Approaches to the Synthesis of Block and Graft Copolymers with Well Defined Segment Lengths

Almar Postma

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Abstract

The synthesis of amine end-functionalised polymers by controlled free radical techniques has been investigated with a focus on methods that provide primary amino end-functionalised polystyrene. The aim of these investigations was to provide precursors to block and graft polyolefins and polyesters by interchain coupling reactions.

The approaches investigated involved developing strategies for the synthesis of phthalimido-functional polymers which can be quantitatively deprotected to yield the desired amino-functional polymers.

Initially synthesis by atom transfer radical polymerisation (ATRP) was explored. A number of approaches based on ω-functionalisation (end-group substitution) and α-functionalisation (functional initiator) were examined. A novel ATRP initiator, *N*-bromomethylphthalimide, provided the most promising results but still had limited applicability because of its low solubility in polymerisation media.

The problems encountered with the ATRP approaches prompted an exploration of techniques based on reversible addition fragmentation chain transfer (RAFT) approach. Novel phthalimidomethyl RAFT agents (trithiocabonates, xanthates) were synthesized. The activity and scope of the new RAFT agents was investigated in polymerisations of styrene, *n*-butyl acrylate, *N*-isopropylacrylamide, *N*-vinylpyrrolidone (trithiocarbonate) and vinyl acetate (xanthate). The syntheses of α-phthalimidomethylpolystyrene were successfully scaled up and hydrazinolysis afforded a range of α-aminomethylpolystyrenes of low polydispersity and controlled molecular weight.

The syntheses of primary amino-functional polymers using the pthalimido-functional RAFT agents necessitated the development of a convenient method for conversion of trithiocarbonate groups to inert chain ends. Thermolysis proved a most simple and efficient method of achieving this for both polystyrene and poly(*n*-butyl acrylate). Thermolysis also provided a means of further characterising the mechanism of the RAFT process.

A simple and efficient method for amino end-group analysis was developed that involved *in-situ* derivatisation with trichloroacetyl isocyanate followed by ^{1}H NMR analysis. The method was shown to be a suitable method for determining a wide range protic end-groups (NH_2, OH, COOH) in synthetic polymers.

Finally, metallocene polyolefin based coupling trials largely with controlled amino-functional polystyrene were conducted as an initial investigation into the production of high value added grafted polyolefins (and polyester). The grafting trials were carried out on a small scale with a view to directing future experiments.

Declaration

I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for an award of any other degree or diploma at UNSW or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others, with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

Almar Postma

Mr. McGuire: I want to say one word to you. Just one word.
Ben Braddock: Yes, sir.
Mr. McGuire: Are you listening?
Ben Braddock: Yes, I am.
Mr. McGuire: Plastics.
Ben Braddock: Just how do you mean that, sir?

- The Graduate (1967)[1]

Publications arising from this thesis

Advances in RAFT Polymerization: The Synthesis of Polymers with Defined End-Groups. Moad, G., Chong, Y.K.; Postma, A.; Rizzardo, E.; Thang, S. H.; *Polymer*, 46, 8458-8468, **2005**. (cited 1)

Thermolysis of RAFT-Synthesized Polymers. A Convenient Method for Trithiocarbonate Group Elimination. Postma, A.; Davis, T. P.; Moad, G.; O'Shea, M. S.; *Macromolecules*, 38, 5371-5374, **2005**. (cited 4)

Approaches to Phthalimido and Amino End-Functional Polymers by Atom Transfer Radical Polymerisation (ATRP). Postma, A.; Moad, G.; O'Shea, M. S.; Davis, T. P.; *React. Funct. Polym.* 66, 137-147, **2006**.

A Simple Method for Quantitative Determination of Protic End-Groups in Synthetic Polymers by ^{1}H NMR Spectroscopy. Postma, A.; Donovan, A. R.; Moad, G.; O'Shea, M. S.; Davis, T. P.; *Polymer* – submitted, **2005**.

Publications arising outside the scope of this thesis

Chain Transfer Activity of ω-Unsaturated Methacrylic Oligomers in Polymerizations of Methacrylic Monomers. Hutson, L.; Krstina, J.; Moad, C.; Moad, G.; Morrow, G. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules*, 37, 4441-4452, **2004**. (cited 6)

Binary Copolymerization with Catalytic Chain Transfer. A Method of Synthesizing Macromonomers Based on Monosubstituted Monomers. Chiefari, J.; Jeffery, J.; Krstina, J.; Moad, C. L.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules,* 38, 9037-9054, **2005**.

A Multidisciplinary Approach to the Use of Pyridinyl Dithioesters and Their N-Oxides as CTAs in the RAFT Polymerization of Styrene. Not the Chronicle of a Failure Foretold? Alberti, A.; Benaglia, M.; Guerra, M.; Gulea, M.; Hapiot, P.; Laus, M.; Macciantelli, D.; Masson, S.; Postma, A.; Sparnacci, K. *Macromolecules*, 38, 7610-7618, **2005**.

An ESR Approach to the Estimation of the Rate Constants of the Addition and Fragmentation Processes Involved in the RAFT Polymerization of Styrene. Alberti, A.; Benaglia, M.; Fischer, H.; Guerra, M.; Laus, M.; Macciantelli, D.; Postma, A.; Sparnacci, K.; *J.Am.Chem.Soc.* - submitted.

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APPENDIX 1 ..... A1

1 Introduction

1.1 General Introduction

Free-Radical polymerisation is one of the most convenient ways of synthesizing polymers on an industrial scale and has become an important process for the commercial production of polymers, with approximately 70% of vinyl polymers being produced this way.[2] Its versatility stems from several factors: (a) tolerance to impurities and to trace amounts of oxygen and water, (b) the capability of polymerising a wide range of monomers (*e.g.* styrene, vinyl acetate, (meth)acrylates, (meth)acrylamides) with a range of functional groups (*e.g.* COOH, OH, NR_2, $CONR_2$) and (c) its compatibility with a wide range of reaction conditions (it can be conducted under (mini)emulsion, suspension as well as standard bulk and solution conditions).[3,4]

This gives free-radical polymerisation a competitive advantage over other techniques such as group transfer and ionic polymerisation, which require ultra-pure reagents, anhydrous conditions and work with only a limited range of commercially interesting monomers. However, there are some associated disadvantages of free radical polymerisation which include the broad molecular weight distributions that can only be controlled to a limited extent by choosing the initiator concentration or through the use of transfer agents. Furthermore, the control of polymer architecture and the synthesis of block, graft and end-functional polymers with chain length, composition and composition distribution remains difficult. This inability to precisely control the microstructure of the polymer chain restricts the control the macroscopic properties of the bulk polymer.

In the last 10 years these limitations have been mostly dissolved with the advent of living radical polymerisation (LRP). There are currently three main techniques: nitroxide mediated polymerisation (NMP),[5] atom transfer radical polymerisation (ATRP)[6] and reversible addition fragmentation chain transfer (RAFT).[4,7] These methods seek to combine the robustness and versatility of radical polymerisation with the structural control of living polymerisation. Out of

these three main LRP techniques, RAFT is arguably the most versatile and convenient of the systems. RAFT is also the only technique where the addition of the RAFT agent to a system should in principle not influence the kinetics of that system. Existing technological/industrial processes and their recipes can be kept as is, to which the RAFT agent can be added as a magic ingredient, turning a bland dish to a gastronomic delight.

Living radical polymerisation techniques are readily applied to the synthesis of end-functional polymers. In an ideal living radical system all chain ends are retained and no new chains are formed and therefore are inherently pertinent to the introduction of end-functionality to radical polymers. Two main processes can be distinguished; α-and ω-functionalisation approaches. These are further outlined in chapter 2. These methodologies hold relevance to the design of the functional initiators (the alkoxyamines for NMP or the halo compound for ATRP) and chain transfer agents (in the case of RAFT). They may be designed with a view to directly providing the polymer chains with the desired functionality or indirectly by transformation of dormant polymer chain ends postpolymerisation. Chain functionality can thus be introduced into the polymer by adjusting the structure of the functional initiator or chain transfer agent.

There are many issues and synthetic implications to consider as each method has its own mechanistic limitations and complexities. It is important, for example, to recognise that not all RAFT agents work with equal efficiency in all circumstances. This is often overlooked by the polymer chemist who may prematurely become discouraged. Finding a system which provides an end-functional polymer with controlled molecular weights, polydispersities whilst minimising any compromises in end-group purity and therefore eventual properties, for whatever application, can be a fundamental investigation in itself.

Recent developments in the production of segmented polymers using controlled or living polymerisation techniques have resulted in the ability to make new materials by manipulation of new arrangements and building blocks of known monomers or segments. The advent of controlled free radical polymerisation has also allowed the production of materials that have only previously been possible via rigorous polymerisation methods such as anionic polymerisation.

Living radical polymerisation techniques immediately lend themselves to the synthesis of block and graft (segmented) copolymers by the production and exploitation of controlled end-functional polymers

1.2 Aims of This Work

Reactive extrusion (REX) has been used to produce polymers from monomers (by bulk polymerisation), functional polymers (via free radical grafting of monomers onto polymers), block and graft copolymers (via interchain copolymer formation through the reaction of functional polymers in the melt). However, on the whole the materials produced by REX are of a relatively inconsistent composition and/or molecular weight distributions, reflected in their often resultant variable properties.

An opportunity exists to utilize controlled free radical polymerisation methods to provide feed stocks for the formation of segmented polymers that can subsequently be produced by reactive extrusion. Although end-functionalised, block, graft and brush copolymers of polyolefins exist, the majority of these products rely on involved processes and are not cost effective. It was proposed that this could be made possible by synthesising controlled end-group polystyrene as a reactive feed stock, in an efficient and cost effective manner and, furthermore, by taking into account the morphological characteristics of the proposed olefin substrates. This thesis aims to approach the synthesis of cost effective graft copolymers via interchain coupling of reactive functionalities on polyolefins (or polyesters) and radically controlled polymers.

Initially this study was focussed on using metallocene catalysed LLDPE as the polyolefin substrate, these materials have been available for some time but little actual work has been published on their modification by reactive extrusion. Their relatively narrow polydispersity and chemical homogeneity makes them ideal substrates for studying their behaviour in reactive extrusion and simplifies the understanding of the chemistry involved. The added benefit is that they have an improved solubility in a greater range of organic solvents, which is

governed by their comonomer content/density. This allows a wider use of characterisation techniques which would otherwise have been difficult to apply. However, one complication that does arise with metallocenes having a narrow polydispersity is that it goes hand in hand with low melt viscosities, making it harder for them to be processed. The merging of controlled living radical polymerisation techniques and controlled polymer architecture metallocenes would provide an opportunity to develop a process to synthesize cost effective engineered graft copolymers on a larger scale by reactive extrusion.

The main focus of this thesis has undoubtedly been on the synthesis of well-defined amino-functionalised polystyrene (as well as investigating the possibilities with other monomers), driven by the breath and outcomes of the results uncovered. The degree of control over molecular weights, molecular weight distribution and the resulting chemical functionality of the polymer chains was investigated and largely dictated by the method used. The ultimate aim of producing controlled end-functionalised feed stocks for segmented polymers necessitated a thorough understanding of and implicated the importance of each control. With a view to scaling up, the system adopted would need to be robust, efficient, replicable and cost effective, especially with the desired applicability in a bulk commodity area. The integrity of the end-functional polymer would have to be assessed in terms of end-group purity, with it harbouring minimal residual unwanted functionalities from the radical process adopted. Furthermore, there was also the continual aim of being able to effectively analyse the polymers produced, especially in terms of end-group quantitation and qualitative determination.

1.3 Outline of Thesis

This thesis aims to investigate the synthesis of end-functional polymers by controlled free-radical polymerisation techniques, the subsequent use of these polymers in the interchain coupling of reactive extrusion functionalised polyolefins, for the formation of graft and block copolymers. The following chapters outline the methodology and approach underlying this investigation

with an impetus to contribute to the understanding of a continually expanding area.

Chapter 2. Literature review

This chapter reviews the area of conventional free radical polymerisation, the three major methods of living radical polymerisation, the grafting of reactive monomers by reactive extrusion and the synthesis of graft copolymers. The chapter starts by introducing the essential features of classic radical polymerisation, which existed before the advent of living radical polymerisation, and its application to end-group control. This is followed by a discussion of the three main controlled radical polymerisation techniques: nitroxide mediated polymerisation (NMP), atom transfer radical polymerisation (ATRP) and the more recent reversible addition-fragmentation chain transfer (RAFT) polymerisation. A particular emphasis is placed on the application of these techniques to the synthesis of α- and ω-end-functional polymers and to examples that provide architectural control over the polymers. The penultimate section reviews the functionalisation of polyolefins with reactive monomers by reactive extrusion. The focus is on two commercially important monomers, maleic anhydride and glycidyl methacrylate. The factors required for achieving efficient grafting in melt reactors and an overview of the characterisation of the graft functionalised polymers are examined. The final section looks at the synthesis of graft copolymers by interchain coupling of reactive polymer functionalities largely in the melt, highlighting the choice of functionalities, system optimization and examples of graft copolymer synthesis found in the literature.

Chapter 3. Approaches to phthalimido and amino end-functional polystyrene by ATRP

Approaches to the synthesis of amine end-functional polystyrenes through intermediary phthalimido end-functional polystyrenes were explored.

Phthalimido groups can be quantitatively converted to amine groups by hydrazinolysis according to an Ing-Manske procedure. Approaches based on α-functionalisation (functional initiator) and ω-functionalisation (end-group substitution) were examined. Initially, well defined low molecular weight ω-bromopolystyrenes were prepared by atom transfer radical polymerisation (ATRP) with copper (I) bromide, 4,4'-di-(nonyl)-2,2'bipyridine (dNbpy) and 1-bromoethylbenzene initiator, these were subsequently transformed into ω-phthalimidopolystyrenes by substitution with potassium phthalimide and consequently deprotected to the amine. However, elimination of the terminal bromine to form an unsaturated chain end was observed as a side reaction, on substitution. A more successful approach was developed in which various α-phthalimidopolystyrenes were successfully prepared using phthalimido-functional initiators. Phthalimido-functional bromoisobutyrate derivatives proved very effective in yielding very low polydispersity polystyrene ($\overline{M}_w / \overline{M}_n$ ~1.1). The conversion of the derived α-phthalimidopolystyrene to an α-aminopolystyrene was problematic because of concomitant cleavage of the isobutyrate ester linkage during hydrazinolysis and other side reactions. *N*-(bromomethyl)phthalimide was successfully used as an ATRP initiator to prepare low polydispersity α-pthalimidopolystyrene ($\overline{M}_w / \overline{M}_n$ ~1.3) and hence, α-aminopolystyrene with a high degree of end-group purity.

Chapter 4. Approaches to phthalimido and amino end-functional polymers by RAFT

This chapter continues with the study of amine end-functional polymer synthesis by using the RAFT approach to circumvent some of the observed problems with the ATRP system. The use of phthalimide derivatives as transfer agents in polymerisations with RAFT was explored. Phthalimidomethyl trithiocarbonates were used as RAFT agents to provide end-functional polystyrene (PS), poly(*n*-butyl acrylate) (PBA), poly(*N*-isopropylacrylamide) (PNIPAAm) of controlled molecular weight (1k–100k g mol^{-1}) and with control over polydispersity. *N*-vinyl pyrrolidinone (NVP) polymerisation was also briefly investigated. A

phthalimidomethyl xanthate RAFT agent was used to provide end-functional poly(vinyl acetate) (PVA). The phthalimide functionality of the polystyrene products was converted to amine end-groups by hydrazinolysis. Scaling up of the polymerisation was also investigated as well as the effectiveness of the RAFT agents employed.

Chapter 5. Investigations into the efficient removal of the RAFT moiety

This chapter is concerned with developing a method for the clean removal of the RAFT group. Several approaches are studied, namely radical-induced reduction/radical exchange, aminolysis (in conjunction with reduction by zinc and acetic acid) and thermolysis. ^{1}H NMR and GPC analysis is applied in studying these processes. Thermolysis provided a simple and efficient way of eliminating trithiocarbonate groups from polymers made by the RAFT process. For polystyrene with chain end [~CHPhCH_2CHPh-S(C=S)SBu] the product has a comparatively inert 1,3-diphenylpropenyl chain end (~CHPhCH=CHPh) which is most likely formed by a concerted elimination mechanism. In the case of poly(*n*-butyl acrylate) with chain end [~CH(CO_2Bu)CH_2CH(CO_2Bu)-S(C=S)SBu] the analogous elimination reaction is a minor pathway. The thermolysis product has a macromonomer chain end [~CH(CO_2Bu)CH_2C(CO_2Bu)=CH_2] which may arise by consecutive C-S bond homolysis, intra- or intermolecular transfer and β-scission. Thermolysis was followed by thermogravimetric analysis, ^{1}H NMR and gel permeation chromatography.

Chapter 6. End-group determination by TAI derivatisation

This chapter investigates a simple method for the determination of protic end-groups in synthetic polymers. The method involves in situ derivatisation with trichloroacetyl isocyanate (TAI) in an NMR tube and observation of the imidic hydrogen signals of the derivatised products by ^{1}H NMR spectroscopy. The signals observed are characteristic of the end-group and appear in a normally clear region of the NMR spectrum (δ 7.5-11). The method was used to

determine hydroxyl, amino and carboxyl groups and was applied to the characterisation of polymers formed by both conventional and living radical polymerisation (RAFT, ATRP, NMP), to end-functional poly(ethylene oxide) and to polyethylene-block-poly(ethylene oxide). The derivatisation was found to facilitate analysis of amine functional polymers by gel permeation chromatography (GPC) which is often rendered difficult by specific interaction of the amine group with the GPC column.

Chapter 7. Polyolefin Graft Copolymers from Amino End-functionalised Polystyrene: Trials and Future Directions

Initially the synthesis of functionalised polyolefins by the grafting of monomers (maleic anhydride and glycidyl methacrylate) in the melt under reactive extrusion conditions is described. They are produced as precursors for the synthesis of graft copolymers largely with amine end-functionalised polystyrenes but also with an acid functionalised polystyrene. The grafting levels of the reactive monomers on (metallocene) linear low density polyethylenes are analysed by FTIR and UV spectrometry, the polymers are also further analysed by GPC. Small scale coupling experiments are conducted in the melt and in solution with a view to assessing the system and to direct future trials. Additionally the formation of polyester-polystyrene block copolymer is briefly investigated via the coupling of polyester oligomers with amine end-functional polystyrene. The success of the graft copolymer formation is assessed using GPC with UV and RI detection.

Chapter 8. General conclusions

This chapter summarises the results obtained in the previous chapters and discusses some options for future directions

Parts of this thesis have been submitted, are in press or have been published elsewhere:

Chapter 3. [8]

Chapter 4. [9,10]

Chapter 5. [10,11]

Chapter 6. [12]

1.4 References

1. in memory of H. H. T. M. Ketels (1960-1999), who in his own way was a Mr. McGuire, and me, Ben Braddock.
2. Otsu, T. *J. Polym. Sci., Part A: Polym. Chem. 38*, 2121-2136.
3. Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization;* Pergamon, Elsevier Science Ltd: Oxford, U.K., 1995.
4. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379-410.
5. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.
6. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
7. Alternatively RAFT could be written as fragmentation-addition reversible chain transfer (FARCT). This acronym contains all the initial letters, unlike RAFT in which the letter 'c' of chain is omitted.
8. Postma, A.; Moad, G.; O'Shea, M. S.; Davis, T. P. *React. Funct. Polym.* **2005**, *66*, 137-147.
9. Postma, A.; Evans, R. A.; Moad, G.; O'Shea, M. S.; Davis, T. P. *Macromolecules* **2005**, to be submitted.
10. Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458-8468.
11. Postma, A.; Davis, T. P.; Moad, G.; O'Shea, M. S. *Macromolecules* **2005**, *38*, 5371-5374.
12. Postma, A.; Donovan, A. R.; Moad, G.; Mulder, R.; O'Shea, M. S.; Davis, T. P. *Polymer* **2005**, submitted.

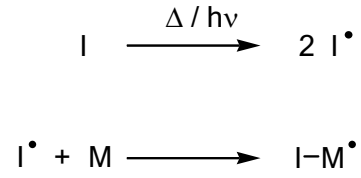
Man: Oh look, this isn't an argument.
Mr Vibrating: Yes it is.
Man: No it isn't. It's just contradiction.

- "*Argument Clinic",* Monty Python's Flying Circus

2 Literature Review

2.1 Radical polymerisation

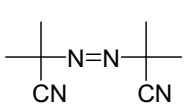
Conventional free radical polymerisation is a chain reaction which comprises three main processes; initiation, propagation and termination.[1] An additional process, chain transfer, also occurs under certain conditions. Initiation involves at least two-steps. The first is the formation of primary radicals ($I^{\bullet}$). This usually involves the decomposition of an initiator (I) by thermolysis or photolysis to produce radicals in pairs as shown in Scheme 2.1. However, primary radicals can also be formed by a redox reaction.



Scheme 2.1. Initiation by either thermolysis of photolysis.

The second step is the addition of the radicals ($I^{\bullet}$) to the vinyl monomer to initiate propagation by formation of $I\text{-}M^{\bullet}$ so that the polymer starts to grow. The primary radicals can also undergo termination by combination or disproportionation with each other or with other radicals leading to an overall loss in radicals and a reduction in initiator efficiency. When they react with propagating radicals the reaction is called primary radical termination. The primary radicals can also undergo fragmentation or rearrangement to produce secondary radicals which can react by similar pathways.

Some common initiators used in radical polymerisation are the azo-initiators, for example, azobis(isobutyronitrile) (AIBN) (**1**), water soluble initiator 4,4'-azobis(4-cyanovaleric acid) (**2**), 1,1'-azobis(1-cyclohexanenitrile) (VAZO88™) (**3**). Peroxide initiators are also quite commonly used, examples including, dibenzoyl peroxide (BPO) (**4**), di-t-butyl peroxylate (DBPOX) (**5**) and 2,5-bis(t-butylperoxy)-2,5-dimethylhexane (DHBP) (**6**).



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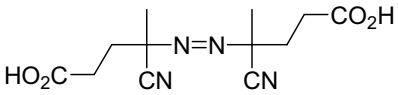

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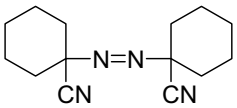

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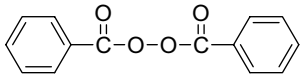

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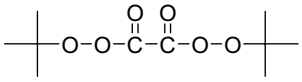

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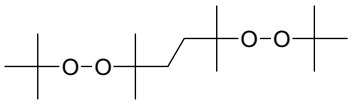
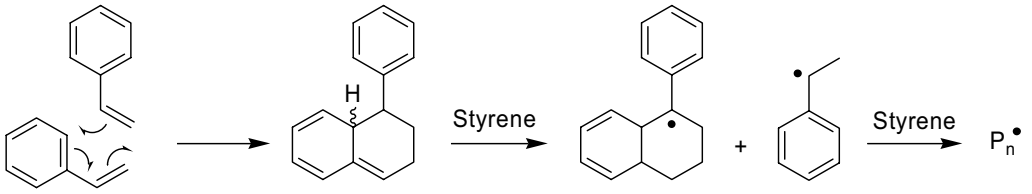


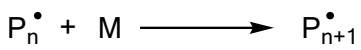
6

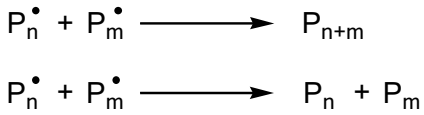
Some monomers, like styrene, also undergo thermally initiated polymerisation by monomer derived radicals without the need of added initiator (Scheme 2.2).



Scheme 2.2. Initiation of styrene by thermal Diels-Alder reaction, hydrogen donation and formation of the initiating radical (Mayo mechanism).

Propagation involves sequential addition of monomer to the polymeric radical ($P_n^{\bullet}$) to produce a new polymeric radical ($P_{n+1}^{\bullet}$), one repeat unit longer, see Scheme 2.3. The propagation process is repeated over and over to increase the chain length of the polymer. The majority of propagation events occur as "head-to-tail" addition, where the attacking radical adds to the least-substituted-end of the monomer double bond.





Scheme 2.3. Propagation and termination (radical-radical combination and disproportionation).

Termination is the process by which radicals are irreversibly destroyed, to leave an inactive or 'dead' polymer. This process can occur by either combination of

two radicals to provide a polymer with the length equal to the sum of the two radicals or by disproportionation, to produce two polymer chains of the same length as the original radicals, as shown in Scheme 2.3. Disproportionation, however, involves hydrogen atom transfer from one radical to the other, leaving an unsaturated end-group on one of the polymer chains. This may react further if attacked by another radical. Overall the radical concentration is reduced thus terminating the chain reaction. For an ideal radical polymerisation the polydispersity (PD*) will be, 2, for termination by disproportionation or chain transfer, or 1.5, for termination by combination. [1]

Chain transfer, first recognized by Flory[2] in 1937, terminates a propagating radical but does not terminate the chain reaction since there is no overall change in the radical concentration. A new radical is formed which can re-initiate propagation. As shown in Scheme 2.4 the propagating radical ($P_n^{\bullet}$) reacts with a transfer agent (T) to terminate one chain and leave a radical ($T^{\bullet}$) which can reinitiate a new monomer to produce another radical ($P_m^{\bullet}$). Transfer agents are usually used to control polymerisation by lowering the molecular weight and the rate of polymerisation and can also be used to control the nature of the end-group.

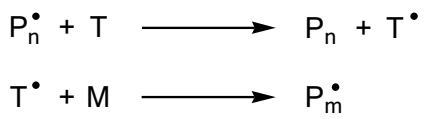
---

* Polydispersity is the ratio of the weight average $\overline{M}_w$ to the number average molecular weights $\overline{M}_n$:

PD= $\overline{M}_w / \overline{M}_n$

- The number average molecular weight or molar mass is simply the total weight of the sample divided by the number of molecules in the sample: $\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum n_i}$, where n_i is the number of chains of length *i*, w_i is the weight of chains of length *i* and M_i is the molecular weight of a chain of length *i*.

- The weight average molecular weight is the sum of the weights of chains of each molecular weight multiplied by their molecular weight divided by the total weight of the sample: $\overline{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$.



Scheme 2.4. Chain transfer of radical from growing polymer chain to another molecule (*e.g.* solvent, monomer).

The steps of conventional radical polymerisation, outlined above, occur concurrently and the time it takes for an individual polymer chain to be initiated, to propagate and then to terminate is of the order of seconds. However, the consumption of monomer can take from minutes to days. In order to consume the monomer to high conversion a continuous supply of radicals is required to maintain a relative constant radical concentration. This has the consequence of firstly forming high molecular weight material even during the initial stages of the reaction (and normally throughout the polymerisation) with chains of different degrees of polymerisation (DP♦) being formed at the later stages due to changing reactant concentration and rate constants. The molecular weight distribution (MWD) of the final polymer will be spread over a range of DPs, resulting in a polymer with a broad polydispersity PD >1.5 (Figure 2.1).

The polymer end-groups are derived from a range of possible sources like the initiation process, from termination by disproportionation (unsaturated double bonds) as well as from chain transfer agents. In the absence of chain transfer agent there is greater difficulty in controlling the polymer end-groups. The lack of control over polymer molecular weight, architecture, chain composition, and end-groups spurred research into finding ways of overcoming these confines.

♦ The degree of polymerisation is the number of repeat units in a chain.

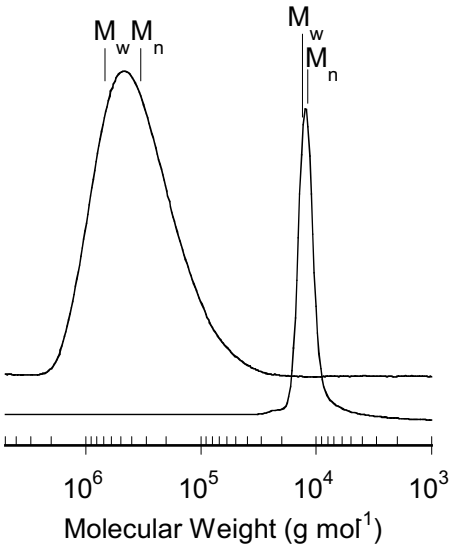


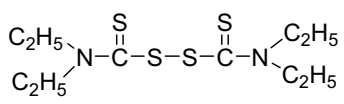
Figure 2.1. Molecular weight distributions for a conventional (broad) and living radical polymerisation (narrow). Note: $\overline{M}_w$ is always greater than $\overline{M}_n$. Reprinted with permission.[3]

Since the aim of this thesis is not primarily focussed on the mechanisms and kinetic issues of free radical polymerisation the reader is directed to comprehensive reviews on the free-radical polymerisation chemistry process in books by Moad and Solomon,[1] Rempp and Merrill,[4] where this topic is discussed more thoroughly.

2.2 Living radical polymerisation

There was an upsurge in interest in living polymerisation in the '80s when radical chemistry was applied to the then established living polymerisation techniques involving, anionic, coordination or group transfer mechanisms. Living radical polymerisations (LRP) do not meet the requirements of the term "living" as defined by Szwarc.[5] Since they involve radicals as intermediates they must involve a finite amount of termination. They were therefore considered less "alive" than that of the classical living polymerisation techniques and were therefore referred to as pseudo- / quasi-living,[1] controlled rather than living[6] or *living* was surrounded by quotations or placed in italics.[7,8] The criteria for living

polymerisation can be stated as follows. Living polymerisations, if taken to full conversion, should continue to polymerise on further addition of monomer, the number average molecular weight should be linearly dependant on conversion, the molecular weight should be controlled by stoichiometry, the number of polymer chains should remain constant during polymerisation, the chain length distribution should be low (*i.e.* near monodisperse) (Figure 2.1), and chain-end-functionality should be quantitatively retained. Living radical systems can meet all or most of these criteria



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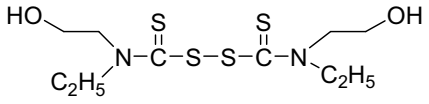

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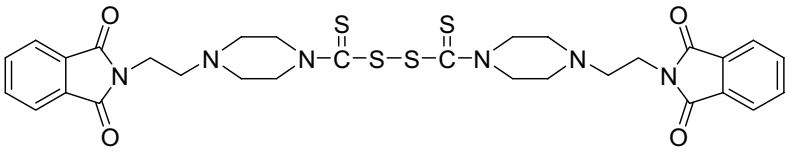

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Initial work by Otsu and Yoshida[9] utilized control agents they called “iniferters”, that had the property of being initiators, transfer agents and chain terminators. One class of iniferters included certain diaryl-, dibenzoyl-, dixanthogen- and dithiuram- disulphides. The mechanism of polymerisation is illustrated by considering dithiuram disulphide (**7**): Initiation of the polymerisation is by homolytic photodissociation of the S-S bond to form a pair of dithiocarbamyl radicals which can add to monomer (albeit slowly). Transfer from a propagating radical to the unreacted iniferter to give a dithiocarbamyl radical can also occur. Termination ends polymerisation by the initiating radicals combining with a propagating polymer radical. The reaction is reversible only under photochemical conditions. Since the dithiocarbamyl end-groups are thermally stable but photochemically labile, only photo-initiated polymerisations could be described as living radical polymerisations.

The iniferter systems weren’t perfect and they only displayed limited living characteristics with particular monomers, under certain reaction conditions, with side reactions occurring and polydispersities not narrowing significantly.

However, it uncovered interesting results and introduced the importance of reversible termination, giving insight into the requirements for living radical polymerisation that would later form the basis of nitroxide mediated (NMP) and atom transfer polymerisation (ATRP). The mechanistic step of transfer to the polymeric iniferter was not important because the transfer constants were low. Such transfer reactions are important with macromonomer and thiocarbonylthio based reversible addition-fragmentation chain transfer (RAFT) agents. These topics will be discussed in sections 2.2.2, 2.2.3 and 2.2.4.

Iniferters do however, allow control over polymer end-functionality by the nature of the iniferter mechanism, hence dithiocarbamates like (**8**) and (**9**) have been used to prepare hydroxyl[10] and amino[11] telechelic polymers (Figure 2.4), respectively. However, end-group purity is compromised by slow loss of the living chain ends due to the occurrence of various side reactions.[12,13]

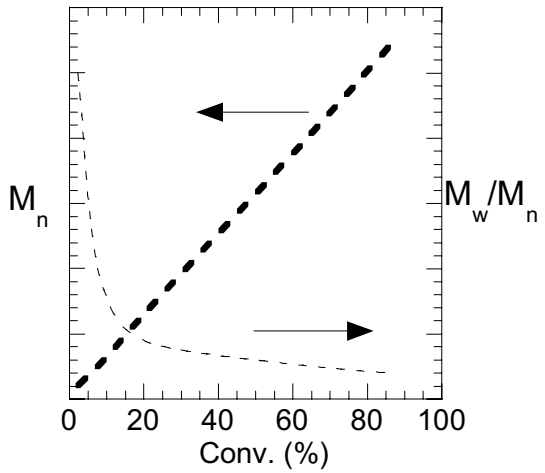


Figure 2.2. Evolution on molecular weight ($\overline{M}_n$) and polydispersity with monomer conversion.

A linear increase in molecular weight $\overline{M}_n$ with monomer conversion combined with a low PD (<1.5, Figure 2.1) as shown in Figure 2.2, with a first order kinetic plot (not shown) is often considered a test for living systems. However these tests are not particularly definitive since first order kinetic plots are observed in conventional, non living radical polymerisation under steady state conditions. Living radical polymerisation systems always have <100% living ends since

termination events alway occur. Moreover, systems with 100% living chain ends may show a non-linear increase in molecular weight with conversion when initiation is slow compared to propagation.[14] A better test for the degree of livingness is the percentage of living functional end-groups.

Determining the amount of end-groups in low molecular weight polymers can easily be examined with NMR but this presents a challenge in accuracy when the DP exceeds 100. A way to circumvent this is to perform a chain extension test in conjunction with chromatographic analysis (*e.g.* GPC≈). The resulting polymer, acting as a macroinitiator, further polymerises more monomer and if the living chain end purity is high, the final polymer correspondingly will have increased in molecular weight quantitatively.

2.2.1 End-functional polymers

As discussed, LRP should provide predictable molecular weights with narrow molecular weight distributions and chain ends capped by functionalities. More importantly, the end-functionality should be quantitative with all chains carrying both an initiator derived α end and terminated with an ω end-group (Figure 2.3). Under specific conditions, functionality can also be placed in other key parts of the polymer chain (Figure 2.4). Functionalities should be selected to be compatible with LRP processes.

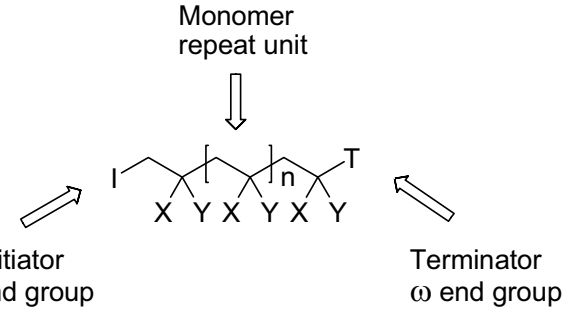


Figure 2.3. Structural features of an ideal living radically polymerised polymer, showing α and ω functionalities.

≈ Gel permeation chromatography also known as size exclusion chromatography (SEC)

α-functionalisation: The α-functionalisation approach can be imparted using LRP by either the use of a functional initiator; the initiator fragment of the alkoxyamine nitroxide mediated polymerisation (NMP), the organic fragment of the organohalide initiator for atom transfer radical polymerisation (ATRP) or by the radical leaving group from transfer agents (*e.g.* reversible-addition fragmentation *chain* transfer or RAFT). All chains should contain the functionality although other sources of initiation will reduce the level of functionality (*e.g.* thermal initiation of styrene or the use of an additional non-functional initiator). See sections 2.2.2.2, 2.2.3.2 and 2.2.4.3 for specific examples of α-functionalisation.

ω-functionalisation: It is possible to introduce ω-functionalisation using NMP by placing the functionality in the nitroxide fragment of an alkoxyamine, in the Z group of the RAFT agent or by chemical transformation of the halo-end of a dormant ATRP polymer chain (this can also be applied to both the RAFT Z group and the nitroxide). The level of functionality will be dependant on the quantitativeness of the transformation chemistry applied as well as the polymerisation process introducing it. Termination by disproportionation and radical-radical termination will reduce functionality, and any other chain transfer processes to species present in the polymerisation medium will contribute to the loss of end-functionality. Living radical polymerisation allows the control over formation of block copolymers at the ω chain end, thus functional monomers, short oligomers or blocks can be considered another method for ω-functionalisation. Removal of the dormant chain ends of NMP, ATRP and RAFT provides another route to functionalisation, the functionality being dependant on the method of removal. See sections 2.2.2.1, 2.2.3.1 and 2.2.4.2 for specific examples of ω-functionalisation.

The use of the functional initiator **2** has been applied to making polymers with mono functional end-groups such as monocarboxy-terminated polystyrene prepared under nitroxide mediated polymerisation.[15] Using functional nitroxide (**10**, p23) in conjunction with a functional initiator, a di-end-functional or telechelic polymer could be made.

It should be remembered that in attempting to prepare monofunctional polymers, any termination will give rise to a difunctional impurity. Equally, preparation of difunctional polymer will give some monofunctional impurity due to disproportionation.

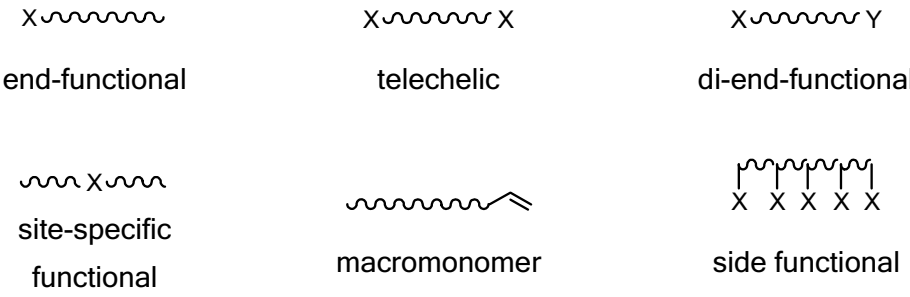


Figure 2.4. End-functional polymers synthesized by living radical polymerisation.

End-functionality plays an important role in the polymer's ultimate property and therefore use, for example it can effect the polymer's thermal stability,[16] and if reactive, will allow the polymer to couple with other functionalities forming grafts or blocks, cross-linking or giving it a curing property. The ω end, being living, can further chain extend, thereby allowing the formation of functional blocks (when functional monomers are used).[17,18] Control over the synthesis of blocks, grafts and other polymer architectures (Figure 2.5) has become increasingly important in producing high value added materials for nanotechnology, biomaterials, blend modifiers and improving or expressing particular polymer properties by self-assembly.[19,20]

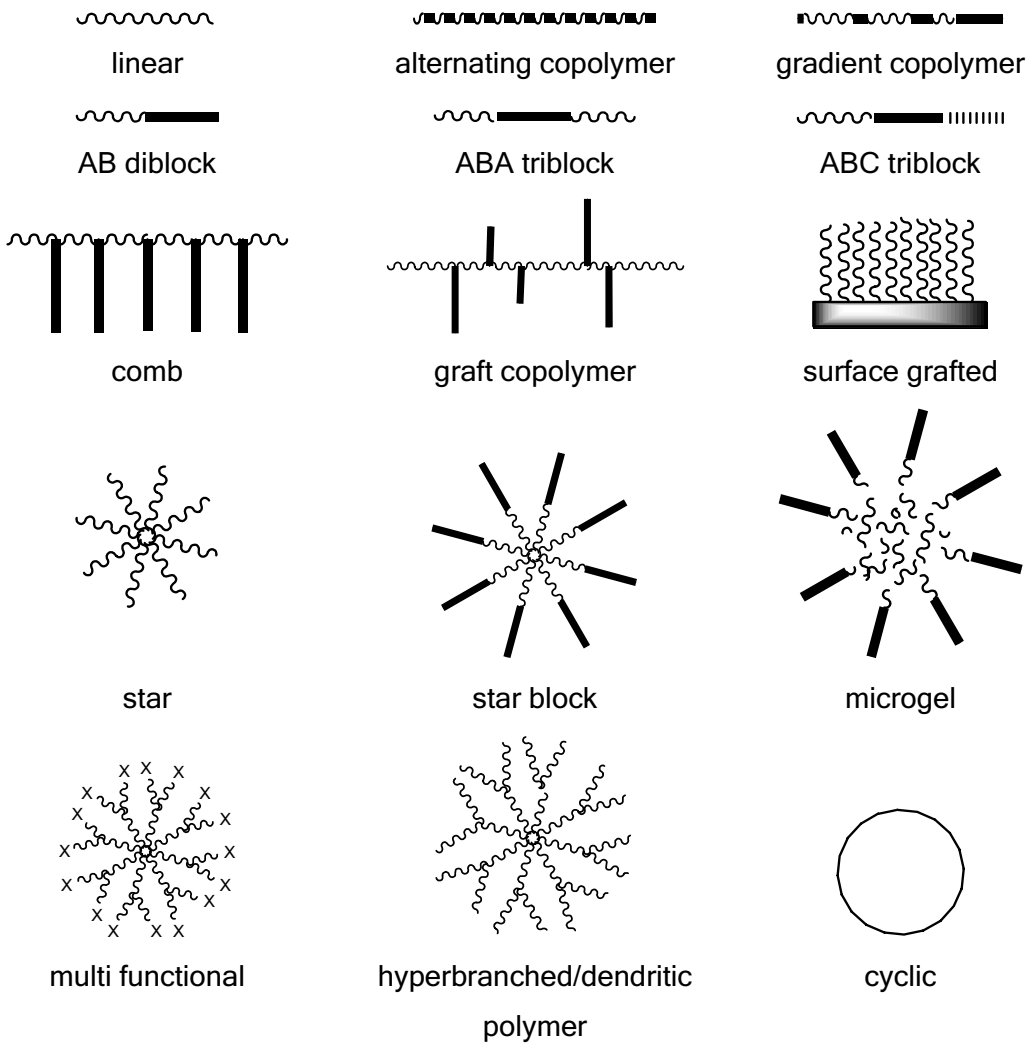


Figure 2.5. A variety of polymer architectures permitted by living radical polymerisation.

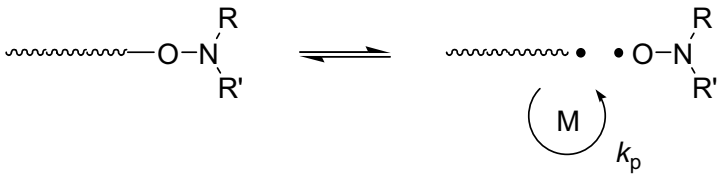
Although these architectures can be made by other non radical polymerisation techniques (*i.e.* ionic, group transfer polymerisation), LRP's versatility and ability to utilize a larger range of vinyl monomers, allows a greater variety of polymer functionality, monomer compositions, well defined architectures and end-group functionalisation.

2.2.2 Nitroxide-mediated polymerisation (NMP)

It wasn't until the mid '80s that living radical polymerisation attained a further step towards better control. Nitroxide mediated polymerisation (NMP) was born out of earlier nitroxide radical trapping work in studying the formation of initiator derived radicals but was also soon used as a reversible deactivator in radical polymerisation.[21] The initial work focussed on synthesis of acrylic block copolymers and was not widely reported in the open literature. In 1990, Johnson *et al.*[22] showed that it should be possible to use the method to make narrow polydispersity polymers. However, the method did not achieve popularity until 1993 when Georges *et al.*; demonstrated experimentally that it was possible to make low polydispersity polystyrene (down to 1.3-1.2).[23] In this work 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, **10a**) was used as the control agent.

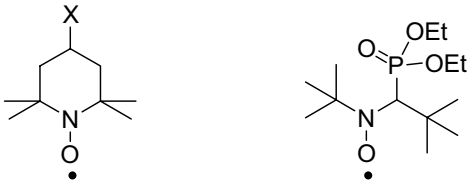
NMP relies on "reversible termination" mechanism involving dissociation - recombination of the C-O bond of the alkoxyamine group) to control polymerisation (Scheme 2.5). Nitroxides provide a process for rapid and reversible deactivation of propagating radicals such that they spend the majority of their time in a dormant state. The concentration of the reactive chain end is low and this reduces the significance of irreversible termination reactions such as combination and disproportionation.

The 'persistent radical effect', is a model developed by Fischer.[24] During polymerisation active (propagating) radicals couple irreversibly, causing an increase in the concentration of mediating (persistent) radicals and an increased concentration of dormant species. This helps maintain livingness but also slows the rate of polymerisation.



Scheme 2.5. Reversible termination equilibrium in nitroxide mediated polymerisation.

NMP was initially restricted to the control of polymerisation of styrenic and acrylic monomers at high temperatures (>110-140 °C). The development of imidazolidinones by Moad and coworkers[25] and later α-H nitroxides, like **11**, by groups Benoit *et al.*[26] and Hawker *et al.*[27-29] permitted better control over the polymerisation of a wider variety of monomers at lower temperatures, but effective control over methacrylates still remains difficult.



10 **11**

a X= H **b** X=OH

End-group control in NMP can be introduced by the alkoxyamine through a functionality either on the nitroxide fragment (ω-functional) or the initiator fragment (α-functional), or in the case of telechelic synthesis (α,ω), in both fragments. Functionality built into alkoxyamines can provide polymers with end-group incorporation levels of >95% for molecular weights up to 75k.[28] Interconversion of end-groups is also possible, however it is likely that functionality levels will be lower due to the additional step(s) required.

2.2.2.1 ω- Functionalisation

ω-End-group functionality brought onto the chain via the functional nitroxide fragment of the alkoxyamine can be problematic under certain conditions. According to Priddy *et al.*[30] at 140 °C, at least 10% of polymer chains lose their

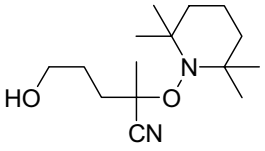
TEMPO functionality to form hydroxylamines. Under these conditions, for example, functionality on TEMPO (*i.e.* hydroxyl, **10b**) would be lost. Decomposition has been found to be reduced by steric factors such as bulky substituents on the nitroxide as well as being effected by the composition of the polymer.[31,32]

The reversible coupling in NMP allows for block formation[33] and subsequently has been applied in introducing short blocks or single functional monomer units onto the polymer chain, in particularly, comonomers like maleic anhydride and maleimide derivatives, that don't propagate under the reaction conditions used.[32] The use of functional allylic sulphide transfer agents (*e.g.* (**23**) and (**24**) section 2.2.4) have been used to end cap the polymer under nitroxide mediated conditions giving a vinyl group as well as the functionality of the incorporated allylic sulphide.[34]

Nitroxides can also exchange with transfer agents like thiols[21] (leaving a hydrogen) or functional dithiuram disulphides (leaving a functional dithiocarbamate),[35] this would evidently allow the interconversion of NMP and RAFT polymerisation. The heating of an alkoxyamine with another (functional) nitroxide gives nitroxide exchange, the purity of the end-functionality being dependent on the relative stabilities of the alkoxyamine and the excess nitroxide.[21,36,37]

Reductive transformation of the nitroxide end-groups is also a way of achieving ω-functionality. Reduction of poly(methacrylic acid) terminated with a nitroxide with zinc and acetic acid, has provided the polymer chain with a ω-terminal hydroxyl.[21]

2.2.2.2 α- Functionalisation



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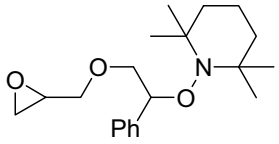
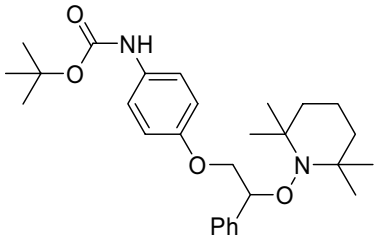


13[38]

Functional initiator fragments, to introduce α functionality, have been designed into alkoxyamines, either by direct synthesis or *in situ* with a functional azo- or peroxy- initiator. Examples of hydroxyl (**12**) and epoxide (**13**) initiator functional alkoxyamines have been made. NMP is compatible with hydroxy, tertiary amino, epoxy and several other functionalities, although carboxylic functionalities have been found to be problematic.



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The synthesis of the functionalised TEMPO initiator (**14**) *via* a bromo-substituted alkoxyamine, incorporating an aromatic amine protected by a t-butoxycarbonyl (*t*-Boc) group has been achieved.[39] Functionalisation after polymerisation was confirmed by ^{1}H, ^{13}C NMR and titration after *t*-Boc deprotection. It was also found that the *t*-Boc functionalisation didn't affect the initiation ability of the nitroxide to styrene.

A review published by Hawker *et al.*[40] highlighted strategies for controlling polymeric structure and synthetic strategies for producing functionalised polymers employing nitroxides and alkoxyamines.

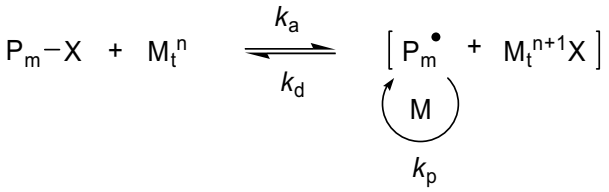
2.2.3 Atom transfer radical polymerisation (ATRP)

ATRP was generated from the initial work of atom transfer radical addition (ATRA), a radical technique for adding an organic halide to an alkene utilizing a metal complex catalyst, discovered in 1945 by Kharasch[41] and was later refined by Asscher[42] and Minisci.[43] Around 1995 separate research groups started to publish results on using ATRA for controlling polymerisation; Wang and Matyjaszewski,[44] Kato and coworkers[45] and Percec and Barboiu.[46]

The ATRP process can be generally described as a radical polymerisation with reversible termination by transfer to a ligand-metal complex. This usually involves the transfer of a halogen (typically bromine) from a dormant initiator or polymeric chain to a transition metal salt. A free radical is generated when the transition metal is oxidised by the halogen transferring, this free radical then adds of monomer. The catalyst♠ is regenerated by the reduction of the oxidised transition metal complex, the polymer chain becomes dormant and the chain end is terminated with the halogen. (Scheme 2.6). ATRP like NMP is also governed by the persistent radical effect.

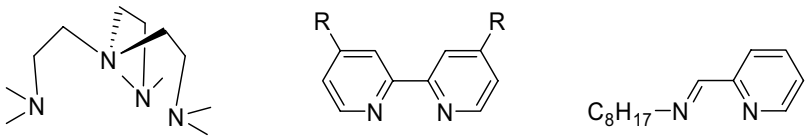
The metal catalysed living radical process is very successful in controlling the polymerisation of a range of (meth) acrylic, (meth) acrylonitrile and styrenic monomers (a range greater than that of NMP) and has been popularised by it being used in the synthesis of new polymer architectures. It is also versatile enough to synthesize end-functionalised polymers by using a functional initiator method or an end-capping method. ATRP does have some drawbacks, however; as it contains a transition metal catalyst and a halogen end-group the polymer prepared will be contaminated with some unremoved catalyst and the terminal halogen introduced in the polymer can be easily eliminated at elevated temperatures and under basic conditions. Also, the polymerisation of vinyl esters and halides is too slow and control over acrylic acids is problematic as it competes with the ligand forming a strong complex with the transition metal catalyst and thereby deactivating it.[6,47,48]

♠ The metal-ligand species is strictly not a catalyst, as some is irreversibly oxidized due to radical termination side reactions.



Scheme 2.6. General mechanism of ATRP polymerisation, (M_t^n) transition metal coordinated by ligands and halogen (X).

Of the transition metals halides used in ATRP (iron, nickel, palladium, ruthenium) copper (I) is the more efficient catalyst and the most studied.[49] The catalysts are complexed with ligands, the ligands playing the role of solubilizing the transition metal catalyst and modulating the redox potential of the M_t^n / $M_t^{n+1}X$ cycle (Scheme 2.6). Commonly used ligands are amino based (*e.g.* Me_6TREN, **15**), bipyridyl (*e.g.* bipyridine (bpy) R=H, 4,4'-di-(nonyl)-2,2'bipyridine (dNbpy) R=C_9H_{19}, **16**) and Schiff base *N*-alkyl-2-pyridylmethanimine (*e.g. N*-(*n*-octyl)-2-pyridylmethanimine, **17**) systems.



15 **16** **17**

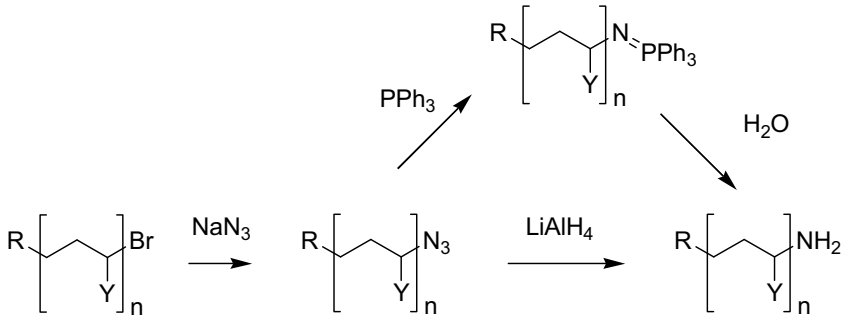
The chemistry of metal catalyzed living radical polymerisation has been reviewed by Kamigaito *et al.*[47,50] and Matyjaszewski *et al.*[48]

2.2.3.1 ω- Functionalisation

ATRP polymers - in their dormant state - retain a ω-terminal halogen (usually bromine) which has been used as a handle in post polymerisation transformation, to provide stability or introduce functionality to the polymer chain. Chain end-functionalisation on the ω-terminus will be reduced by the incidence of various side reactions. Since ATRP is a radical process, a certain amount of radical-radical termination will also occur. This cannot be removed but can be minimized by appropriate tuning of the polymerisation conditions to reduce the loss of halo end-groups. Another source of halogen loss is the

elimination of HBr, catalysed by copper (II), as observed in the (co)polymerisation of styrene.[51,52] Also observed is chain transfer to the ligand in the copper (I) aliphatic amine ligand catalyst system, resulting in an unsaturated end-group.[53]

Two main approaches for the transformation of end-groups are based on radical or chemical (non-radical) means. Radical transformation of end-groups can be performed by simply adding a non-propagating monomer or an addition-fragmentation transfer agent to the end of the polymerisation. Some of the end-functionalities that have been achieved are: macromonomer,[54] vinyl,[55] hydroxy,[55,56] epoxy[55] and succinic.[54] Maleic anhydride and the addition-fragmentation transfer agents have given high functionalisation (>95%), with the less active non-propagating monomers being prone to side reactions.[56] The addition of a functional nitroxide can also confer end-functionality,[56] although with methacrylates this results in disproportionation to give chain end unsaturation.[54] The complete removal of either bromine or chlorine from an ATRP polymer to leave a hydrogen has been successfully performed on styrene and (meth)acrylates polymers by radical induced reduction with tri-*n*-butyltinhydride and an initiator.[57]



Scheme 2.7. End-group substitution and transformation to an amine.

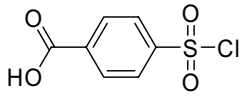
Chemical end-group transformation can also achieve high end-functionality levels, the substitution with azide, primary amine, thiol and carboxylate salts giving >95% displacement. Polystyrene made by ATRP has been transformed into ω amino polystyrene by simple nucleophilic substitution of the bromine into an azido group with sodium azide and a further reduction with lithium aluminium

hydride ($LiAlH_4$) to the amino.[58] An alternate method uses the conversion of the azide into the phosphoranimine and subsequent hydrolysis to form the amine end-group. This was necessary for poly methylacrylate since the ester pendant groups would otherwise undergo reduction with $LiAlH_4$ (Scheme 2.7).[59] Substitution with potassium phthalimide to provide a hyperbranched polystyrene with amine functionality has been attempted with partial success. Substitution of both the chlorine end-groups and chlorine pendant groups has been found to be incomplete and further reduction of the amine via the Gabriel synthesis[60] resulted in gelation.[61] Amino-alcohols, mercapto-alcohols are a means to hydroxyl end-functionality[56] and carboxylic acids[62] can also react with the bromine to bring in functionality, the later two requiring basic conditions.

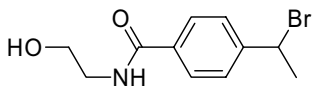
However, substitution reactions with phenolates and alcoholysis can give HBr elimination, reducing end-functionality levels.[63]

2.2.3.2 α- Functionalisation

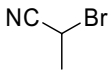
A wide range of initiators can be used in ATRP so long as the initiator has a labile halogen and radical stabilising groups. Various organohalides which are regularly exploited are the, α-halo esters (**21**, **22**), benzyl (**19**) and sulphonyl halides (**18**), also simple compounds like α-halo nitriles (**20**), carbon tetrachloride and chloroform have been used.



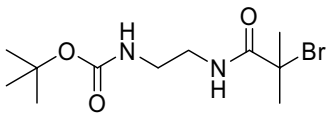
18[48]



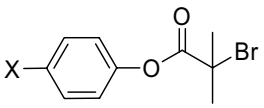
19[63]



20[64]



21[53,65]



22[66]

a X=NH_2 **b** X=NO_2 **c** X= CO_2H

Initiators have been further developed to possess a variety of functionalities: hydroxyl (**19**), amine (**20**, **22b** - precursor to amine) (**21** - protected amine) and

other reactive functionalities. Primary and secondary amines as well as carboxylic acids require protection as they may interfere with the ligand/catalyst system,[67] however, with the appropriate design of catalyst systems these functional initiators may be tolerated.[48] Aromatic amines (**22a**) and acids (**18**, **22c**) are tolerated. Polystyrene synthesised with 2-bromopropanenitrile (**20**) and the *t*-Boc derivative (**21**) gave primary amine functionality on deprotection with $LiALH_4$ reduction and trifluoroacetic acid (TFA) under mild conditions, respectively.

Removal of the terminal halogen is required before the deprotection to give amines, carboxylate salts and thiols, as these groups are known to undergo nucleophilic substitution with organohalogens.[56]

The synthesis of telechelic polymers is possible through the combination of α and ω-functionalisation[68] and by post ω-functionalisation of a polymer produced by bis halofunctional initiators. Chain coupling of α functional polystyrene using atom transfer radical coupling (ATRC) has produced hydroxyl telechelic polystyrene[69] as well as carboxyl and aldehyde telechelic.[70] This procedure works by terminating two active propagating chains by combination in the absence of monomer, and relies on their preference to combine as opposed to disproportionating. Telechelic purity is limited by the ratio of combination:disproportionation.

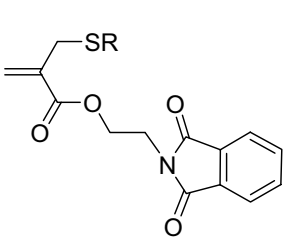
The strategies of end-functionalisation of ATRP polymers is thoroughly discussed in a review by Coessens *et al.*[71]

2.2.4 Reversible addition-fragmentation chain transfer (RAFT)

Living radical polymerisations based on degenerative or reversible transfer are the most dynamic by nature since the number of radicals in these systems is determined by the addition of initiator, similar to conventional free-radical polymerisation. The term “degenerative” refers to the fact that there is no effective change in the overall energy of the process, the radical being transferred from one chain to the other and the effective number of radicals

remaining constant. Examples of reversible (degenerate) transfer exist in the work with alkyl iodides (*e.g.* 1-phenylethyl iodide) to mediate the polymerisation.[72,73] More recently organotellurium mediated radical polymerisation (TERP)[74] has been shown to be an example of degenerative transfer (a mixture of reversible transfer and dissociation-combination), able to polymerise (meth)acrylates and styrene with excellent control.

Allyl sulphides, although not showing true reversible characteristics, also work under an addition-fragmentation mechanism but are normally used to synthesise macromonomers or to introduce end-functionality, as has been done by Meijs *et al.*[75] with a phthalimido functional allylic sulphide (**23**) and could equally be done with (**24**) to potentially synthesize amino end-functional polymers. Equally, allyl bromide has been used to produce α-bromo functionalised macromonomers from the α-bromo methacrylate, in emulsion systems.[76]



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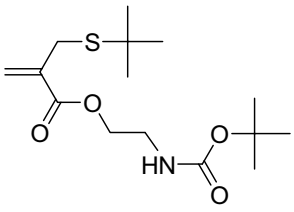
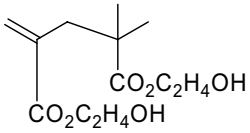


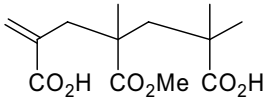
24

Macromonomers, oligomeric chains terminated with a reactive carbon-carbon double bond, were the first to be used as RAFT agents (Scheme 2.8). The macromonomers were usually synthesized by the use of cobalt complexes[77-79] in catalytic chain transfer (CCT) of methacrylates,[80] these macromonomers could be made to homo- or copolymerise under certain conditions but were found to behave mostly as chain transfer agents in an addition-fragmentation type mechanism.[81,82] Since macromonomers demonstrated low chain transfer activity, only starve feed conditions allowed the transfer reaction to compete with the monomer propagation rate, giving such polymerisations a living character and allowing for block and graft copolymer formation.[83] Hydroxyl and acid end-functional polymers have be synthesized with the use of functional di- (**25**) and tri- (**26**, **27**) macromonomers.[84] Macromonomers inherently having

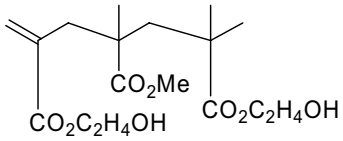
reactive double bonds can be synthesized to reasonable purity by various methods including CCT[85] and by high temperature polymerisation with chain transfer to polymer,[86] however, more reactive transfer agents were required to give full control.



25[84]



26[84]



27[84]

These were found in sulphur based transfer agents, structures similar in many ways to the macromonomers and earlier iniferters but with (depending on structure) superior transfer constants because of the high reactivity of the thiocarbonylthio group towards the propagating radical. The potential of these xanthates in organic synthesis was recognized with the Barton-McCombie process.[87] Zard and co workers[88,89] further developed this chemistry. In 1998, the CSIRO group discovered that a range of the thiocarbonylthio compounds (dithioesters, trithiocarbonates, dithiocarbamates and xanthates) could be used to control polymerisation and provide the characteristics of living polymerisation.[90,91] At about the same time Charmot, Zard and coworkers developed the use of xanthates to control polymerisation and initially called the process macromolecular design by interchange of xanthate (MADIX) agents.[92]

It must be understood that the mechanism of RAFT is significantly different from that of NMP and ATRP, as it does not rely on reversible termination of the propagating radical or the influence of deactivation-activation and the persistent radical effect, to determine the rate of polymerisation. Nor does RAFT provide the initiating radicals as is provided by the alkoxyamines for NMP, or the organo-halo compound in ATRP. RAFT imparts its control through reversible chain transfer steps by which it sets up deactivation-activation equilibria. The reversible transfer mechanism can be broken up into two parts, see Scheme 2.8:

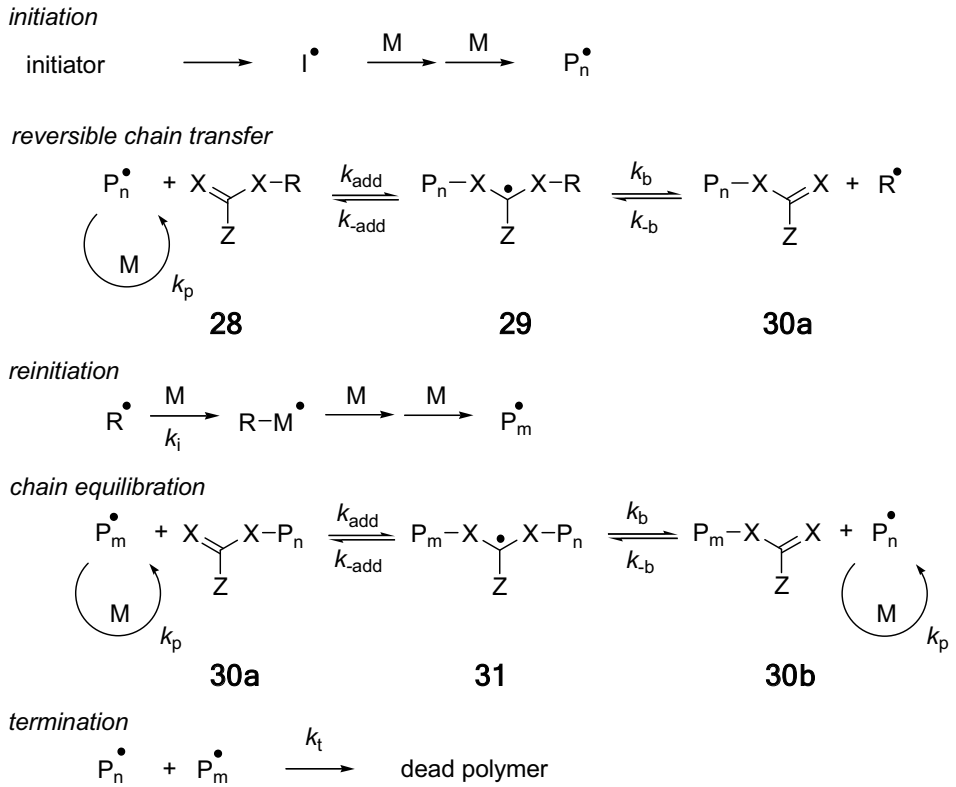
Firstly the reversible chain transfer or pre-equilibrium step, where the RAFT agent is transformed into a polymeric macroRAFT agent. This occurs after

initiation with the propagating radical ($P_n^{\bullet}$) adding to the thiocarbonylthio of **28** forming the intermediate (**29**) which fragments off the leaving/reinitiating group ($R^{\bullet}$) leaving the macroRAFT (**30a**). Radical ($R^{\bullet}$) reinitiates monomer forming the new propagating radical ($P_m^{\bullet}$).

Secondly, when the initial RAFT agent is consumed, the chain equilibration mechanism becomes the dominant step, where ($P_m^{\bullet}$) adds to (**30a**) giving the intermediate (**31**) which can rapidly equilibrate between (**30a**) and (**30b**), setting up a fast equilibrium between propagating radicals ($P_n^{\bullet}$ and $P_m^{\bullet}$). The dormant macroRAFT agents thus provides equal opportunity for all propagating radicals to grow, thus narrowing the chain length dispersity and providing the greater majority of chains with a thiocarbonylthio ω-end-group as well as an α-R group.*

Radicals are not formed or lost in the reversible transfer steps and thus a source of free radicals is required to initiate and maintain the polymerisation. They also account for the formation of dead polymer, as is the case for the kinetics of conventional radical polymerisation.

* Some of the α end-groups will be initiator derived



Scheme 2.8. General mechanism of RAFT polymerisation.

It is a process that is simple to perform, is robust and has minimal sensitivity to impurities.[3] It can be used with a large range of monomers, in a wide range of solvents and reaction conditions, providing control over molecular weight and at the same time giving very narrow polydispersities (<1.1) and can give end-functionality to the polymer.[93-95] The RAFT moiety, which stays dormant, can also be further re-activated for chain extension and block synthesis and complex architectures.[17,96] This property may be used in end capping a polymer with a functional monomer or a short block of functional monomers.[18]

2.2.4.1 Choice and design of RAFT agent

Since the advent of RAFT in the late 90s a wide variety of RAFT agents have been designed and tested under varying conditions and with a broad range of

monomers, with different degrees of success over the control of polymerisation. The initial successful thiocarbonylthio RAFT agents (ZC(=S)SR) were based on dithioesters,[91] with later arrivals of trithiocarbonates, dithiocarbonates (xanthates) and dithiocarbamates. [17,90,94,95,97] The RAFT agent's effectiveness at LRP is strongly dependant upon the properties of the R and Z groups and on the monomer being polymerised. It is also important that the RAFT agent has a C=S bond reactive to radical attack and the radical leaving group (R•) should efficiently reinitiate polymerisation (Figure 2.6). The intermediate **29** should partition in favour of products and both intermediates **29** and **31**should fragment rapidly.[98,99]

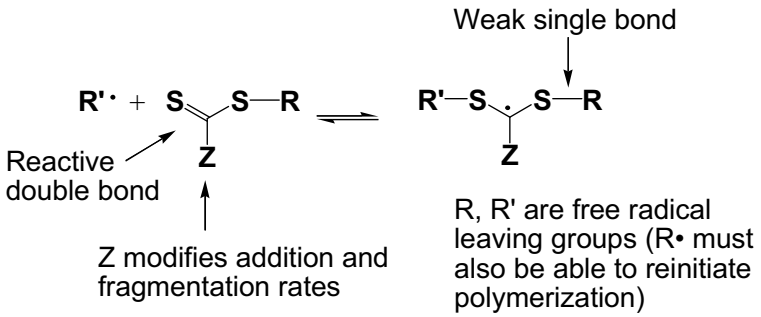


Figure 2.6. Important structural features required for a successful RAFT agent.

The radical leaving/reinitiating group R and the activating/deactivating C=S modifier group Z should be chosen to tune the RAFT agent to suit the polymerisation conditions.[100] Efficient fragmentation for the R group is observed in substituents that are better homolytic leaving species than the attacking radical $P_n^{\bullet}$. For example where R is a benzyl (-CH_2Ph), the leaving benzyl radical is a better leaving group than the styryl or acrylyl propagating radical, but a poor leaving group with respect to the methacrylyl radical, as is observed with the almost inert activity with these types of RAFT agents in MMA polymerisation.[98,101] Electron withdrawing groups, radical stabilizing groups and sterically bulky groups on R also enhance the rate of fragmentation of intermediate **29**, *e.g.* a triphenylmethyl radical would make a excellent leaving group. However, the radical (R•) must also be able to reinitiate polymerisation, therefore, the triphenylmethyl radical being a poor reinitiator would make it a bad choice as an R group. A more suitable group would be a cyanoisopropyl R group, as it contains an electron withdrawing group, it is a radical stabilizing

tertiary species and reinitiates polymerisation well. A general guideline for the choice of R groups is illustrated in Figure 2.7.

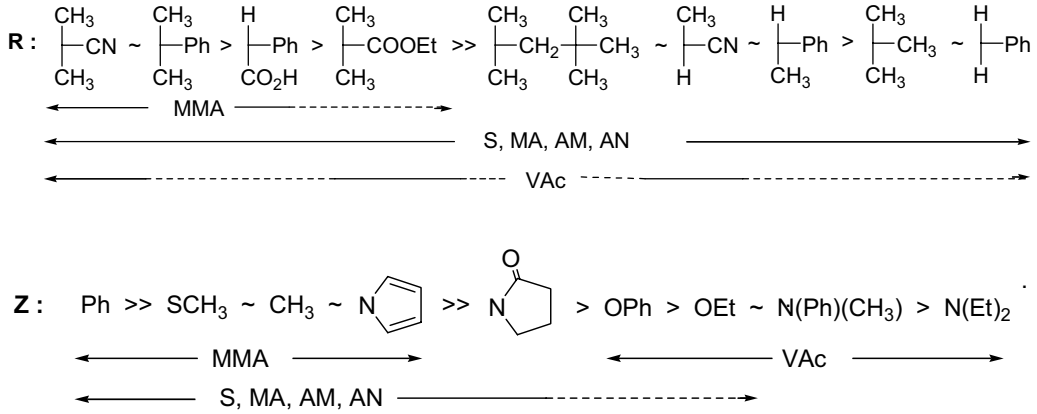


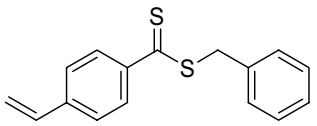
Figure 2.7. Guidelines for the design of RAFT agents, selection of appropriate R and Z groups. Z (L→R), addition rates decrease and fragmentation rates increase. R (L→R), fragmentation rates decrease. Dashed lines indicate reduced control. AM – acrylamides, AN – acrylonitriles, MA – methyl acrylates, MMA – methyl methacrylates, S – styrenics, VAc – vinyl acetate. Reprinted with permission.[3]

The Z group strongly influences the rate of free radical addition on to the C=S in species **28** with electron withdrawing groups enhancing the reactivity of the RAFT group.[99] This is observed in the difference between the relatively low activity for *O*-alkyl xanthates or *N*,*N*-dialkyl dithiocarbamates which can form more easily the zwitterionic canonical forms, compared with the markedly more active forms which have an oxygen or nitrogen lone pair less available for delocalization by being next to an electron withdrawing group of part of an aromatic system. Considering these options and the trend revealed in Figure 2.7, the majority of (meth)acrylate, (meth)acrylamide and styrenic systems could be controlled with a single RAFT agent (a tertiary cyanoalkyl trithiocarbonate or dithiobenzoate) and vinyl monomers could be controlled with another RAFT agent (a cyanoalkyl xanthate). Different RAFT agent designs are dictated by: desired end-functionality, polymer architecture, ease of preparation and compatibility with the reaction medium.[3,102]

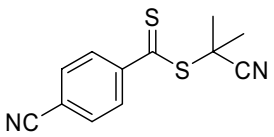
Reviews on RAFT have been published by Davis *et al.*[103], Rizzardo *et al.*[100] and a recent review by Moad *et al.*[3] fully describe the intricacies of RAFT polymerisation.

2.2.4.2 ω- Functionalisation

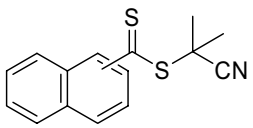
The RAFT polymerisations' great advantage over other LRP processes is its wide compatibility with functionalities, making it ultimately suitable for the synthesis of end-functional polymers. By incorporating the functionalities into either (or both) the R and Z groups of the RAFT agent, the key feature of RAFT living polymerisation is that the thiocarbonylthio group on the initial RAFT agent is retained in the final polymer product (*i.e.* macroRAFT agents). The synthesis of ω functional polymers with RAFT can be approached in two ways: design of a functionality into the Z group or by transformation of the thiocarbonylthio group.



32[104]



33[105]

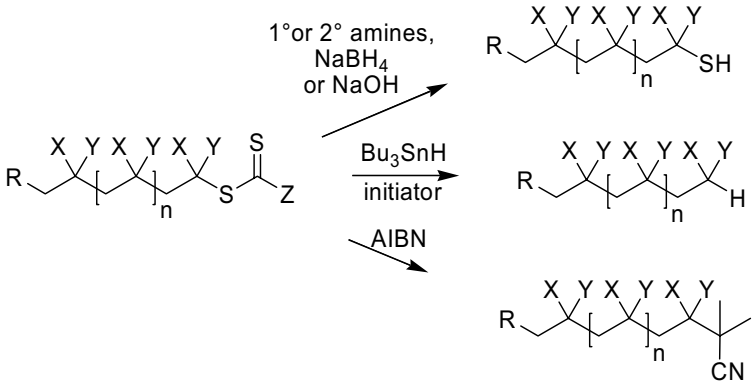


34[105]

Functionality brought into the Z group does have the inherent disadvantage in that there is a potential lability of the C-S bond in the corresponding RAFT end-group under certain conditions (discussed below) with consequential loss of end-functionality. This would explain the limited amount of examples of functional Z groups as compared to the numerous approaches via the R group.

The majority of Z functionalisation examples are from the work on star polymers[96,106,107] although other functionalities have been used, *e.g.* a styrenic functional (**32**), aromatic cyano (**33**) and a naphthyl (**34**). The lability of the C-S bond in the Z group does allow for the opportunity to study the polymerisation kinetics of systems where the growth of polymer chains cannot be directly measured, unless cleaved.

Transformation of the post polymerised thiocarbonylthio group can be performed in a variety of ways, both radical and chemical. This is analogous with the example given previously with the radical-induced reduction of the terminal halo group of the ATRP polymer with tri *n*-butyltinhydride (to provide a hydrocarbon end-group) (section 2.2.3.1). This too has been used to remove the thiocarbonylthio group in RAFT polymers.[108,109] Similarly, radical exchange[98] has recently been used as a means of changing the functionality of the Z group, where an initiator is used to displace the thiocarbonylthio-Z group.[110] Of these existing processes, only the radical-induced reactions are known to provide desulphurization by complete end-group removal/transfer. Treatment with oxidizing agents (*e.g.*, NaOCl,[91] H_2O_2,[91] tBuOOH[111]) are less controlled methods of removing/transforming the end-groups resulting in various (partially)oxidized end-groups. UV irradiation also gives limited purity of the end-group functionality.[93]

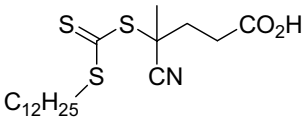


Scheme 2.9. ω-functionalisation by Z group transformation.

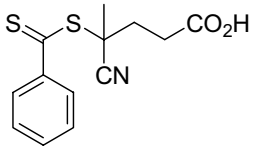
Thiocarbonylthio groups are known to be transformed by reacting them with nucleophiles (*e.g.* amine,[17,91,104,106,112-114] hydroxide,[115,116] borohydride[117,118]) providing a thiol end-group, as highlighted in Scheme 2.9. Thiol end-group oxidation to the disulphide causes high molecular weight impurities (chain coupling). This has been found to occur under aminolysis conditions and can be minimised by carefully degassing reaction media or by the use of sodium dithionite.[119] Chemistry on compounds containing thiocarbonyl groups reacting with nucleophiles has been reviewed by Castro.[120]

2.2.4.3 α- Functionalisation

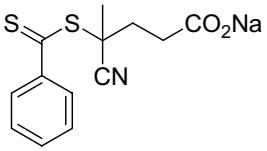
Several functional RAFT agents with the functionality in the R group have been synthesized and used successfully. Unprotected functionalities reported in the literature include: carboxylic acid (**35**, **36**), sodium carboxylate (**37**) and hydroxyl (**38**). These RAFT agents can further be modified to form other functional RAFT agents like (**39** and **40**). Primary or secondary amine end-functional polymers cannot be directly synthesised as they would undergo facile reactions with thiocarbonylthio groups, these would have to be in a form of a protected group like a 9-fluorenylmethyl carbamate (Fmoc), *t*-butyl carbamate (*t*-Boc) or a phthalimide with subsequent deprotection.[121]



35[3]



36[91,93,122]



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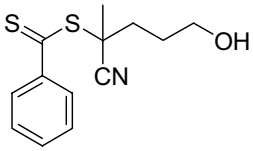
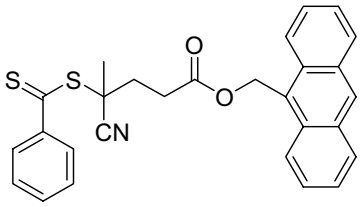


38[91,93,119]



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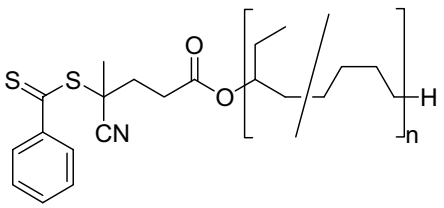
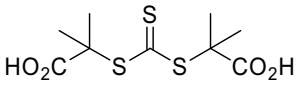


40[124]

Of interest in regards to the use of RAFT in polyolefin chemistry, de Brouwer *et al.*[124] has applied the RAFT technology in preparing a poly[(ethylene-*co*-butylene)-*block*-(styrene-*co*-maleic anhydride)]. This was achieved by first modifying commercially available ethylene/butylene copolymer, (BEP) Kraton L-1203, into the polyolefinic macroRAFT agent (**40**), which was then used in controlling the polymerisation of an equimolar mixture of styrene and maleic anhydride monomer to give the block copolymer.

It must be remembered that initiation and termination steps are responsible for a fraction of chain ends and if the aim is to achieve a very high degree of end-functionality, an initiator should be chosen with the same functionality as the R group of the RAFT agent.



41[125]

The synthesis of telechelic polymers by RAFT can be approached by applying bis-functional trithiocarbonate RAFT agents, Lai *et al.*[125] had success with polymerising styrene, acrylates and acrylamides with **41**, however, methacrylates were not controlled and yielded broad polydisperse polymers. This can be attributed to the 2-carboxy-2-propyl radical being a poor leaving group with respect to the poly methacrylate propagating radical as is observed with the corresponding ester (2-ethoxycarbonyl-2-propyl radical).[98] The bis-acid functional macromonomer (**26**) could in principle also be used to synthesize telechelic carboxy poly(methyl methacrylate)s, however, these macromonomers have low transfer constants (~0.3 at 60 °C)[84] and can only afford narrow polydisperse polymers in a starve feed batch process.[81,82]

Living radical polymerisation has currently established itself as a dominant technique with versatility and precise control over well defined polymer structures. The three popular systems, NMP, ATRP and RAFT, provide the polymer and material scientist a “tool box” from which to tackle different approaches for designing polymers with novel architectures. However, these “tools” are not without their limitations and shortcomings. The Holy Grail in the field of free radical polymerisation has yet to achieved, this being the combined control over architecture and also stereochemistry.

2.3 Reactive extrusion – grafting of polyolefins

Polyolefins have found numerous applications, from cheap bulk commodity plastics like packaging materials and thermoplastic elastomer rubbers (ethylene,

propylene, butadiene (EPM and EPDM), to high value added materials in coatings and high tensile strength fibres. Polyolefin's greatest advantage is its ease of processing, chemical inertness and low solubility, allowing its application in storage of chemicals and solvents, non surface fouling and in food contact products. This is due to the non polar hydrocarbon polymer chains lacking any polar interactions as well as its low reactivity to forming covalent bonds. However, this property also complicates its adhesion to substrates and miscibility with other polymers. The standard method for overcoming this is by improving the hydrocarbons interfacial tension through the addition of functionality by grafting, block formation or end-functionalisation.[126] Small amounts of functionality (0.5-2 wt%) already increases interactions with other functional polymers or materials dramatically, while the polyolefins retains most of its original properties.[127,128]

Two main ways of functionalising polyolefins is by: (a) free radical grafting of functional monomers onto the backbone, usually performed by reactive extrusion; or (b) through block or random copolymerisation of suitable functional monomers.[129]

It is worth noting that although reactive extrusion has been used in industry and academia for over 30 years, until recently, much of the knowledge has been kept "in-house".[129] The recent drive in understanding the extrusion process has been reflected by the increase in the number of publications. Kowalski[130] and Brown[131] give a review of the relevant research done in industry and a summary of the patent literature, respectively. A comprehensive survey of the reactive extrusion field can be found in the volumes edited by Xanthos[132] and Al-Malaika[133] giving an overview of the work done in the literature and patents till the early 1990's, and a recent volume on functionalisation of polyolefins by Chung.[134]

Some of the more important advantages of reactive extrusion over alternative processes with regard to polyolefin graft copolymers include:[129,135]

a) no or limited use of solvents,

b) simple product isolation,

c) short reaction times,

d) continuous process,

Some potential disadvantages or difficulties associated with reactive extrusion include:

e) the need to achieve intimate mixing of reactants and substrates,

f) the high reaction temperatures necessary to form a polymer melt,

g) polymer degradation/crosslinking that may accompany the melt.

h) limited control over the free-radical polymerisation process.

In particularly for the case of polyolefin extrusion, the environmental and economic benefits of extrusion far outweigh the disadvantages.

Free-radical grafting[136] in the melt environment usually involves the polymer substrate, vinyl monomer to be grafted and the free radical initiator. The primary free-radicals are generally generated by thermal decomposition of the initiator at melt temperatures. The radical formed preferably undergoes transfer by hydrogen abstraction from the polymer backbone forming a macroradical, but can also react with the unsaturated group of the vinyl monomer producing a monomer radical which undergoes further reactions with monomers present, with undesirable homopolymer formation. This propagating monomer/oligomer/polymer radical usually has limited hydrogen abstracting capacity and thus rarely grafts onto the polymer backbone.

With the macroradical formed it can continue to react in three ways dependant on the structure: chain scissioning (common with PP), crosslinking (common with HDPE) and grafting (under the right conditions in presence of monomer). When the macroradical reacts with a monomer, the monomer is grafted and effectively forms a small branch. This branched macroradical may continue to react with more monomers forming a longer branch, or it may hydrogen abstract with the same or another polymer backbone forming a new macroradical, which

can repeat the grafting cycle. It can also terminate in several possible ways, giving crosslinking as part of the product.

2.3.1 Maleation of polyolefins

Polyolefins (PO) are the most popular and favoured substrates for reactive extrusion experiments and this is largely attributed to their low cost, ready availability and large commercial applications. This, accompanied with a reactive bulk commodity chemical like maleic anhydride (MAh)[137] makes for a high performance-cost effective product, improving the property of polyolefins and more importantly allowing for further reaction from the maleic anhydride grafted group.

There are a number of interdependent factors that govern grafting efficiency, yield and control of the nature of the grafted product. The most important factors in reactive extrusion are:[129,132,135]

Mixing efficiency – determined by screw design, temperature, pressure, solubility of the initiator/monomer and the polymer substrates rheological properties. This factor is of critical importance not just to the homogeneity of the final product but to the success of any experiment. The effect of the mixing efficiency will determine the local reactant concentration levels and this will effect the formation of homopolymer and grafted oligomer formation.

Temperature – higher processing temperatures will generally favour polyolefin degradation, reduce initiator half-life, modify the specificity of reactions and will also influence solubility and rheological parameters.

Pressure – high pressure can lead to enhanced solubility of monomer and/or initiator in the polyolefin substrate and can lead to less degradation by chain scission.

Residence time and residence time distribution – determined by throughput rate, screw speed, screw design and screw length to diameter ratios (L/D).

Vacuum venting – removal of unused monomers, solvents, coagents and other volatiles by the application of vacuum to the polymer melt.

Polymer – the type of polyolefin: ethylene propylene (EP), low density poly ethylene (LDPE), linear low density poly ethylene (LLDPE), high density poly ethylene (HDPE), polypropylene (PP), metallocenes. Its molecular weight, molecular weight distribution, end vinyl content, residual catalyst, additives and associated rheological parameters need to be taken into account for processing conditions.

Monomer – monomer concentration, solubility in polymer substrate, volatility, reactivity towards initiators and substrate derived radicals and susceptibility toward homopolymerisation. High monomer concentrations can result in improved grafting yield but can also result in homopolymerisation due to phase separation.

Initiator – half-life, concentration, solubility, volatility, partition coefficient in polymer and monomer, reactivity and specificity of the initiator derived radicals, side reactions, initiator derived by-products and also the toxicity of the initiator.

Coagents – comonomers, transfer agents, solvents inhibitor and extraneous additives that are added to improve grafting and reduce crosslinking/scissioning.

Screw/extruder design – selection of screw design is critical in achieving the required effectiveness to suit the process required. In a modular designed reactive extruder the selection, placement and arrangement of screw elements and barrel sections largely determines the mixing efficiency, residence time, shear heating, pressure and effectiveness of volatilisation. The use of a single screw, co and counter rotating screws, full intermeshing, partial intermeshing, fully self wiping, partially self wiping, backmixed drag flow extruder,[138] etc. all effect the outcome of the processing variables. This particular topic has been discussed at greater length in the literature.[132,133,139]

A review on the synthesis of graft copolymers by reactive extrusion by Moad[129] provides a comprehensive summary of the work done in the field of polyolefin reactive extrusion, as well as some of the more important papers on grafting to

HDPE,[140-142] LDPE,[143] LLDPE[135,140,142,144,145] and EP copolymers.[140,142] The paper by Ganzeveld and Janssen[141] highlights well the effect of changing initiator level, monomer level, screw speed, barrel temperature and mixing on maleic anhydride grafting levels onto HDPE in a twin screw extruder. Emphasising the need for good mixing, increasing the initiator level below the level at which crosslinking occurs and increasing the number of fully filled chambers in the extruder, will contribute to increased grafting. However, it must be noted that increasing the screw speed will increase the effect of mixing, and thus grafting, but will give the competitive effect of reducing the residence time. Machado *et al.*[146] monitoring of maleic anhydride grafting onto polyolefin (PE, EP and PP) along the extruder length also emphasised the use of appropriate levels of peroxide to MAh and the introduction of peroxide into the extruder after the MAh has had a chance to dissolve into the molten PE matrix. It was also noted that although PE is prone to crosslinking under grafting conditions, a sufficiently long enough screw with an appropriate design would degrade the crosslinked network after most of the peroxide is consumed.

Work on the maleation of polyolefins, conventional linear low density polyethylene and a metallocene ethylene-*co*-butene copolymer, by reactive extrusion has been touched on by Bray *et al.*[135] and Gaylord *et al.*[145] A paper published by Premphet *et al.*[147] describes grafting work onto an elastomeric ethylene-*co*-octene copolymer in a twin screw extruder attaining only 1% grafting of MAh while effectively reducing gel formation by using dimethyl formamide. Bray *et al.*[135] focussed on attaining high grafting efficiency (up to 85%) with minimal crosslinking, this was achieved by passing a previously maleated material (non-vacuum vented to retain unused MAh) through another MAh grafting cycle. The first pass achieved 67% efficiency (2.3% grafted) with the second pass achieving 109% efficiency (3.6% grafted) (value greater than 100% because of conversion of unreacted MAh left from first pass). It was suggested that the first addition of MAh compatibilised the monomer for the second addition. Strait *et al.*[148] reported grafting efficiencies of up to 70% and between 0.75 and 2.0 w% of the graft copolymer comprising MAh, by introducing a maleic anhydride/2-butanone solution into the reactive extruder through liquid injection, also producing a product of low yellowness

discolouration and odour. This procedure was also utilised by Bray and coworkers[135] in their grafting experiments. On the contrary Gross *et al.*[149] increased their grafting efficiency by multi point addition of maleic anhydride (dissolved with peroxide in acetone). Acetone was also considered to be the preferred stripper agent for removing volatiles.

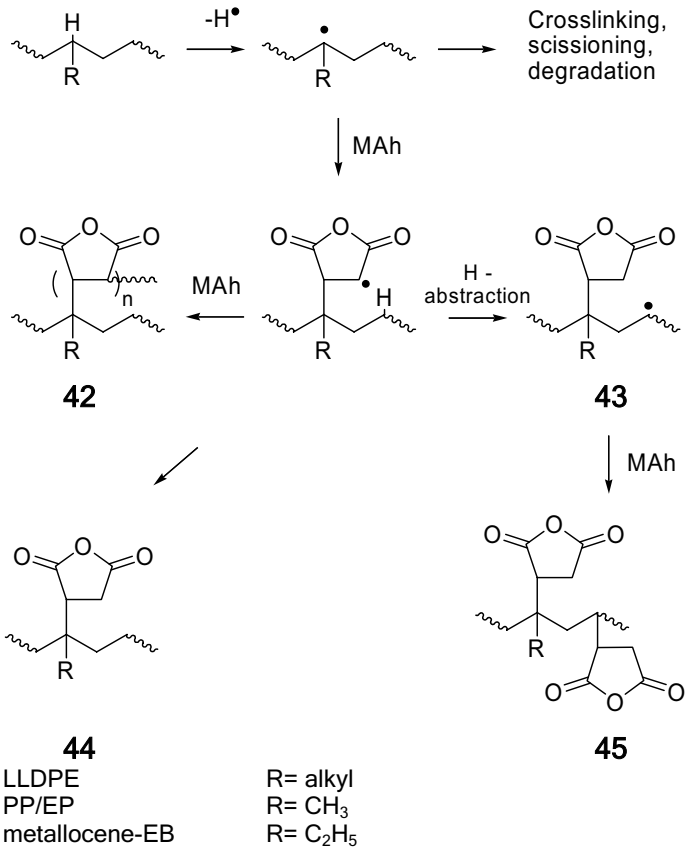
Crosslinking has been shown in earlier studies[130,150] to accompany grafting to some degree and was noticed by gel formation in the melt and further showing up as insoluble residues. The work emphasises greater mixing, reagent introduction and control over initiator in overcoming crosslinking. Machado *et al.*[142] point out that the polyolefin structure effects crosslinking, chain scissioning and grafting levels: polyethylenes favouring crosslinking, polypropylenes favouring scissioning, ethylene/propylene rubbers show varying degrees of both scissioning and crosslinking. Also maleic anhydride graft levels were observed to decrease with propene content greater than half.

It is generally believed that maleic anhydride grafting starts with hydrogen abstraction of the polyolefin backbone by an alkoxy radical, leaving a radical open for the maleic anhydride to react onto. Heinen *et al.*[140] has unambiguously established with thorough ^{13}C NMR studies on ^{13}C enriched MAh grafted onto PE, PP and EP copolymers, that maleic anhydride reacts predominantly onto the methine site rather than the methylene site and forms both oligomer blocks of ~2 units (**42**) and single units (**44**, Scheme 2.10) for HDPE and LDPE. Single units were found to occur predominantly with EP with higher propylene content and occurred exclusively with PP. However, commercially MAh grafted polyolefins cannot be easily characterized by ^{13}C NMR as it is not sensitive to non-labelled MAh units at typically low grafting levels of ~2 wt%. Bray and coworkers[135] found from FTIR analysis that the C=O stretch position for the maleic anhydride grafted LLDPE to be characteristic of oligo-maleic anhydride (**42**) and not of a single succinic anhydride group (**44**). De Roover *et al.*[151,152] concluded that a substantial amount of MAh grafts in PP were found to be oligomeric, based on the difference in oligomer signals at 1784 cm^{-1} and single succinic units signals at 1792 cm^{-1}. However, single succinate unit grafts (**44**) were reported by Premphet,[147] applying the De Roover's FTIR technique.

Russell *et al.*[153] and Sipos *et al.*[154] suggested a mechanism for clustered single unit grafts (**45**), through intra-molecular hydrogen abstraction, based on their work with polyethylene model substrates (squalene, eisocosane) and peroxide induced grafting.

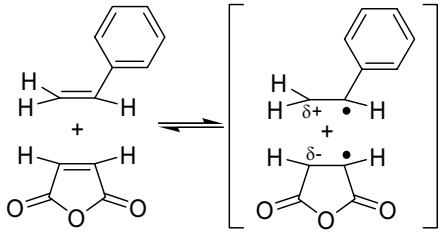
FTIR determination of single units and oligomers is generally considered unreliable as the signals positions of mono- and oligo-succinics units are close with regards to the broadness and complexity of the observed signals, also illustrated by the additional contradictory conclusions on the nature of MAh grafts by the groups performing these studies.

The characterization of the succinic moiety clustering of two different commercial maleated EP has been investigated by fluorescence labelling techniques.[155] Singly or double labelling with 1-naphthalenemethylamine (Np) and/or 1-pyrenemethylamine (Py) allowed the determination of the amount of clustering and spacing to be measurable between the two samples. The Np/Py energy transfer pair allows the use of fluorescence resonance energy transfer (FRET) to be used as a "spectroscopic ruler", measuring the distance between the labelled MAh grafts in a cluster. Solution FTIR spectroscopy verifies the quantitative coupling of amines with the grafted anhydrides.



Scheme 2.10. Maleic anhydride grafting onto polyolefins.

It should be remembered that when grafting onto polyolefins, peroxide derived radicals have been shown to have a greater tendency to abstract hydrogens from the polymer backbone compared to azonitrile type initiators.[129,136] Furthermore, azonitriles usually have a very short half-life and won't find the time to react with the substrate under the residence time and high temperature conditions of melt extrusion, with the likely formation of terminated species over propagation/abstraction.



Scheme 2.11. Proposed styrene-maleic anhydride charge transfer complex.

The use of a coagent, like styrene, in increasing the graft efficiency of maleic anhydride onto PP[136] and LLDPE has been studied previously.[144,150] It has been proposed from NMR studies and grafting results that electron rich monomers, styrene in this case, form a charge transfer complex (CTC) (Scheme 2.11) with maleic anhydride by monoelectronic transfer from the vinyl group onto the maleic anhydride double bond.[136] The result is that the electron poor, symmetrical character of the double bond of maleic anhydride is reduced, increasing its grafting reactivity for macroradicals. The greater rates of copolymerisation of these CTCs compared to the homopolymerisation of MAh can result in longer chain grafts, increasing the level of MAh grafting in localised parts of the polyolefin chain. However, the efficient trapping of radical sites on the macroradicals results in an increased number of grafts along the chain. All of these are considerations for the further reaction of the maleic anhydride groups on the polyolefin chains.

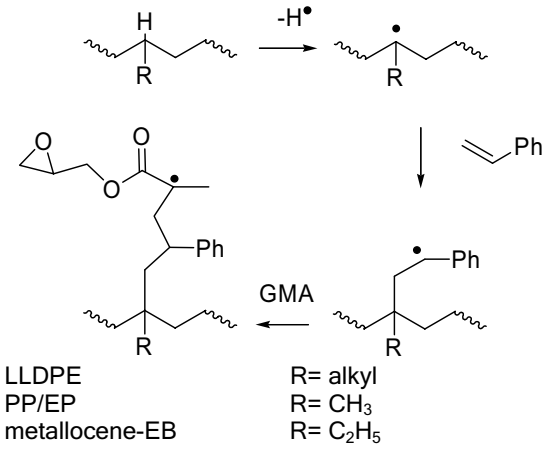
2.3.2 Grafting of glycidyl methacrylate onto polyolefins

Glycidyl methacrylate (GMA) modified polyolefins can, as in the case of maleic anhydride, improve the property of the base polyolefin and allow for both electrophiles and nucleophiles to react onto the epoxy group. Because of this versatility, GMA grafting under melt conditions onto HDPE,[143,156-158] LDPE,[143] LLDPE[156] and EP[143,159-161] has been investigated by several groups.

Work has also been done in improving the grafting of GMA onto polyolefins by using styrene as a coagent.[160] The grafting reactivity of GMA alone is poor, however with styrene, as in the case of MAh, its grafting levels are improved.

Unlike styrene-MAh grafting, where a charge transfer complex is proposed to form (Scheme 2.11), with GMA, styrene acts as a mediator as it is more reactive towards macroradicals (Scheme 2.12). Once a styrene unit is attached, the resulting styryl radical is more favourable for GMA monomer to add on to, the styrene effectively forming a bridge between the PO and GMA.[136]

Cartier *et al.*[162] have reported grafting yields onto HDPE in a batch mixer increasing to 3-fold and conversions of grafted GMA to the polymerised species over 80% using styrene as a coagent. Grafting of GMA was reported to be lower in a comparison experiment in a twin screw extruder, this was reasoned to be caused by a lower residence time in the extruder system compared with air induced grafting in the non-nitrogen blanketed batch mixer. Their earlier batch mixer/twin screw extruder work on ethylene-propylene rubber showed similar grafting levels as with HDPE, with GMA monomer to grafted species conversions of >80%.[160]



Scheme 2.12. Styrene-mediated radical grafting of glycidyl methacrylate (GMA) onto polyolefins.

Cartier *et al.*[162] disclosed in their patent that DHBP was favoured over BPO for GMA grafting at 180 °C. On the contrary it has been observed that BPO is more effective at grafting GMA than DHBP at lower temperatures in a twin screw extruder.[163] It is likely that in the case of Cartier *et al.*[162] the extruder melt temperature was too high with the result that the majority of the BPO initiator

was spent before it reached the grafting zone, effectively giving it a false lower grafting efficiency.

2.3.3 Analysis of grafted polyolefins

Analysis of grafting levels of MAh or GMA in polyolefins can be troublesome mainly due to the polyolefins low solubility in common solvents (with the exception of some short branched metallocenes) and also the low grafting levels commonly achieved with both MAh and GMA in the melt. Except for the studies on model compounds, little accurate measurement is achievable with either ^{1}H or ^{13}C NMR. Acid-base titration would normally have to be performed on hot solutions of polyolefins in an appropriate solvent making the technique difficult and consequently of low reproducible accuracy.[129]

The majority of MAh and GMA graft level quantification and identification to date is done using FTIR spectroscopic methods. Quantitative spectroscopic analysis are generally measured on melt pressed films, the level of grafted monomer is determined by the intensity of the C=O infrared absorption bands of MAh (1784-1792 cm^{-1}) or GMA (1730 cm^{-1}) relative to a band that is attributable to the PO backbone. A calibration curve based on standards with known concentrations of the functional monomer is then used to convert the absorption band intensities to concentrations. It must be remembered that the intensity and position of the band used as the PO reference band will depend not only on the type of PO but also on the grade of PO.[129,135,151,152]

Characterization of maleic anhydride grafted onto EP by fluorescence[164] and verification of the quantitative coupled amine functionalised chromophore by solution FTIR[155] has allowed for an accurate measurement of grafting levels and grafting microstructure. The fluorescence/UV work illustrates the rapid quantitative reactivity of amines to maleic anhydride groups attached to a polymer backbone, a reaction which is exploited in interfacial reactions of amine end-functional polymers for interchain grafting (section2.4).

2.4 Graft copolymers

Besides the block copolymers, mentioned in the previous sections, as examples of segmented polymers, graft copolymers provide another approach to the synthesis of elastomeric copolymers. The grafted functional side chains in the graft copolymer provide the polyolefin with the required interactive properties, these properties are tuneable by the number of grafted chains (n) and the molecular weight of the chains (Figure 2.8). The desired polyolefin properties are usually retained if the number of grafts (n) and the chain lengths are kept below a critical point. If the pendant chain length is sufficiently long, phase separation occurs and new properties are observed.[165]

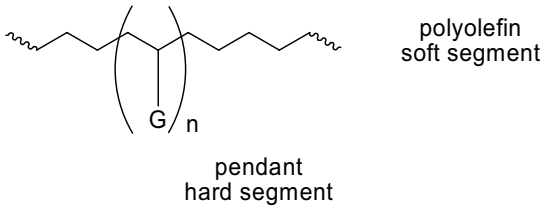


Figure 2.8. Graft copolymer represented by a soft polyolefin backbone with, on average, n random grafted (G) hard segment side chains.

The resultant polyolefin graft copolymers usually serve as effective interfacial agents (*e.g.* polyolefin blend compatibilisers) but have recently also gained greater interest, along side with other types of copolymers, in the control over nano-structured blend morphologies (Figure 2.9) and resulting applications.[19]

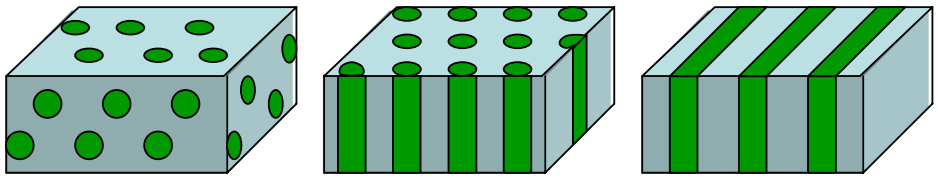


Figure 2.9. Morphology changes with copolymer composition changes.

A review by Schellekens and Klumperman[166] on polyolefin block and graft copolymers highlights the three methods of grafting: grafting-through, grafting-from and grafting-onto as: *grafting-through* defined as the copolymerisation of the polyolefin monomer with a macromonomer, *grafting-onto* defined as attaching growing polymer chains onto the polyolefin backbone, and *grafting-*

from is growing the polymer off of the polyolefin backbone (*i.e.* employing LRP to achieve the controlled grafting). The work described in synthesizing graft copolymers in this thesis is mainly concerned with the "grafting onto" approach (Scheme 2.13) as it lends itself easily to scaled reactions on a reactive extruder.

Macosko and coworkers have investigated the reactive blending kinetics of a range of mid and terminal functional polymer systems. General conclusions from their work can be summarized as follows:[167-169]

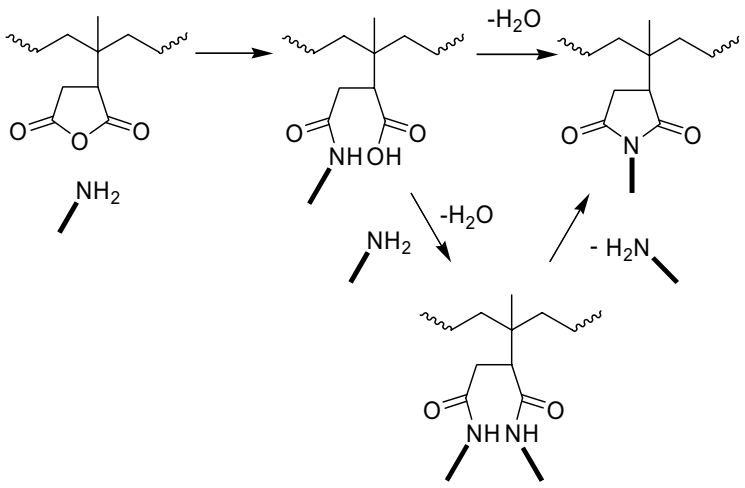
a) Decreasing reactive systems; aliphatic amine/anhydride >> aromatic amine/anhydride > acid/epoxy > acid/oxazoline > amine/epoxy > hydroxyl/(anhydride or acid) > acid/amine.

b) Only the amine/anhydride and acid/epoxy giving significant conversion within 2 minutes.

c) Terminal-terminal functionalities reacted faster than mid-terminal, the mid functionality being partially shielded by the polymer chain.

d) Flow was also found to increase the interfacial rate constant dramatically in a heterogeneous blend than over the static system.

The reactions between aliphatic amine end-functional polystyrene and anhydride end-functional hydrogenated polybutadiene were observed to be rapid (<5 minutes) and conversions high in their melt blending experiments performed in the MiniMAX mixer at 200 °C.



Scheme 2.13. Grafting onto: interfacial succinic-amine coupling reaction.

Several other groups have looked at interfacial grafting of reactive functionalities. Glycidyl methacrylate grafting followed by an interchain coupling reaction in a multistep reactive extrusion process has been performed on a co-rotating, intermeshing twin screw extruder using polyamide (PA6).[170] A polyamide amine functionality reacting with the epoxide group forms the interchain graft junction on the HDPE backbone. Lambla and coworkers also looked at the transesterification of anionically synthesised hydroxy end-functional polystyrenes (PD<1.1) onto ethylene-co-methylacrylate[171] and the grafting of PP with GMA and subsequential interfacial reaction of the functionalised PP with poly(butylene terephthalate).[172] Batch mixer experiments on the hydroxy end-functional polystyrene uncovered that the lower molecular weight polymers ($\overline{M}_n$=1700 and 3000 g mol^{-1}) had a higher reactivity towards grafting than that of the higher molecular weight polymer ($\overline{M}_n$=8000 g mol^{-1}). It was also noticed that the yield of grafting increased with an increase in temperature, increase in mixing speed and the addition of small amounts (1-2 wt%) of hexadecane or 1,2,4 trichlorobenzene, the solvent enhancing miscibility, diffusion and interfacial mixing. The upper critical molecular weight of polystyrene at 8000 g mol^{-1} could be increased in a twin screw extruder, their conjecture being that the Haake batch mixers are considered to be poorer mixing devises as compared to twin screw extruders.

Perego and Albizzati[173] patented a process of obtaining high yields of graft copolymers under melt conditions (single screw extruder) or in solution with maleated PP or PE and using amine or hydroxy functionalised anionic polystyrenes from $\overline{M}_n$=21000-60000 g mol^{-1}. Gallucci *et al.*[143] studied the crosslinkability of PE-*g*-GMA by the use of successful interfacial reaction of hexamethylenediamine and 1,3,5-benzenetricarboxylic acid onto GMA epoxy groups. PE-*g*-MAh was also efficiently crosslinked with the diamine

Oxazoline reactive groups have been investigated for their use in the interfacial chemical bonding in polypropylene and acrylonitrile-*co*-butadiene-*co*-acrylic acid rubber (NBR) under batch mixer conditions.[174] The interfacial reaction through the carboxylic acid group and the oxazoline grafts on the PP giving an amido-ester linkage. The resulting graft copolymer gaining a >13 fold improvement in impact property above the brittle-tough transition (notched Charpy test) and the impact properties were found to be irrespective of the effect of rubber particle size.

Various approaches based on living free radical polymerisation combined with polyolefin chemistry will in the future be applied in the synthesis of well defined graft copolymers, as the field of controlled radical polymerisation advances at a dramatic rate.

Without any doubt the ability to synthesize well grafted polymers, such as polyolefins, with any appreciable success, reproducibility, efficiency and, most importantly, cost effectiveness poses many challenges. Any approach that enables this based on living free radical polymerisation will certainly help to clarify and enrich this area allowing challenges to be overcome and consequently with the realisation of new materials and applications.

2.5 References

1. Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization;* Pergamon, Elsevier Science Ltd: Oxford, U.K., 1995.
2. Flory, P. J. *J. Am. Chem. Soc.* **1937**, *59*, 241-253.
3. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379-410.
4. Rempp, P.; Merrill, E. W. *Polymer Synthesis;* 2nd rev. ed. ed. Hüthig & Wepf Verlag: Basel, Germany, 1991.
5. Szwarc, M. *Nature* **1956**, *178*, 1168.
6. Matyjaszewski; Krzysztof *Curr. Op. Solid State Mater. Sci.* **1996**, *1*, 769-776.
7. Percec, V.; Tirrell, D. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*(10), Special Issue: Living or Controlled?
8. Szwarc, M.; Levy, M.; Milkovich, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 2656-2657.
9. Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982** , *3*, 127.
10. Reghunadhan, C. P.; Clouet, G. *J. Macromol. Sci.- Rev. Macromol. Chem. Phys.* **1991**, *c31*, 311-340.
11. Clouet, G.; Juhl, H. J. *Macromol. Chem. Phys.* **1994**, *195*, 243-251.
12. Turner, S. R.; Blevins, R. W. *Macromolecules* **1990**, *23*, 1856-1859.
13. Lambrinos, P.; Tardi, M.; Polton, A.; Sigwalt, P. *Eur. Polym. J.* **1990**, *26*, 1125-1135.
14. Matyjaszewski, K.; Gaynor, S.; Greszta, D.; Mardare, D. S. T. *J. Phys. Org. Chem.* **1995**, *8*, 306-315.
15. Baumert, M.; Mülhaupt, R. *Macromol. Rapid Commun.* **1997**, *18*, 787-794.
16. Costa, L.; Camino, G.; Guyot, A.; Bert, M.; Clouet, G.; Brossas, J. *Polym. Degrad. Stab.* **1986**, *14*, 85-93.
17. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243-245.
18. Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T. T.; Gilbert, R. G.; Serelis, A. K.; Such, C. H.; Hawkett, B. S. *Macromolecules* **2005**, *38*, 2191-2204.
19. Ruzette, A.-V.; Leibler, L. *Nature Materials* **2005**, *4*, 19-31.

20. Caruso, F. *Adv. Mater.* **2001**, *13*, 11-22.
21. Solomon, D. H.; Rizzardo, E.; Cacioli, P. US 4,581,429, April 8, 1986; *Chem. Abstr. 102*, 221335q.
22. Johnson, C. H. J.; Moad, G.; Solomon, D. H.; Spurling, T. H.; Vearing, D. J. *Aust. J. Chem.* **1990**, *43*, 1215-1230.
23. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987-2988.
24. Fischer H. *J. Am. Chem. Soc.* **1986**, *108*, 3925-3927.
25. Chong, B. Y. K.; Ercole, F.; Moad, G.; Rizzardo, E.; Thang, S. H.; Anderson, A. G. *Macromolecules* **1999**, *32*, 6895-6903.
26. Benoit, D.; Grimaldi, S.; Finet, J. P.; Tordo, P.; Fontanille, M.; Gnanou, Y. *ACS Symposium Series*ACS: 1998; Vol. 685, pp 225-235.
27. Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904-3920.
28. Rodlert, M.; Harth, E.; Rees, I.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4749-4767.
29. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.
30. Howell, B. A.; Li, I. Q.; Priddy, D. B.; Smith, P. B.; Ellaboudy, A. *Thermochim. Acta* **1999**, *340-341*, 279-283.
31. Goto, A.; Kwak, Y.; Yoshikawa, C.; Tsujii, Y.; Sugiura, Y.; Fukuda, T. *Macromolecules* .
32. Harth, E.; Hawker, C. J.; Fan, W.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 3856-3862.
33. Miura, Y.; Hirota, K.; Moto, H.; Yamada, B. *Macromolecules* **1999**, *32*, 8356-8362.
34. Rizzardo, E.; Meijs, G.; Thang, S. H. *Macromol. Symp.* **1995**, *98*, 101-123.
35. Beyou, E.; Chaumont, P.; Chauvin, F.; Devaux, C.; Zydowics, N. *Macromolecules* **1998**, *31*, 6828-6835.
36. Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722-8728.
37. Turro, N. J.; Lem, G.; Zavarine, I. S. *Macromolecules* **2000**, *33*, 9782-9785.
38. Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules*

1997, *30*, 4238-4240.

39. Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183-188.
40. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.
41. Kharasch, M. S.; Jensen, E. V. U. W. H. *Science* **1945**, *102*, 128.
42. Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963**, 3921-3927.
43. Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165-171.
44. Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614-5615.
45. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721-1723.
46. Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970-7972.
47. Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371-377.
48. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
49. Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665-3668.
50. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689-3745.
51. Lutz, J.-F.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2002**, *203*, 1385-1395.
52. Lutz, J.-F.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 897-910.
53. Sadhu, V. B.; Pionteck, J.; Voigt Dieter; Komber, H.; Fischer, D.; Voit, B. *Macromol. Chem. Phys.* **2004**, *205*, 2356-2365.
54. Bon, S. A. F.; Steward, A. G.; Haddleton, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2678-2686.
55. Coessens, V.; Pyun, J.; Miller, P. J.; Gaynor, S. G.; Matyjaszewski, K. *Macromol. Rapid. Commun.* **2000**, *21*, 130-109.
56. Snijder, A.; Klumperman, B.; van der Linde, R. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2350-2359.
57. Coessens, V.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 66-70.
58. Matyjaszewski, K.; Nakagawa, Y.; Gaynor, S. G. *Macromol. Rapid Commun.* **1997**, *18*, 1057-1066.

59. Coessens, V.; Nakagawa, Y.; Matyjaszewski, K. *Polymer Bulletin* **1998**, *40*, 135-142.
60. Gabriel, S. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 2224-2236.
61. Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955-970.
62. Muehlebach, A.; Rime, F. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3425-3439.
63. Malz, H.; Komber, H.; Voigt, D.; Hopfe, I.; Pionteck, J. *Macromol. Chem. Phys.* **1999**, *200*, 642.
64. Ji, S.; Hoye, T. R.; Macosko, C. W. *Macromolecules* **2005**, *38*, 4679-4686.
65. Sadhu, V. B.; Pionteck, J.; Voigt, D.; Komber, H.; Voit, B. *Macromol. Symp.* **2004**, *210*, 147-155.
66. Haddleton, D. M.; Waterson, C. *Macromolecules* **1999**, *32*, 8732-8739.
67. Matyjaszewski, K. *Controlled/Living Radical Polymerization: Progress in ATRP, NMP and RAFT,* Symposium series 768 ed.; Matyjaszewski, K., Editor; American Chemical Society: Washington DC, 2000.
68. Zhang, H.; Jiang, X.; van der Linde, R. *Polymer* **2004**, *45*, 1455-1466.
69. Sarbu, T.; Lin, K.-Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9694-9700.
70. Yurteri, S.; Cianga, I.; Yagci, Y. *Macromol. Chem. Phys.* **2003**, *204*, 1771-1783.
71. Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337-377.
72. Goto, A.; Ohno, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 2809-2814.
73. Yutani, Y.; Tatemoto, M. JP Eur. Pat. Appl. EP048937OA1, 1991.
74. Yamago, S.; Iida, K.; Yoshida, J. *J. Am. Chem. Soc.* **2002**, *124*, 13666-13667.
75. Meijs, G. F. ; Morton, T. C.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1991**, *24*, 3689-3695.
76. Bon, S. A. F.; Morsley, S. R.; Waterson, C.; Haddleton, D. M. *ACS Polym. Prep., Div. Polym. Chem.* **1999**, *40*, 391-392.
77. Cacioli, P.; Hawthorne, D. G.; Laslett, R. L.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci. Chem.* **1986**, *A23*, 839-852.

78. Heuts, J. P. A.; Roberts, G. E.; Biasutti, J. D. *Aust. J. Chem.* **2002**, *55*, 381-398.
79. Gridnev, A. A.; Ittel, S. D. *Chem. Rev.* **2001**, *101*, 3611-3659.
80. Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V.; Belgovskii, I. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1981**, *19*, 879.
81. Krstina, J.; Moad, G.; Rizzardo, E.; Winzor, C. L.; Berge, C. T.; Fryd, M. *Macromolecules* **1995**, *28*, 5381-5385.
82. Krstina, J.; Moad, C. L.; Moad, G.; Rizzardo, E.; Berge, C. T.; Fryd, M. *Macromol. Symp.* **1996**, *111*, 13-23.
83. Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1996**, *29*, 7717-7726.
84. Hutson, L.; Krstina, J.; Moad, C. L.; Moad, G.; Morrow, G. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2004**, *37*, 4441-4452.
85. Chiefari, J.; Jeffery, J.; Krstina, J.; Moad, C. L.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2005**, *38*, 9037-9054
86. Chiefari, J.; Jeffery, J.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 7700-7702.
87. Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc. Perkin Trans. 1* **1975**, 1574-1585.
88. Delduc, P.; Tailhan, C.; Zard, S. Z. *Chem. Commun.* **1988**, 308-310.
89. Zard, S. Z. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 672-685.
90. Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. Australia PCT Int. Appl. WO 98/01478, January 15, 1998; *Chem. Abstr. 128*, 115390.
91. Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559-5562.
92. Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol. Symp.* **2000**, *150*, 23-32.
93. Rizzardo, E.; Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 297-307.
94. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977-6980.
95. Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.;

Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993-1001.

96. Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071-2074.
97. Destarac, M.; Charmot, D.; Franck, X.; Zard, S. Z. *Macromol. Rapid. Commun.* **2000**, *21*, 1035-1039.
98. Chong, B. Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256-2272.
99. Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273-2283.
100. Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *ACS Symposium Series*ACS: 2000; Vol. 768, Chapter Ch. 20, pp 278-296.
101. Moad, G.; Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromol. Symp.* **2002**, *182*, 65-80.
102. Barner, L.; Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Aust. J. Chem.* **2004**, *57*, 19-24.
103. Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365-375.
104. Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y. *Macromolecules* **2003**, *36*, 7446-7452.
105. Benaglia, M.; Rizzardo, E.; Alberti, A.; Guerra, M. *Macromolecules* **2005**, *38*, 3129-3140.
106. Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505-1513.
107. Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tet. Lett.* **2002**, *43*, 6811-6814.
108. Chen, M.; Ghiggino, K. P.; Smith, T. A.; Thang, S. H.; Wilson, G. J. *Aust. J. Chem.* **2004**, *57*, 1175-1177.
109. Chen, M.; Ghiggino, K. P.; White, J.; Thang, S. H.; Wilson, G. J. *J. Org. Chem.* **2005**, *70*, 1844-1852.
110. Perrier, S.; Takolpuckdee, P.; Mars, C. A. *Macromolecules* **2005**, *38*, 2033-2036.
111. Vana, P.; Albertin, L.; Barner, L.; Davis, T. P.; Barner-Kowollik, C. *J.*

Polym. Sci., Part A: Polym. Chem. **2002**, *40*, 4032-4037.

112. Thomas, D. B.; Convertine, A. J.; Hester, R. D.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2004**, *37*, 1735-1741.
113. Favier, A.; Ladaviere, C.; Charreyre, M.-T.; Pichot, C. *Macromolecules* **2004**, *37*, 2026-2034.
114. Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458-8468.
115. Schilli, C.; Lanzendorfer, M. G.; Muller, A. H. E. *Macromolecules* **2002**, *35*, 6819-6827.
116. Llauro, M.-F.; Loiseau, J.; Boisson, F.; Delolme, F.; Ladavière, C.; Claverie, J. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5439-5462.
117. Sumerlin, B. S.; Lowe, A. B.; Stroud, P. A.; Zhang, P.; Urban, M. W.; McCormick, C. L. *Langmuir* **2003**, *19*, 5559-5562.
118. McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312-325.
119. Lima, V.; Jiang, X.; Brokken-Zijp, J.; Schoenmakers, P. J.; Klumperman, B.; van der Linde, R. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 959-973.
120. Castro, E. A. *Chem. Rev.* **1999**, *99*, 3505-3524.
121. Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Chemistry*; John Wiley & Sons. Inc.: New York, 1991.
122. Thang, S. H.; Chong, B. Y. K.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Lett.* **1999**, *40*, 2435-2438.
123. Chen, M.; Ghiggino, K. P.; Mau, A. W. H.; Rizzardo, E.; Thang, S. H.; Wilson, G. J. *Chem. Commun.* **2002**, 2276-2277.
124. de Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3596-3603.
125. Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *54*, 6754-6756.
126. Lohse, D. J.; Datta, S.; Kresge, E. N. *Macromolecules* **1991**, *24*, 561-566.
127. Lin, C.-W.; Lee, W.-L. *J. Appl. Polym. Sci.* **1998**, *70*, 383-387.
128. Trivedi, B. C.; Culbertson, B. M. *Maleic Anhydride*, 1st ed.; Plenum Press: New York, 1982.
129. Moad, G. *Prog. Polym. Sci.* **1999**, *24*, 81-142.
130. Kowalski, R. C. *Reactive Extrusion: Principles and Practice*; Xanthos, M., Editor; Hanser Publishers: Munich, 1992; pp 7-32.

131. Brown, S. B. *Reactive Extrusion: Principles and Practice*; Xanthos, M., Editor; Hanser Publishers: Munich, 1992; p 75.
132. Xanthos, M. *Reactive Extrusion: Principles and Practice*; Hanser Publishers: Munich, 1992.
133. Al-Malaika, S. *Reactive Modifiers for Polymers*, 1st ed.; Chapman and Hall: London, 1997.
134. Chung, M. T. C. *Functionalization of Polyolefins ;* 1st ed. Academic Press: London, 2002.
135. Bray, T.; Damiris, S.; Grace, A.; Moad, G.; O'Shea, M.; Rizzardo, E.; Van Diepen, G. *Macromol. Symp.* **1998**, *129*, 109-118.
136. Hu, G.-H.; Flat, J. J.; Lambla, M. *Reactive Modifiers for Polymers,* 1st ed.; Al-Malaika, S., Editor; Chapman and Hall: London, 1997.
137. Trivedi, B. C.; Culbertson, B. M. *Maleic Anhydride*, 1st ed.; Plenum Press: New York, 1982.
138. Grenci, J.; Todd, D. B. *Int. Polym. Proc.* **2000**, *15*, 147-156.
139. Rauwendaal, C. *Polymer Mixing: A Self-Study Guide*, 1st ed.; Hanser: Munich, 1998.
140. Heinen, W.; Rosenmöller, C. H.; Wenzel, C. B.; de Groot, H. J. M.; Lugtenburg, J.; van Duin, M. *Macromolecules* **1996**, *29*, 1151-1157.
141. Ganzeveld, K. J.; Janssen, L. P. B. M. *Polym. Eng. Sci.* **1992**, *32*(7), 467-474.
142. Machado, A. V.; Covas, J. A.; van Duin, M. *Polymer* **2001**, *42*, 3649-3655.
143. Gallucci, R. R.; Going, R. C. *J. Appl. Polym. Sci.* **1982**, *27*, 425-437.
144. Samay, G.; Nagy, T.; White, J. L. *J. Appl. Polym. Sci.* **1995**, *56*, 1423-1433.
145. Gaylord, N. G.; Mehta, R.; Mohan, D.; Fumar, V. *J. Appl. Polym. Sci.* **1992**, *44*, 1941-1949.
146. Machado, A. V.; van Duin, M.; Covas, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3919-3932.
147. Premphet, K.; Chalearmthitipa, S. *Polym. Eng. Sci.* **2001**, *41*, 1978-1985.
148. Strait, C. A.; Tabor, R. L.; Lancaster, G. M. US 4,927,888, May 22, 1990.
149. Gross, L. H.; Bartlett, T. M. US 4,857,600, August 15, 1989.
150. Gaylord, N. G. *Reactive Extrusion: Principles and Practice*; Xanthos, M.,

Editor; Hanser Publishers: Munich, 1992; p 55.

151. De Roover, B.; Sclavons, M.; Carlier, V.; Devaux, J.; Legras, R.; Momtaz, A. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 829-842.
152. Sclavons, M.; Carlier, V.; De Roover, B.; Franquinet, P.; Devaux J.; Legras, R. *J. Appl. Polym. Sci.* **1996**, *62*, 1205-1210.
153. Russell, K. E. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2273-2280.
154. Sipos, A.; McCarthy, J.; Rossell, K. E. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3353-3362.
155. Zhang, M.; Duhamel, J.; van Duin, M.; Meessen, P. *Macromolecules* **2004**, *37*, 1877-1890.
156. Liu, T. M.; Evans, R.; Baker, W. E. *Annu. Tech. Conf-Soc. Plast. Eng.* **1995**, *53*, 1564-1571.
157. Liu, N. C.; Xie, H. Q.; Baker, W. E. *Polymer* **1993**, *34*, 4680-4687.
158. Torres, N.; Robin, J. J.; Boutevin, B. *J. Appl. Polym. Sci.* **2001**, *81*, 581-590.
159. Zhang, X.; Yin, Z.; Li, L.; Yin, J. *J. Appl. Polym. Sci.* **1996**, *61*, 2253-2257.
160. Hu, G.-H.; Cartier, H. *J. Appl. Polym. Sci.* **1999**, *71*, 125-133.
161. Al-Malaika, S.; Kong, W. *J. Appl. Polym. Sci.* **2001**, *79*, 1401-1415.
162. Cartier, H.; Hu, G.-H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2763-2774.
163. Peeters, G. Personal Communications.
164. Németh, S.; Jao, T.-C.; Fendler, J. H. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1723-1732.
165. Holden, G. *Understanding Thermoplastic Elastomers*; Hanser Publishers: Munich, 2000.
166. Schellekens, M. A. J.; Klumperman, B. *J. Macromol. Sci.- Rev. Macromol. Chem. Phys.* **2000**, *C40*(2&3), 167-192.
167. Jones, T. D.; Macosko, C. W.; Moon, B.; Hoye, T. R. *Polymer* **2004**, *45*, 4189-4201.
168. Jeon, H. K. ; Macosko, C. W.; Moon, B.; Hoye, T. R.; Yin, Z. *Macromolecules* **2004**, *37*, 2563-2571.
169. Orr, C. A.; Cernohous, J. J.; Guegan, P.; Hirao, A.; Jeon, H. K.; Macosko, C. W. *Polymer* **2001**, *42*, 8171-8178.
170. Hu, G.-H.; Sun, Y.-J.; Lambla, M. *Polym. Eng. Sci.* **1996**, *36*, 676-684.

171. Hu, G.-H.; Lambla, M. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 97-107.
172. Sun, Y.-J.; Hu, G.-H.; Lambla, M.; Kotlar, H. K. *Polymer* **1996**, *37*, 4119-4127.
173. Perego, G.; Albizzati, E. EP485982, May 20, 1992.
174. Liu, N. C.; Baker, W. E. *Polymer* **1994**, *35*, 988-994.

3 Approaches to Phthalimido and Amino End-Functional Polystyrene by ATRP

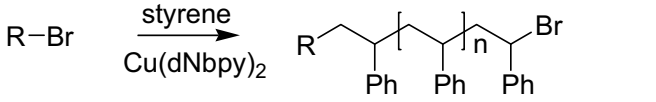
3.1 Introduction

This chapter details the investigation of the two approaches for obtaining primary amine end-functionalised polystyrenes using the atom transfer radical polymerisation (ATRP) technique; ω-functionalisation by halogen end-group transformation and α-functionalisation involving the use of a functional initiator.

End-functional polymers with controlled architecture and molecular weight are currently of great importance in industry and academia and are particularly valued because of their potential applications in surface science and biomedical areas. Because end-groups are retained, living polymerisation processes are, by their nature, particularly suited to the synthesis of end-functional polymers and in addition provide control over the polymerisation and are a means to build specific architecture for these applications. Thus various living radical methods, including nitroxide-mediated polymerisation (NMP),[1] atom transfer radical polymerisation (ATRP)[2] and reversible addition-fragmentation chain transfer (RAFT) with macromonomers[3,4] or thiocarbonylthio compounds,[5,6] have all been successfully adapted for this purpose.

The synthesis of end-functional polymers by ATRP has been outlined in several reviews[2,7,8] and continues to be an area of intense interest for both mono-end-functional and telechelic polymers.[9-11] There are two basic approaches to the synthesis of end-functional polymers[7] termed ω-functionalisation and α-functionalisation. In the first, the bromo functionality introduced by the ATRP initiator is transformed post-polymerisation to introduce a functional group at the ω-chain end. The second approach makes use of an appropriately designed

functional initiator to directly introduce the desired functional group (R) at the α-chain end (refer to Scheme 3.1, for example using initiators **1**-**7**).



α end group ω end group

Scheme 3.1

This chapter is focused on the synthesis of polymers with primary amine end-groups by ATRP. The polymers have a range of applications in biomedical and materials science, however, our interest was the synthesis of block and graft copolymers with well defined segment lengths.[12-14] There have been a number of previous papers on the synthesis of polymers with primary amine end-groups.[12,13,15-18] Primary amine-functional polymers have previously been prepared by anionic polymerisation[12,13,16-18] free radical telomerisation,[19] and by ATRP.[15,20-25] They have also been prepared by conventional radical polymerisation with the use of a functional iniferter,[26] functional transfer agents[27,28] or functional initiators.[29,30] Living polymerisation processes generally require that primary amines are protected during the polymerisation process due to their potential reactivity to the controlling moiety of the polymerisation.

In this chapter we explore the introduction of the latent amine functionality as a phthalimido-group.[31-33] Approaches based on ω-functionalisation and α-functionalisation were examined.

3.2 Experimental

3.2.1 General

Solvents were of AR grade and were distilled before use. All chemicals and monomers were purchased from Aldrich unless stated otherwise. Styrene was purified by filtration through neutral alumina (70-230 mesh), to remove inhibitors and flash distilled immediately prior to use. *N*-(bromomethyl)phthalamide (**1**)

was obtained from Aldrich (97%) and was used without purification. ^{1}H NMR spectra were obtained with a Bruker Advance DRX500, Bruker Av400 or a Bruker AC200 spectrometer on samples dissolved in deuterochloroform, processed with XWin-NMR 3.5 or Mestre 2.3. Chemical shifts are reported in ppm from TMS. Gel permeation chromatography (GPC) was performed with a system comprising a Waters Associates liquid chromatograph equipped with differential refractometer and a set of 3×Mixed C columns and a mixed E PLgel column (each 7.5 mm×30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22±2 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) ranging from 600 to 7.5 × 10^6 g mol^{-1}. A third order polynomial was used to fit the $\log_{10}$M *vs* time calibration curve, which was approximately linear across the molecular weight range 2 × 10^2–2 × 10^6 g mol^{-1}. Conversions reported were determined gravimetrically unless stated otherwise.

3.2.2 Homogeneous ATRP of styrene in bulk

The following procedure is typical:

A solution comprising styrene (1.82 g, 1.75×10^{-2} mol), cuprous bromide (25 mg, 1.75×10^{-4} mol), 4,4'-di-(nonyl)-2,2'bipyridine (dNbpy) (143 mg, 3.49×10^{-4} mol) and the appropriate bromo-initiator, was prepared in ampoules (concentrations are shown in Table 3.1 and Table 3.2). Solutions were degassed by three freeze-evacuate-thaw cycles, and the ampoules were sealed and heated in an isothermal oil bath at 110±1 °C for the periods indicated.

3.2.3 Heterogeneous ATRP of styrene in bulk

A mixture comprising styrene (7.48 g, 7.18×10^{-2} mol), cuprous bromide (0.42 g, 2.90×10^{-3} mol), bipyridine (bpy) (0.90 g, 5.76×10^{-3} mol) and *N*-(bromomethyl)phthalimide (1.38 g, 5.75×10^{-3} mol) were placed in a Schlenk flask. The mixture was degassed by nitrogen sparging for 30 minutes and then

heated in an isothermal oil bath at 110±1 °C, with stirring and samples were taken at 0.6, 1.4, 2.3 and 3 hours. Samples were evaporated to dryness dissolved in chloroform and filtered through silica (*ca* 0.5 mL) to remove residual copper catalyst before analysis by NMR. A further sample was evaporated to dryness, diluted with THF and analysed by GPC. Molecular weights and conversions obtained are shown in Table 3.3.

3.2.4 Transformation of ω-bromopolystyrene to ω-phthalimidopolystyrene

The ω-bromopolystyrene (0.85 g) and potassium phthalimide (1.72 g, 9.28×10-3 mol; approx 10 eq. with respect to bromo end-groups) were dissolved in *N,N*-dimethylformamide (DMF) (10 mL). The mixture was stirred at 80 °C under argon for 16 h. The reaction mixture was precipitated into methanol (200 mL) once, the polystyrene collected by filtration and dried in a vacuum oven.

3.2.5 Hydrazinolysis of phthalimidopolystyrene to aminopolystyrene

Phthalimide end-functional polystyrene (0.3 g) and hydrazine monohydrate (0.075 g, 1.50×10^{-3} mol; approx 10 eq. with respect to the phthalimide) were dissolved in DMF (10 mL). The mixture was stirred at 80 °C under argon for 16 h (on the addition of the hydrazine the solution yellowed due to formation of phthalyl hydrazide). A catalytic amount of 1 M HCl (aq) was added to free the amine. The reaction mixture was precipitated into methanol (200 mL), the polystyrene collected by filtration and dried in a vacuum oven. The same procedure was used for both α- and ω-phthalimidopolystyrenes. NMR analysis showed that the phthalimide end-group was quantitatively removed in each case.

3.2.6 Trichloroacetyl isocyanate derivatisation of aminopolystyrene[34]

The amine end-functional polystyrene (50 mg) was dissolved in $CDCl_3$ (0.5 mL) in a standard 5 mm NMR tube and its ^{1}H NMR spectrum was recorded. One drop of trichloroacetylisocyanate (TAI) (~10 μL) was added and the tube shaken. The ^{1}H NMR spectrum was then obtained. The signals for the derivatised end-group of ω-aminopolystyrene appeared at δ 7.83 (amidic NH) and 8.27 (imidic NH) Figure 3.2), those of α-aminomethylpolystyrene appeared at δ 7.50 (amidic NH) and 8.21 (imidic NH). Excess TAI, being aprotic, exhibits no signals in the ^{1}H NMR spectrum. Reaction with extraneous water yields trichloroacetamide with signals δ 5-6.

3.2.7 Reduction of ω-bromopolystyrene

The procedure was executed as previously described.[35] Polystyrene (0.50 g, $\overline{M}_n$ =3100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.31), tri-*n*-butylstannane (0.47 g), AIBN (1.5 mg) and toluene (1.5 mL) were placed in an argon-flushed ampoule. The contents were degassed by three freeze-evacuate-thaw cycles, sealed and heated in a constant temperature bath at 70 °C for 3 h.

3.2.8 Synthesis of phthalimidomethyl 2-bromo-2-methylpropanoate (2)

N-(hydroxymethyl) phthalimide (8.86 g, 0.05 mol), triethylamine (5.66 g, 0.055 mol), were dissolved in THF (100 mL) and stirred at room temperature. Bromoisobutyryl bromide (6.8 mL, 0.055 mol) was slowly added and the reaction was stirred for a further 16 h. The white precipitate of triethylammonium bromide was removed by filtration to leave a yellow solution from which the THF was evaporated to leave a yellow oil (14.3 g, crude yield = 88%). The product was dissolved in dichloromethane (100 mL) and washed sequentially with 2×100 mL of each; deionized water, saturated Na_2CO_3(aq), deionized water, dilute HCl(aq), deionized water and brine. The solution was dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation to

give a pale yellow oil that spontaneously crystallized on standing. The product was recrystallized from ethanol to give pale beige needles. Yield = 9.02 g (55.3%), mp = 92-93 °C.

^{1}H NMR ($CDCl_3$) δ: 1.90 (s, 6H, 2 × C**H**$_3$), 5.79 (s, 2H, N-C**H**$_2$-O), 7.80 (m, 2H, phthalyl aromatic), 7.92 (m, 2H, phthalyl aromatic).

^{13}C NMR ($CDCl_3$) δ: 30.5 (2 × (**C**H$_3$)), 54.9 (Br-**C**(CH$_3$)$_2$), 62.0 (N-**C**H$_2$-O), 124.0 (2 × *o*-Ph, **C**H), 131.7 (2 × Ph, **C**), 134.7 (2 × *p*-Ph, **C**H), 166.4 (2 × N-(**C**=O)C), 170.6 (O-(**C**=O)-C).

MS (ES+) m/z 325.9 (MH^+) ($C_{13}H_{12}BrNO_4$ requires 324.99).

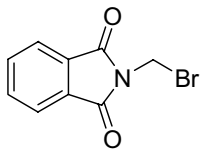
3.2.9 Synthesis of phthalimidoethyl 2-bromo-2-methylpropanoate (3)

The procedure as described for (**2**) above was used with *N*-(hydroxyethyl) phthalimide (9.55 g, 0.05 mol) as the starting material. The product was recrystallized from ethanol to give off-white needles. Yield = 6.91 g (40.6%), mp = 61-62 °C.

^{1}H NMR ($CDCl_3$) δ: 1.87 (s, 6H, 2 × C**H**$_3$), 4.02 (tr, J = 5.3 Hz, 2H, C**H**$_2$-N), 4.42 (tr, J = 5.3 Hz, 2H, C**H**$_2$-O), 7.74 (m, 2H, phthalyl aromatic), 7.85 (m, 2H, phthalyl aromatic).

^{13}C NMR ($CDCl_3$) δ: 30.6 (2 × (**C**H$_3$)), 36.7 (**C**H$_2$-N), 55.5 (Br-**C**(CH$_3$)$_2$), 63.0 (**C**H$_2$-O), 123.3 (2 × *o*-Ph, **C**H), 132.0 (2 × Ph, **C**), 134.1 (2 × *p*-Ph, **C**H), 168.0 (2 × N-(**C**=O)C), 171.4 (O-(**C**=O)-C).

MS (ES+) m/z 339.9 (MH^+) ($C_{14}H_{14}BrNO_4$ requires 339.01).



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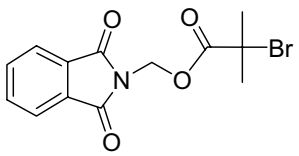

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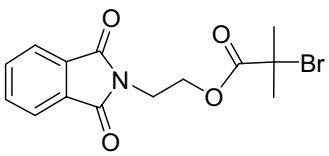

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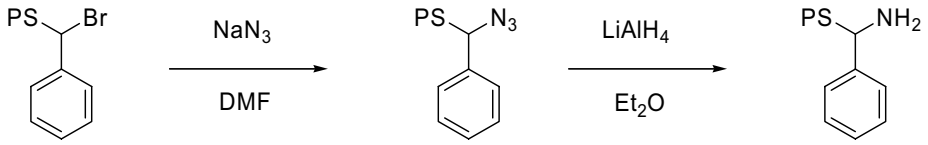
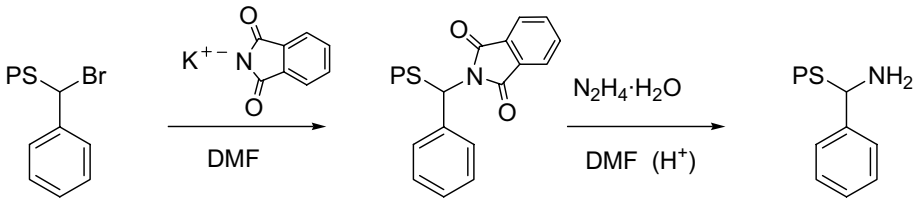
3.3 Results and discussion

3.3.1 Approaches based on ω-functionalisation

The conversion of ATRP-produced, ω-halo-functional polymers, to ω-amino-functional polymers has previously been reported by Matyjaszewski and coworkers.[15,22] They used sodium azide or trimethylsilyl azide/potassium fluoride to convert ω-bromo-functional polymers to the corresponding ω-azido-functional polymers by nucleophilic substitution. The primary amine functional polymer was then obtained from polystyrene by reduction with lithium aluminium hydride (Scheme 3.2).[15] Azide end-functional poly(methyl acrylate), which is sensitive to lithium aluminium hydride reduction, has also been converted to the corresponding amine end-functional polymer by hydrolysis of the phosphoranimine formed on reaction with triphenylphosphine.[22]



Scheme 3.2



Scheme 3.3

It was decided to explore the use of the Ing-Manske procedure,[36] an improvement on the Gabriel synthesis,[37] to prepare ω-aminopolystyrene from bromoterminated polystyrene. The proposed process is shown in Scheme 3.3. Nucleophilic substitution of the bromine end-groups of the polymer formed by ATRP with potassium phthalimide gives a ω-phthalimidopolystyrene. Deprotection by hydrazinolysis then provides the required amine end-group. Weimer *et al.*[38] have applied such a method to a hyperbranched polymer prepared by self-condensing vinyl ATRP of 4-(chloromethyl)styrene. In this

particular case, a phthalimido functionalised polymer was successfully prepared by substitution of the chloro pendant- and chloro end-groups. However, attempted deprotection to the amine led to a cross-linked product.

We prepared ω-bromopolystyrene by ATRP essentially as described by Wang and Matyjaszewski.[39] The details and initiator/catalysts concentrations used are provided in Table 3.1. We observed that polystyrene formed after longer reaction times and higher conversions contained a substantial fraction of unsaturated end-groups. In any radical polymerisation there will be some termination by radical-radical reaction.[40] All termination products whether formed by combination or disproportionation will lack the terminal bromine functionality. It has been reported that under some conditions the unsaturated product formed by disproportionation can be detected by NMR.[41,42] However, the unsaturated disproportionation product, if present, should be accompanied by an equal amount of similar molecular weight polystyrene with a saturated chain end. Since radical-radical termination during styrene polymerisation is mainly (~95%) by combination,[43] a *ca* 20-fold greater amount of the combination product, we conclude, therefore, that the observed unsaturated product (~30% of chains for the experiment shown in Figure 3.1) cannot be formed by disproportionation. The finding that polydispersities are very narrow ($\overline{M}_w / \overline{M}_n$ ~1.1, see Table 3.1) indicates that the product is also not formed continuously during polymerisation. Furthermore, the bromo end-group by itself appeared stable at 110 °C in styrene solution for the polymerisation times indicated.

Matyjaszewski and coworkers[40,44] have reported that slow elimination catalyzed by deactivator [copper (II)] complicates the formation of higher molecular weight polystyrene. This is a probable explanation for the observed unsaturated product. Their experiments,[44] however, suggest that there should be substantially less elimination (<10% for 85% conversion for similar initiator and catalyst concentrations) than what was observed in our experiments (~30% for 70% conversion - Table 3.1). Since the elimination is catalyzed by copper (II), this result may indicate the presence of copper (II) impurity in the cuprous bromide used.

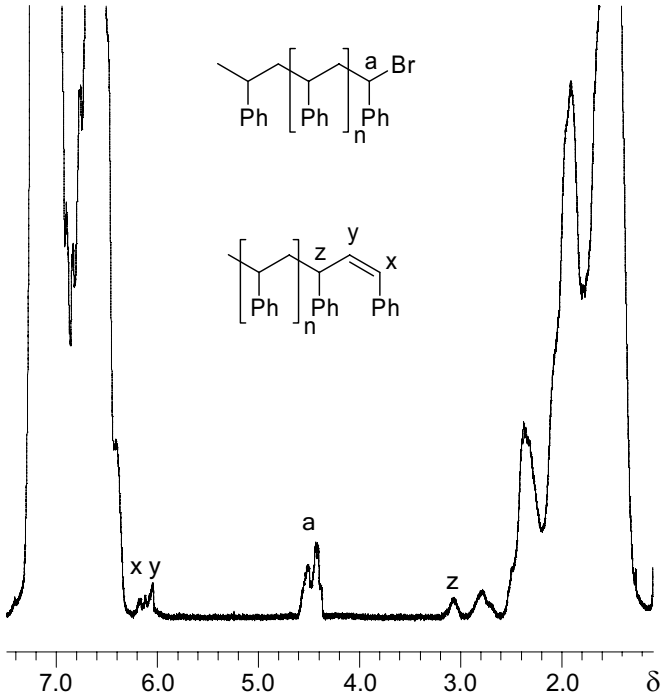
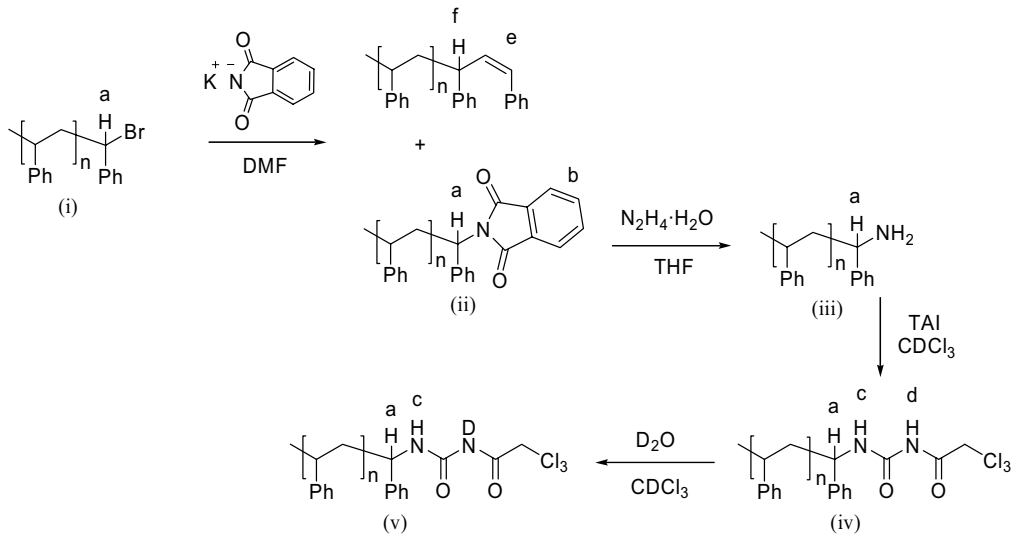


Figure 3.1. ^{1}H NMR spectra of high conversion polystyrene formed by ATRP with (1-bromoethyl)benzene as initiator (7 h, 68% conversion, see Table 3.1). Signal assignments for unsaturated chain end are based on those reported for the model compound, 1,3,5-triphenylpropene,[45] and previously published spectra.[42,46-48]

Low molecular weight ω-bromopolystyrene with no detectable fraction of unsaturated end-groups (<5%) was synthesized using CuBr/dNbpy catalyst at low conversion (Table 3.1). The NMR spectrum of this material is shown in Figure 3.2(i). Attempts to make low molecular weight product at high conversion by using higher initiator concentration and longer reaction times invariably gave product contaminated with unsaturated chain ends (Table 3.1). Polystyrene prepared under similar conditions with CuBr/dNbpy catalyst and other initiators (e.g. **3**, **4**) also contained this unsaturated impurity. However, the polymer prepared with **1** as initiator and CuBr/bpy catalyst appeared to be free of this by-product.



Scheme 3.4

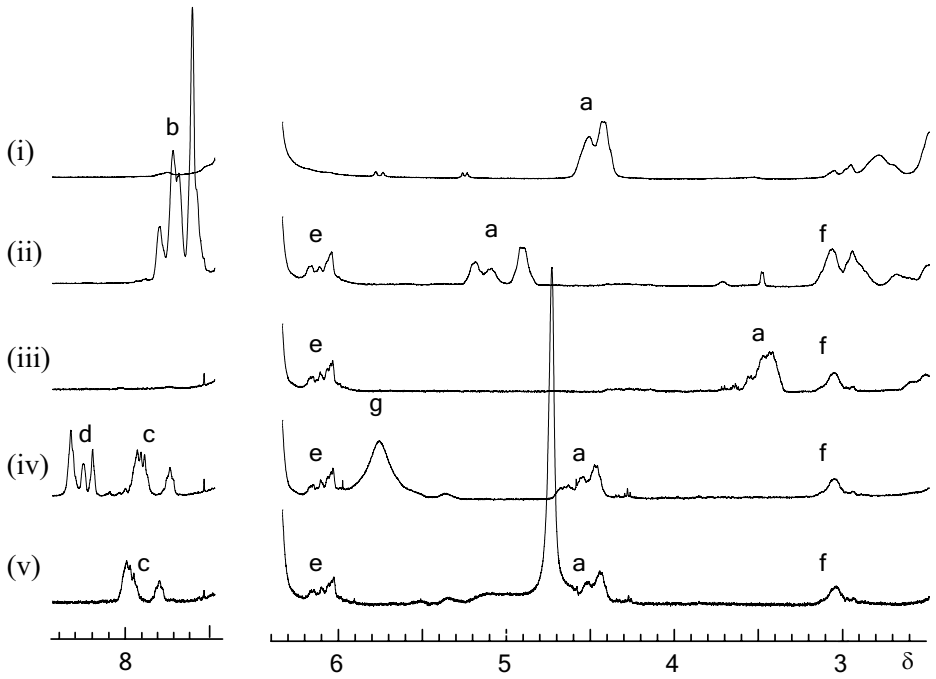


Figure 3.2. The Ing-Manske procedure followed by ^1H NMR. Signal assignments are as follows: (a) methine adjacent to modified functional group, (b) aromatic protons of phthalimide group, (c) -NH α to chain end, (d) acidic -NH proton of derivatising agent, (e) terminal proton of a 1,3-diphenylpropen-3-yl end-group, (f) methine of 1,3-diphenylpropen-3-yl end-group, (g)

trichloroacetamide signal. From top to bottom the spectra correspond to the starting material and the products of four reaction steps shown in Scheme 3.4.

Deprotection (conversion of the phthalimide group to the amine) appeared to be quantitative. The reaction was followed by ^{1}H NMR (Figure 3.2 and Scheme 3.4) which shows the clean shift of methine signal (a) adjacent to the modified functional group, and the disappearance of the phthalimido aromatics (b). Derivatisation of the amine end-group with trichloroacetyl isocyanate (TAI) provided further confirmation of the amine end-group and verified the quantitation.[34]

Even though it was initially possible to produce polystyrene free of unsaturated by-product, the subsequent substitution reaction was accompanied by elimination to give an olefinic end-group thus reducing the end-group purity. Others have also found that elimination of the terminal bromine with other nucleophiles can be competitive with nucleophilic displacement.[2] Their reactions also provided polymer with unsaturated end-groups. For example, elimination is observed in the attempted synthesis of ω-mercaptopolystyrene by nucleophilic reaction of ATRP-formed ω-bromopolystyrene with thiourea in DMF.[49] It appears there is less elimination with use of THF as a solvent.[50]

Different reaction conditions for the substitution reaction (*e.g.* use of other solvents, lower reaction temperatures) might be explored to reduce the extent of elimination. However, the efficiency of ω-functionalisation processes will always be limited by side reactions that occur during ATRP or during the post-polymerisation end-group modification process, we therefore turned our attention to the α-functionalisation approach (section 3.3.2).

Table 3.1. Atom transfer radical polymerisation with (1-bromoethyl)benzene in bulk styrene at 110 °C [St]/[CuBr]/[dNbpy] = 100/1/2.

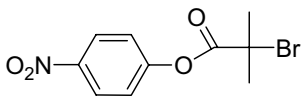
Time (h)	[M]/[I][a]	$\overline{M}_n^{Calc}$ [a] (g mol^{-1})	$\overline{M}_n$ (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv.[b] (%)	Vinyl[c] (%)
1	96.9	1720	1290	1.10	15	< 5[e]
3	99.7	2170	1760	1.08	19	< 5[e]
7	100	7890	7370	1.08	74	33
24	97.9	9920	10040	1.14	95	48
48	97.5	10140	10600	1.10	98	57
7	19.9	1600	1120	1.11	68	31
7	19.9	1590	1120	1.11	68	25
7	100	7890	7370	1.08	74	21

[a] $\overline{M}_n^{Calc}$ ~ [M]/[I]$_o$×Conv×104+(molecular weight of ATRP initiator). [b] NMR conversion. [c] Percentage vinyl end-groups=[1,3-diphenylpropen-3-yl]/([1,3-diphenylpropen-3-yl]+[bromo])×100. [e] Unsaturated end-groups not detectable.

3.3.2 Approaches based on α-functionalisation

In the α-functionalisation approach, the functionality is present in the initiator and ideally, all chains should possess that functionality. In the case of styrene polymerisation, the occurrence of thermal initiation will result in some non-functional chains. The fraction of non-functional chains can be minimized by restricting the synthetic procedure to low molecular weight polymers formed over short reaction times.[44] The number of steps required to obtain a primary amine end-group using an α-functionalisation approach are also reduced.

Various approaches to the synthesis of α-amine functional polymers by ATRP have been described previously. Haddleton *et al.*[23] reported on the use of various functionalised phenolic esters of bromoisobutyric acid, including (**4**) and (**5**), with *N*-(*n*-octyl)-2-pyridylmethanimine and cuprous chloride or bromide to obtain good control in methyl methacrylate polymerisations. Summers *et al.* used an *in-situ* formed amine functional initiator (**6**) derived from 1-(4-aminophenyl)-1-phenylethylene and *N,N,N',N",N"*-pentamethyldiethylenetriamine/cuprous bromide catalyst,[24] and a similar approach was used to make polystyrene with tertiary amine functionality.[51] It appears aromatic amines are compatible with ATRP, however, the lower reactivity of aromatic amines limits their utility in many applications. For instance, α-aminopoly(methyl methacrylate) has been synthesized using t-BOC functional bromoisobutyramide derivative (**7**) as initiator, to provide a halogen free polymer by hydrogen transfer from excess ligand (*N,N,N',N",N"*-pentamethyldiethylenetriamine) used during the polymerisation.[20,21] However, as a compromise, low and variable efficiency and broad polydispersities were observed.



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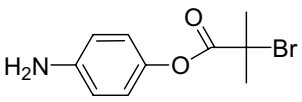

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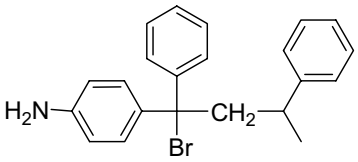

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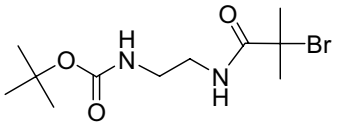

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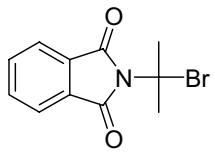
Phthalimido functional initiators synthesized from bromoisobutyroyl bromide[23,25] have previously been employed to synthesize phthalimido end-functional poly(methyl methacrylate) by ATRP with methanimine catalysts. We have found that these initiators are also very effective for ATRP of styrene with dNbpy/CuBr as catalyst. The results are shown in Table 3.2. Very narrow polydispersities and high efficiencies were obtained with (**2**) and (**3**) (Figure 3.3 and Figure 3.4 respectively). However, it was found that the phthalimido end-groups could not

be deprotected to provide the desired amine functionality because of concomitant hydrazinolysis of the isobutyrate ester linkage or intramolecular isomerization reaction of the freed amine. NMR analysis show that resonances attributable to the methylene (**2**) and ethylene (**3**) α to the ester linkage disappeared on attempted hydrazinolysis.

The synthesis of other potentially active initiators (**8**–**11**) were investigated but proved to be problematic. Attempted bromination of their corresponding precursors using *N*-bromosuccinimide (NBS) gave numerous brominated products as difficult-to-remove impurities, which precluded their further exploitation.



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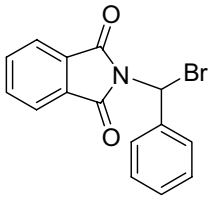

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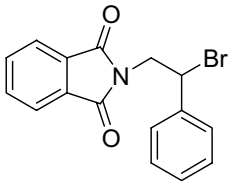

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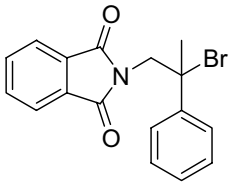

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Table 3.2. Atom transfer radical polymerisation with monofunctional initiators (**1**-**5**) in bulk styrene at 110 °C [St]/[CuBr]/[dNbpy] = 100/1/2.

ATRP Initiators	Time (h)	[M]/[I]	$\overline{M}_n^{Calc}$ [a] (g mol^{-1})	$\overline{M}_n$ (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv.[b] (%)
1	7	98.2	330	310	1.10	0.8
1	7	20.0	770	710	1.19	25
2	7	100	8790	10000	1.09	81
2	7	100	8960	9760	1.10	83
2	7	40.1	3070	3050	1.07	66
2	7	20.1	1200	1010	1.11	42
2	7	20.0	1190	1020	1.11	42
3	7	99.6	9050	10100	1.10	84
3	7	40.0	3290	3110	1.06	71
3	7	20.0	1810	1000	1.09	71
4	7.45	100	2640	2560	1.11	23
4	7.45	20.0	580	340	1.04	14
5	7.45	99.5	4570	6610[c]	1.26	42
5	7.45	22.7	690	880	1.45	18

[a] $\overline{M}_n^{Calc}$ ~ $[M]/[I]_o \times Conv \times 104$+(molecular weight of ATRP initiator). [b] NMR conversion, [c] bimodal distribution.

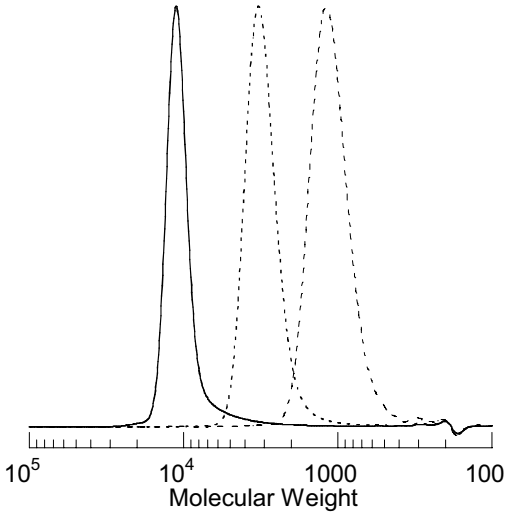


Figure 3.3. GPC traces for the polymerisation of styrene with different concentrations of (**2**) (Table 3.2), normalised peak heights.

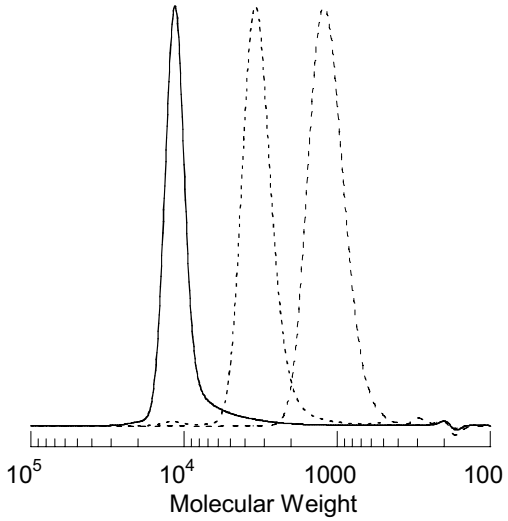
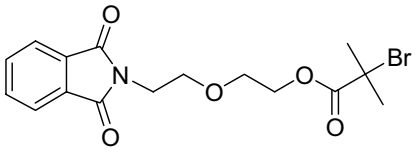


Figure 3.4. GPC traces for the polymerisation of styrene with different concentrations of (**3**) (Table 3.2), normalised peak heights.

Harrisson has noted that the end-group of poly(methyl methacrylate) prepared with initiator (**3**) irreversibly isomerizes to the hydroxyethyl amide on deprotection.[52] Wooley *et al.*[53] recently reported that polymer synthesized with (**12**) gave end-groups analogous to (**2**) and (**3**) but containing an oligo(ethylene

oxide) spacer between the phthalimide and the ester moiety, can be successfully converted to amine end-groups by hydrazinolysis.



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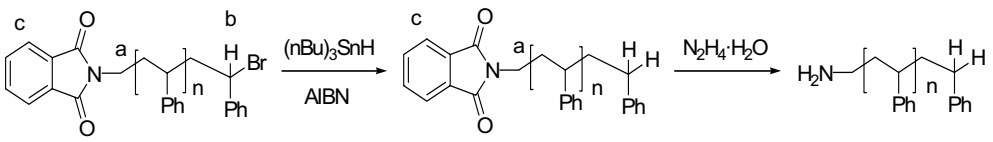


Scheme 3.5

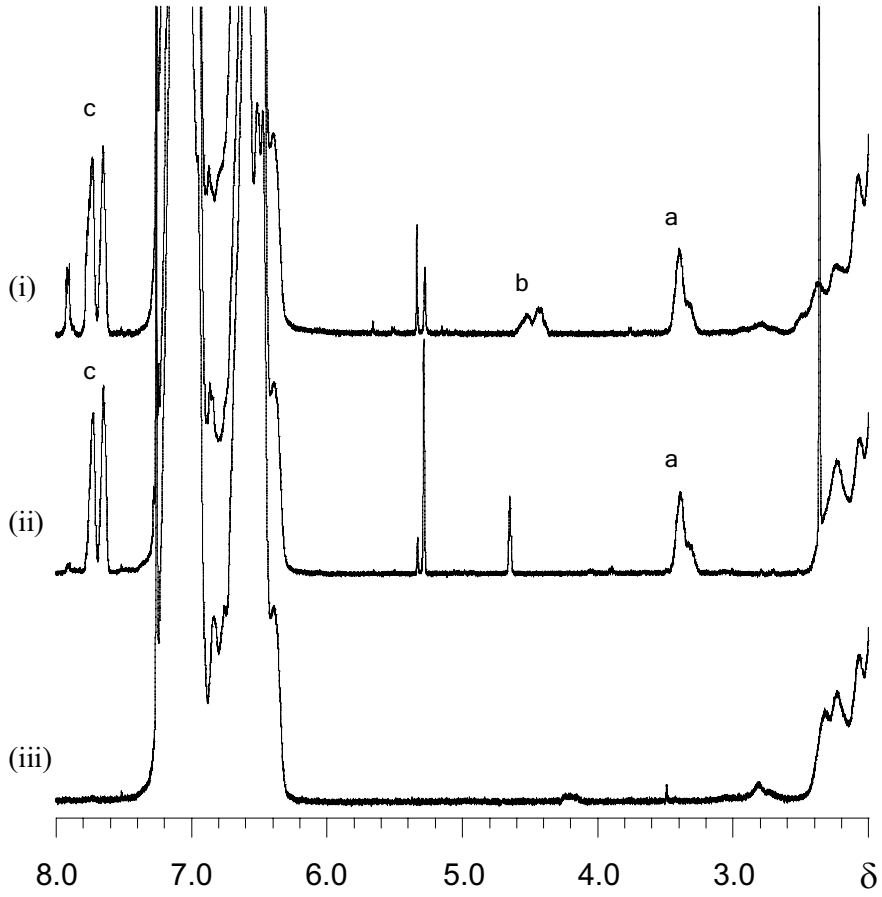


Figure 3.5. ^{1}H NMR spectra of precipitated polystyrene ($\overline{M}_n$=3100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$=1.31) prepared with (**1**) as initiator (i), after removal of bromine end-group under by reduction with tributyl stannane (middle), after deprotection of the amine end-group with hydrazine monohydrate (ii); (a) methylene signal α to phthalimido, (b) methine adjacent to terminal bromo, (iii) phthalimido aromatic signals.

We also explored the use of the commercially available, *N*-(bromomethyl)phthalimide (**1**) as an ATRP initiator, that allowed the synthesis of α-phthalimidopoly(styrene) (Table 3.3, Figure 3.6). The initiator showed a low

efficiency ~0.5 and polydispersities, though still narrow ~1.3, were somewhat broader than those obtained with the bromoisobutyrate initiators (Table 3.3, Figure 3.6). The formation of an, as yet, unidentified phthalimide derivative (observed by NMR) and the poor solubility of the initiator in the polymerisation medium probably account for the low efficiency. The use of a cosolvent for polymerisation to improve initiator solubility (anisole) and other ligands (Me_6TREN) was explored. However, these experiments gave only low conversions (<14%) and oligomeric products, whilst the use of longer reaction times gave a product with unsaturated end-groups and no significant improvement in yield.

Table 3.3. Atom transfer radical polymerisation with N-(bromomethyl)phthalimide (**1**) in bulk styrene at 110 °C [St]/[CuBr]/[bpy] = 25/1/2.

ATRP Initiator	Time (h)	[M]/[I]	$\overline{M}_n^{Calc}$ [a] (g mol^{-1})	$\overline{M}_n$ (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv [b] (%)
1	0.6	12.5	320	780	1.25	6
1	1.4	12.5	850	1840	1.33	47
1	2.3	12.5	1400	2730	1.33	89
1	3	12.5	1460	3110	1.33	93

[a] $\overline{M}_n^{Calc}$ ~ $[M]/[I]_o \times Conv \times 104 +$(molecular weight of ATRP initiator). [b] gravimetric conversion.

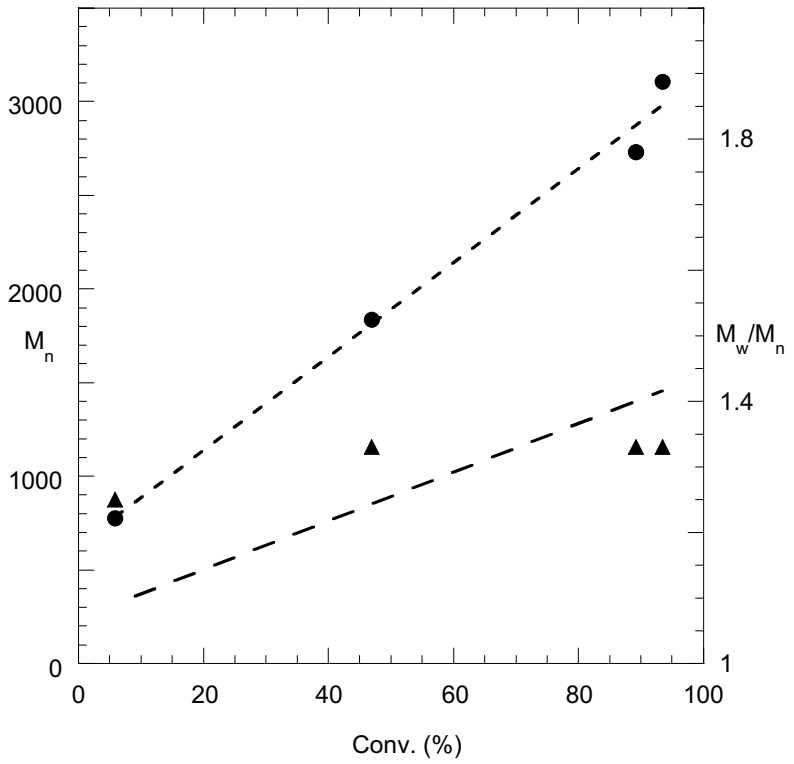


Figure 3.6. Evolution of polydispersity (▲) and molecular weight (●) with conversion for bulk thermal styrene polymerisation at 110 °C in the presence of (**1**) and bpy/CuBr. (---) observed molecular weight best fit, (−−−) calculated molecular weight. For experimental details, see Table 3.3.

Removal of the bromine end-group was required to avoid the possibility of its reaction with hydrazine during the deprotection step with the freed primary amine end-group. The removal of the terminal bromine was achieved by reduction with tri-*n*-butylstannane (AIBN, toluene, 70 °C for 3 hours) to leave a saturated chain end (Scheme 3.5). This reduction was followed by ^{1}H NMR (Figure 3.5), where quantitative disappearance of the methine signal α to the terminal bromine at δ 4.4 was observed (Figure 3.5). Deprotection of the phthalimido end-group to give the amine was achieved by hydrazinolysis in DMF (80 °C for 12 hours). The reaction was followed by NMR by observing the disappearance of the aromatic resonances between δ 7.5 and 8.0 (Figure 3.5). Additionally, derivatisation with trichloroacetyl isocyanate provided confirmation

of the presence of primary amine end-group functionality, these details are discussed in Chapter 6.

3.4 Conclusions

ATRP polymerisation has been applied to the synthesis of α primary amine functional polystyrene. The most successful route involves the use of *N*-(bromomethyl)phthalimide (**1**) as initiator, however its efficiency was found to be somewhat low. Other initiators where the phthalimido group is joined by an ester linkage (**2** and **3**) provided good control over the polymerisation but were not useful for production of a primary amine functional polymer because of the susceptibility of that linkage to hydrolysis during deprotection and consequent loss of the functionality. The compounds (**4, 5** and **6**) are effective ATRP initiators and can be used to produce polymers with a less reactive aromatic amine end-group. The initiator (**7**) was not explored but holds potential for the synthesis of amine end-functional polymers which show sensitivity to basic conditions. Better control would also be expected by using a ligand system other than excess ligand (*N,N,N',N",N'*-pentamethyldiethylenetriamine) which promotes de-halogenisation during the polymerisation, to allow narrower polydispersities to be attained.

Radical-induced reduction with tri-*n*-butylstannane to remove the bromo end-group and hydrazinolysis affords the polymer with the desired α primary amine end-group. Approaches based on ω-functionalisation gave product with lower end-group purity. In the next chapter, the use of RAFT as a way to synthesize polymers with primary amine end-functionality will be discussed.

3.5 References

1. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.
2. Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*,

337-377.

3. Hutson, L.; Krstina, J.; Moad, C. L.; Moad, G.; Morrow, G. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2004**, *37*, 4441-4452.
4. Krstina, J.; Moad, C. L.; Moad, G.; Rizzardo, E.; Berge, C. T.; Fryd, M. *Macromol. Symp.* **1996**, *111*, 13-23.
5. Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. *ACS Symp. Ser.* **2003**, *854*, 520-535.
6. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379-410.
7. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
8. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689-3745.
9. Sarbu, T.; Lin, K.-Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 3120-3127.
10. Yurteri, S.; Cianga, I.; Yagci, Y. *Macromol. Chem. Phys.* **2003**, *204*, 1771-1783.
11. Otazaghine, B.; David, G.; Boutevin, B.; Robin, J. J.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2004**, *205*, 154-164.
12. Kukula, H.; Schlaad, H.; Falkenhagen, J.; Kruger, R. P. *Macromolecules* **2002**, *35*, 7157-7160.
13. Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1998**, *31*, 3759-3763.
14. Dimitrov, I.; Schlaad, H. *Chem. Commun.* **2003**, 2944-2945.
15. Coessens, V.; Nakagawa, Y.; Matyjaszewski, K. *Polymer Bulletin* **1998**, *40*, 135-142.
16. Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206-1212.
17. Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939-945.
18. Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; Desimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.
19. Boyer, C.; Loubat, C.; Robin, J. J.; Boutevin, B. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5146-5160.
20. Sadhu, V. B.; Pionteck, J.; Voigt, D.; Komber, H.; Voit, B. *Macromol. Symp.* **2004**, *210*, 147-155.
21. Sadhu, V. B. ; Pionteck, J.; Voigt Dieter; Komber, H.; Fischer, D.; Voit, B. *Macromol. Chem. Phys.* **2004**, *205*, 2356-2365.

22. Matyjaszewski, K.; Nakagawa, Y.; Gaynor, S. G. *Macromol. Rapid Commun.* **1997**, *18*, 1057-1066.
23. Haddleton, D. M.; Waterson, C. *Macromolecules* **1999**, *32*, 8732-8739.
24. Summers, G. J.; Ndawuni, M. P.; Summers, C. A. *Polym. Int.* **2003**, *52*, 158-163.
25. Lecolley, F.; Waterson, C.; Carmichael, A. J.; Mantovani, G.; Harrisson, S.; Chappell, H.; Limer, A.; Williams, P.; Ohno, K.; Haddleton, D. M. *J. Mater. Chem.* **2003**, *13*, 2689-2695.
26. Clouet, G.; Juhl, H. J. *Macromol. Chem. Phys.* **1994**, *195*, 243-251.
27. Meijs, G. F.; Morton, T. C.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1991**, *24*, 3689-3695.
28. Pierson, R. M.; Costanza, A. J.; Weinstein, A. H. *J. Polym. Sci.* **1955**, *17*, 221-246.
29. Konter, W.; Bömer, B.; Köhler, K. H.; Heitz, W. *Makromol. Chem.* **1981**, *182*, 2619-2632.
30. Serre, B.; Rubio, S.; Sledz, J.; Shue, F.; Chapelet-Letourneux, G. *Polymer* **1981**, *22*, 513-518.
31. Postma, A.; Moad, G.; O'Shea, M.; Davis, T. P. *26th Australasian Polymer Symposium* **2003**, PM40.
32. Postma, A.; Moad, G.; Evans, R. A.; Davis, T. P.; O'Shea, M. *IUPAC - World Polymer Congress MACRO 2004, 40th International Symposium on Macromolecules* **2004**, P2.1-122.
33. Postma, A.; Moad, G.; Evans, R. A.; O'Shea, M. S.; Davis, T. P. *27th Australasian Polymer Symposium* **2004**; pp C1-4.
34. Postma, A.; Donovan, A. R.; Moad, G.; Mulder, R.; O'Shea, M. S.; Davis, T. P. *Polymer* **2005**, submitted.
35. Coessens, V.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 66-70.
36. Ing, H. R.; Manske, R. H. F. *J. Chem. Soc.* **1926**, 2348-2351.
37. Gabriel, S. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 2224-2236.
38. Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955-970.
39. Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
40. Matyjaszewski, K.; Davis, K.; Patten, T. E.; Wei, M. *Tetrahedron* **1997**,

53(45), 15321-15329.

41. Ohno, K.; Goto Atsushi; Fukuda, T. *Macromolecules* **1998**, *31*, 2699-2701.
42. Lutz, J.-F.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 897-910.
43. Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization;* Pergamon, Elsevier Science Ltd: Oxford, U.K., 1995.
44. Lutz, J.-F.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2002**, *203*, 1385-1395.
45. Schreck, V. A.; Serelis, A. K.; Solomon, D. *Aust. J. Chem.* **1989**, *42*, 375-393.
46. Yoshikawa, C.; Goto, A.; Fukuda Takeshi *e-Polymers* **2002,** (013), 1-12.
47. Chiefari, J.; Rizzardo, E. *Handbook of Radical Polymerization*; Matyjaszewski, K.; Davis, T. P., Editor; John Wiley & Sons, Inc.: Hoboken, USA, 2002; pp 629-690.
48. Chiefari, J.; Jeffery, J.; Krstina, J.; Moad, C. L.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2005**, *38*, 9037-9054.
49. Garamszegi, L.; Donzel, C.; Carrot, G.; Nguyen, T. Q.; Hilborn, J. *React. Funct. Polym.* **2003**, *55*, 179-183.
50. Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 9009-9014.
51. Summers, G. J.; Ndawuni, P. M.; Summers, C. A. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2058-2067.
52. Harrisson, S. *Personal Communications* .
53. Harrisson, S.; Wooley, K. L. *Polym. Prep.* **2004**, *45*(2), 545-546.

4 Approaches to Phthalimido and Amino End-Functional Polymers by RAFT

4.1 Introduction

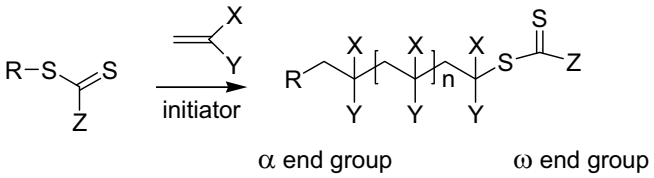
In this chapter we describe the application of RAFT polymerisation in the synthesis of amine end-functional polymers. The method circumvents most of the problems that were observed associated with use of ATRP in this context (Chapter 3).

The synthesis of narrow polydispersity polymers with amine chain ends has recently attracted significant attention due to their potential uses in such fields as surface science, compatibilisation of polymer blends, adhesion and in biomedical applications.[1-4] Our interest in these polymers relates to their potential use in the synthesis of block and graft copolymers with well defined segments by interchain polymer reaction. Polymers with amine chain-ends have advantages with respect to polymers with other reactive functionality (such as hydroxy or thio) because of their greater reactivity.

Several strategies for introducing amine end-group functionality into a chain polymer may be envisaged. End-groups may be incorporated into the chain initiating or chain terminating species through the use of an appropriately designed initiator, transfer agent or chain terminator. The group can be incorporated directly or in a latent form to be converted to the desired functionality in a post polymerisation reaction. Various methods have been exploited to obtain primary amino end-functional polymers, by conventional polymerisation with atom transfer radical polymerisation (ATRP)[5-11] and anionic polymerisation.[12-16] They have also been prepared by functional transfer agents,[17,18] functional iniferters[19] and functional initiators.[20,21] Most processes

require the primary amine group to be protected during the polymerisation process.

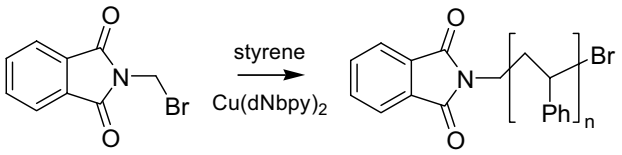
High purity end-functional polymers of can be efficiently synthesized by reversible addition fragmentation chain transfer (RAFT) polymerisation with precise control over the molecular weight and distribution.[22,23] In using RAFT polymerisation to synthesize end-functional polymers, a variety of factors need to be considered. Introducing functionality as the Z activating group[24,25] of the RAFT agent (ω-functionalisation) is not appropriate as it would be lost on later removal of the RAFT moiety from the polymer. The alternative of introducing the functionality as the R leaving/re-initiating group[26,27] of the RAFT agent (α-functionalisation) was therefore employed (Scheme 4.1).



Scheme 4.1

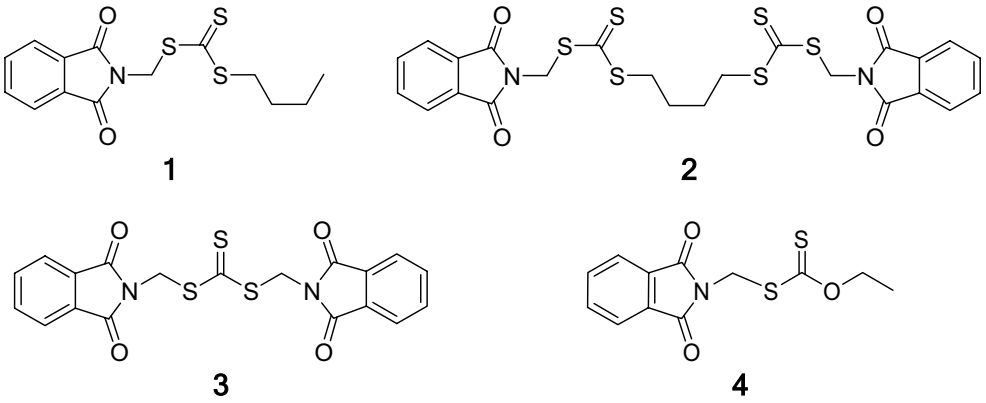
The RAFT process is compatible with a wide range of functional groups including acid, amide, and tertiary amino. However, RAFT is not compatible with unprotected primary or secondary amine functionalities. This is also the case with most other forms of living polymerisation (such as ATRP and anionic polymerisation). The thiocarbonylthio group reacts rapidly with primary and secondary amines to form, in the first instance, a thiol and a dithiocarbamate derivative. It is, therefore, necessary to protect amine end-groups during RAFT polymerisation.

For the present work, a variant on the Gabriel/Ing-Manske procedure[28] was adopted that involved introducing a latent primary amine group as a phthalimidomethyl residue. We have previously used this protection strategy in the design of an ATRP initiator (*N*-(bromomethyl) phthalimide, Scheme 4.2) which was discussed in the previous chapter (Chapter 3).[29]



Scheme 4.2

A related strategy was used by Clouet and Juhl[19] who made use of a phthalimido-functional iniferter in the synthesis of α, ω-primary amino-functional polyisoprene. Phthalimide functionality has also been introduced to polystyrene, poly(*n*-butyl acrylate) and poly(methyl methacrylate) with the use of allyl sulfide chain transfer agents.[17] The phthalimidomethyl trithio- (**1**-**3**) or dithiocarbonate (**4**) RAFT agents investigated in this chapter were synthesized from readily accessible starting materials.



1 **2** **3** **4**

The work described in this chapter is an initial exploration into the activities of the potential RAFT agents. This is done with a focus on firstly their synthesis, their RAFT activities as well as measurement of apparent chain transfer constants. Application to other monomers was also investigated. The following chapter dealing with the RAFT group removal, also further clarified their RAFT behaviour. The amino deprotection step which affords α-amino functionality is also discussed in this chapter.

4.2 Experimental

4.2.1 General

Solvents were of AR grade and were distilled before use. All chemicals and monomers were purchased from Aldrich unless stated. Styrene and *n*-butyl acrylate, were purified by filtration through neutral alumina (70-230 mesh), to remove inhibitors, immediately prior to use. Vinyl acetate (VA) and *N*-vinyl pyrrolidinone (NVP) were flash distilled prior to use, *N*-isopropylacrylamide (NIPAAm) was recrystallised twice from benzene/hexane 3:2 (v:v) and dried under vacuum prior to use. *N*-(bromomethyl)phthalamide was obtained from Aldrich (97%) and was used without purification. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker Advance DRX500, Bruker Av400 or a Bruker AC200 spectrometer on samples dissolved in deuterochloroform, unless stated. Chemical shifts are reported in ppm from external tetramethylsilane. $\overline{M}_n^{NMR}$= number average molecular weight by ^{1}H NMR from the integration of signals attributable to the phthalimido end-group (δ 7.6-8.0) to those for polystyrene aromatics (δ 6.3-7.4) or, for the case of poly(*n*-butyl acrylate), the polymer -OC**H**$_2$CH$_2$CH$_2$CH$_3$ (δ 3.8-4.4); for poly(vinyl acetate), the polymer -CH$_2$C**H**(O)CH$_2$- (δ 4.8-5.2); for poly *N*-isopropylacrylamide, the polymer -C(O)NHC**H**-(*i*-Pr)(*i*-Pr) (δ 3.8-4.0); and for poly *N*-vinyl pyrrolidinone, the total polymer signal (δ 1.2-4.1). High resolution electron impact (HREI), liquid secondary ion mass spectrometry (LSIMS) or high resolution fast atom bombardment (HRFAB) mass spectra were run on a ThermoQuest MAT95XL, positive and negative ion atmospheric pressure chemical ionization (APCI) mass spectra were acquired with a VG Platform mass spectrometer. Gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump and Waters 717 Plus Autosampler equipped with Waters 2414 refractive index detector and 3×Mixed C and 1 mixed E PLgel column (each 7.5 mm×30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22±2 °C. GPC with UV detection was performed on a Waters 2695 Separations Module equipped with Waters 2414 refractive index detector and Waters 2996 photodiode array detector and 3×Mixed C and 1 mixed E

PLgel column (each 7.5 mm×30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 30±2 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) ranging from 600 to 7.5 × 10^6 g mol^{-1}. A third order polynomial was used to fit the $\log_{10}$M *vs* time calibration curve, which appeared to be linear across the molecular weight range 2×10^2–2×10^6. GPC analyses of poly *N*-isopropylacrylamide (PNIPAAm) and poly *N*-vinyl pyrrolidinone (PNVP) were performed using a Shimadzu modular GPC equipped with a SIL-10AD autoinjector and a RID-10A differential refractive index detector. The columns used comprised a Polymer Laboratories 5.0 μm PLgel guard column (50×7.5 mm) followed by four PLgel columns (10^5, 10^4, 10^3, and 500 Å) eluting with and *N*,*N*-dimethylacetamide (DMAc) containing 0.03% w/v LiBr and 0.05% w/v BHT at 40 °C at 1 mL/min. Calibration of the GPCs was performed with narrow polydispersity polystyrene standards ranging from 500 to 10^6 g mol^{-1}. Molecular weights reported in polystyrene equivalents. Thin layer chromatography was run on MERCK aluminium sheet, silica gel 60 F_{254} plates with CH_2Cl_2 as the eluent, unless stated otherwise. The conversions reported in Table 4.2–4.5 were determined by NMR unless stated otherwise.

4.2.2 *S*-*n*-butyl *S'*-phthalimidomethyl trithiocarbonate (1)

The compound was synthesized using the general procedure described elsewhere.[30] Butanethiol (3.0 g, 0.033 mol), carbon disulphide (5.06 g, 0.066 mol) and chloroform (20 mL) were placed in a dry three necked round bottomed flask. Triethylamine (6.9 g, 0.068 mol) was added dropwise with stirring. The solution became yellow/orange as the addition proceeded with formation of the intermediate triethylammonium *S*-*n*-butyl trithiocarbonate. The solution was left to stir at room temperature for 3 hours. TLC R_f = 0.1.

N-(bromomethyl)phthalimide (7.99 g, 0.033 mol) was then added slowly causing the mixture to thicken on formation of the bromide salt. The reaction mixture was stirred overnight and the extent of reaction was confirmed by TLC, R_f = 0.60. The reaction mixture was diluted with an additional 20 mL chloroform prior

to washing sequentially with 2×50 mL of each: deionized water, 2M H_2SO_4 (aq), deionized water and saturated brine. The solution was dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation to give a yellow solid. Yield = 10.39 g (95.9 %), mp = 89-91 °C.

^{1}H NMR ($CDCl_3$) δ: 0.92 (tr, J = 7.2 Hz, 3H, C**H**$_3$-), 1.41 (m, J = 7.3 Hz 2H, CH_3C**H**$_2CH_2CH_2$-), 1.67 (m, J = 7.4 Hz, 2H, CH_3CH_2C**H**$_2CH_2$-), 3.36 (tr, J = 7.4, 2H, (-C**H**$_2$-S), 5.64 (s, 2H, N-C**H**$_2$-S), 7.74 (m, 2H, Ar**H**), 7.87 (m, 2H, Ar**H**).

^{13}C NMR ($CDCl_3$) δ: 13.5 (**C**H_3-), 22.0 (CH_3**C**$H_2CH_2CH_2$-), 29.8 (CH_3CH_2**C**H_2CH_2-), 36.9 (-**C**H_2-S), 41.9 (N-**C**H_2-S), 123.7 (2 × *o*-Ph, **C**H), 131.8 (2 × Ph, **C**), 134.4 (2 × *p*-Ph, **C**H), 166.6 (**C**=O), 220.8 (**C**S_3).

MS (HREI, +VE, +LMR) m/z 325.0260 (M^+) ($C_{14}H_{15}NO_2S_3$ requires 325.0265).

4.2.3 1,4-Bis-((phthalimidomethylsulfanylthiocarbonyl)sulfanyl)butane (2)

1,4 Butanedithiol (2.45 g, 0.02 mol), carbon disulphide (6.09g, 0.080 mol) and chloroform (20 mL) were placed in a dry three necked round bottomed flask. Triethylamine (8.10 g, 0.080 mol) was added dropwise with stirring, the solution became yellow/orange as the addition proceeded with formation of the intermediate triethylammonium salt. An ice bath was used to control the temperature. The mixture was left to stir for an hour, the salt became an immiscible oil on warming to room temperature. The salt dissolved on addition of dichloromethane (20 mL).

To this solution, *N*-(bromomethyl)phthalimide (5.039 g, 0.021 mol) was added slowly, with the mixture thickening on formation of the bromide salt. Reaction was stirred overnight, complete reaction of products was confirmed by TLC, R_f = 0.37. The reaction mixture was diluted with an additional 20 mL chloroform and washed sequentially with 2×50 mL of each: deionized water, 2M H_2SO_4 (aq), deionized water and saturated brine. The solution was then dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation to give a yellow solid (yield 96%). Crystallized from ethanol to give Yield $_{\text{cleanest fraction}}$ = 1.94 g (31.2

%), mp = 179–181 °C. Further fractions, on attempted recrystallization from ethanol, were found to contain significant amounts of decomposition product **6**.

^{1}H NMR ($CDCl_3$) δ: 1.81 (br tr, 4H, -C**H**$_2$-), 3.38 (br tr, 4H, S-C**H**$_2$-), 5.63 (s, 4H, N-C**H**$_2$-S), 7.74 (m, 4H, Ar**H**), 7.86 (m, 4H, Ar**H**).

^{13}C NMR ($CDCl_3$) δ: 27.2 (2 × -**C**H$_2$-), 36.3 (2 × S-**C**H$_2$-), 42.0 (2 × N-**C**H$_2$-S), 123.7 (4 × *o*-Ph, **C**H), 131.8 (4 × Ph, **C**), 134.4 (4 × *p*-Ph, **C**H), 166.6 (4 × **C**=O), 220.4 (2 × **C**S$_3$).

MS (AP-) m / z 592.0 (M^+); (EI, +VE, +LMR) m / z 592.0 (M^+) ($C_{24}H_{20}N_2O_4S_6$ requires 591.9747); (HRFAB, +VE, +LMR) m/z 593.1 (M+1), 724.8786 (M+Cs) ($C_{24}H_{20}N_2O_4S_6$·Cs requires 724.8802).

4.2.4 *S,S'*-bis(phthalimidylmethyl) trithiocarbonate (3)

This compound was prepared according to the general procedure of Leung *et al.*[31] Potassium hydroxide (2.06 g, 0.037 mol), carbon disulphide (6.32g, 0.083 mol) and water (20 mL) were placed in a dry three necked round bottomed flask. The phase transfer catalyst, tetrabutylammonium hydrogensulfate (0.17 g, 5.00×10^{-4} mol), was added with stirring, forming a dark red colour due to the bispotassium trithiocarbonate salt, on the interface. The solution was left to stir at room temperature for 2 hours when *N*-(bromomethyl) phthalimide (1.20 g, 0.005 mol) was added slowly. The resultant orange solution, was left to stir for 24 hours during which time a yellow solid formed. This solid was dissolved in chloroform (30 mL) prior to washing with 3×100 mL of the following, brine, 2M H_2SO_4(aq), deionized water, brine. The solution was dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation. The crude product (1.18 g) was dissolved in hot ethanol (20 mL), the white crystalline solid filtered off and solvent removed to leave a yellow oil that slowly crystallized on standing. R_f = 0.27, yield = 0.461 g (43.0 %), mp = 219–220 °C.

^{1}H NMR ($CDCl_3$) δ: 5.65 (s, 4H, N-C**H**$_2$-S), 7.75 (m, 4H, Ar**H**), 7.88 (m, 4H, Ar**H**).

^{13}C NMR ($CDCl_3$) δ: 42.2 (2 × N-**C**H_2-S), 123.8 (4 × *o*-Ph, **C**H), 131.8 (4 × Ph, **C**), 134.5 (4 × *p*-Ph, **C**H), 166.6 (4 × **C**=O), 217.1 (**C**S_3).

MS (HREI) m/z 427.9947 (M^+) ($C_{19}H_{12}N_2O_4S_3$ requires 427.9959).

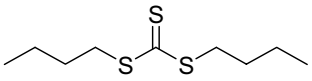
4.2.5 *S*,*S*'-bis(*n*-butyl) trithiocarbonate (5)

S,*S*'-bis(*n*-butyl) trithiocarbonate (**5**) was isolated as a side product from the large scale synthesis of (**1**) when partially hydrolysed (pH 4) *N*-(bromomethyl)phthalimide (Epsilon Chimie) was used. The mother liquor, from the recrystallization of (**1**), was subjected to flash chromatography on silica and the eluent evaporated *in vacuo* to leave a yellow oil (**5**). TLC, R_f = 0.80.

^{1}H NMR ($CDCl_3$) δ: 0.93 (tr, J = 7.4 Hz, 2 × 3H, C**H**$_3$-), 1.43 (m, J = 7.5 Hz, 2 × 2H, CH_3C**H**$_2$$CH_2CH_2$-), 1.68 (m, J = 7.5 Hz, 2 × 2H, CH_3CH_2C**H**$_2$$CH_2$-), 3.36 (tr, J = 7.5, 2 × 2H, -C**H**$_2$-S).

^{13}C NMR ($CDCl_3$) δ: 13.6 (2 × **C**H_3-), 22.1 (2 × CH_3**C**$H_2CH_2CH_2$-), 30.1 (2 × CH_3CH_2**C**H_2CH_2-), 36.5 (2 × -**C**H_2-S), 224.8 (**C**S_3).

MS (HREI, +VE, +LMR) m/z 222.0565 (M^+) ($C_9H_{18}S_3$ requires 222.0571).



5

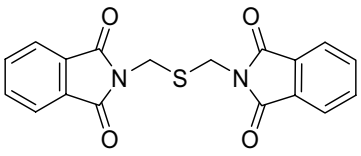
4.2.6 Bis(phthalimidomethyl) sulfide (6)

An additional bi-product, bis(phthalimidomethyl) thioether (**6**), was isolated by recrystallization from the mother liquor as a white, fluffy crystalline solid on standing. TLC, R_f = 0.17 (CH_2Cl_2), mp = 236-237 °C.

^{1}H NMR ($CDCl_3$) δ: 5.14 (s, 2H, N-C**H**$_2$-S), 7.75 (m, 2H, phthalyl aromatic), 7.88 (m, 2H, Ar**H**).

^{13}C NMR ($CDCl_3$) δ: 40.4 (2 × N-**C**H_2-S), 123.6 (4 × *o*-Ph, **C**H), 132.1 (2 × Ph, **C**), 134.2 (2 × *p*-Ph, **C**H), 167.4 (**C**=O).

MS (HREI, +VE, +LMR) m/z 352.0512 (M^+) ($C_{18}H_{12}N_2O_4S$ requires 352.0518).



6

4.2.7 Synthesis of *O*-ethyl *S*-(phthalimidylmethyl) xanthate (4)

Potassium *O*-ethyl xanthate (1.03 g, 6.43×10^{-3} mol) was suspended in chloroform (20 mL) in a dry two necked round bottomed flask. *N*-(bromomethyl)phthalimide (1.00 g, 4.17×10^{-3} mol), dissolved in chloroform (20 mL) was added dropwise with stirring. The solution become pale yellow with the appearance of white KBr salt as the reaction proceeded, forming the title compound. The solution left to stir at room temperature for 18 hours, complete reaction of products was confirmed by TLC, R_f = 0.60.

Additional chloroform (20 mL) was added prior to washing with 2×50 mL of deionized water and 1×50 mL brine. The solution was dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation to give a pale yellow solid. Yield = 1.16 g (98%), mp = 94-95 °C

^{1}H NMR ($CDCl_3$) δ: 1.46 (tr, J = 7.1 Hz, 3H, CH_3CH_2-), 4.68 (q, J = 7.1, 2H, CH_3CH_2-O), 5.33 (s, 2H, N-CH_2-S), 7.75 (m, 2H, Ar**H**), 7.85 (m, 2H, Ar**H**).

^{13}C NMR ($CDCl_3$) δ: 13.7 (**C**H_3CH_2-), 41.2 (N-**C**H_2-S), 70.5 (CH_3**C**H_2-),123.6 (2 × *o*-Ph, **C**H), 131.8 (2 × Ph, **C**), 134.4 (2 × *p*-Ph, **C**H), 166.6 (2 × **C**=O), 210.2 (O**C**S_2).

MS (HREI, +VE, +LMR) m/z 281.0174 (M^+) ($C_{12}H_{11}NO_3S_2$ requires 281.0175).

4.2.8 *S*-(*n*-butyl) *S'*-(1-phenylethyl) trithiocarbonate (7)

This RAFT agent was synthesized and provided by Guoxin Li:

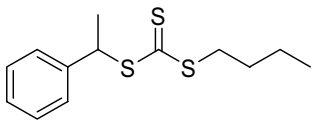
Triethylamine (67.3 g, 0.665 mol) was added dropwise to a solution of 1-butanethiol (30.0 g, 0.333 mol) and carbon disulfide (50.7 g, 0.666 mol) in 200 mL of chloroform while stirring at room temperature. The solution became orange as addition processed. After addition, the mixture was stirred at room temperature for further 3 hrs. TLC showed only one yellow spot, R_f = 0.14.

(1-Bromoethyl)benzene (60.4 g, 0.326 mol) was added dropwise into solution and the mixture was stirred overnight at room temperature (TLC showed only one yellow spot, R_f = 0.65). The reaction solution was dilute with chloroform (200 mL), washed with 2×100 mL of each: H_2O, 2M H_2SO_4, H_2O, and brine and dried over anhydrous $MgSO_4$ for one hour. The mixture was filtered and the filtrate was evaporated to remove all solvent, the resultant product an oily yellow liquid (88.1 g, ~100%).

^{1}H NMR ($CHCl_3$) δ: 1.00 (t, 3H, C**H**$_3$CH$_2$CH$_2$CH$_2$-), 1.50 (m, 2H, CH$_3$C**H**$_2$CH$_2$CH$_2$-), 1.73 (m, 2H, C**H**$_2$-S), 1.81 (d, 3H, C**H**$_3$(CH-)-), 3.41 (t, 2H, -S-C**H**$_2$), 5.41 (q, C**H**), 7.42 (m, 5H, Ar**H**).

^{13}C NMR ($CDCl_3$) δ: 13.7 (**C**H$_3$CH$_2$CH$_2$CH$_2$-), 21.4 (**C**H$_3$CH), 22.1 (CH$_3$**C**H$_2$CH$_2$CH$_2$-), 30.1 (CH$_3$CH$_2$**C**H$_2$CH$_2$-), 36.5 (-**C**H$_2$-S), 50.1 (**C**H), 127.7 (*p*-Ph, **C**H), 127.8 (*m*-Ph, **C**H), 128.7 (*o*-Ph, **C**H) 141.2 (Ph, **C**), 223.1 (**C**S$_3$).

MS (HREI) m/z 270.0562 (M^+) ($C_{13}H_{18}S_3$ requires 270.0565).



7

4.2.9 RAFT polymerisation

RAFT agent **1** (0.0943 g, 2.90×10^{-4} mol) and styrene (9.13 g, 8.76×10^{-2} mol) were combined to form a stock solution, of which 6 equal aliquots of ~1.6 mL were transferred to ampoules, degassed with 4 freeze-pump-thaw cycles, and sealed under vacuum. The ampoules were then heated at 110 °C for 1, 2, 4, 8, 16 hrs and subsequently the polymerisation was quenched in liquid nitrogen. Samples of the monomer/polymer mixture were diluted with THF or $CDCl_3$ (for GPC or NMR analysis respectively). Results can be found in Table 4.2.

4.2.10 RAFT polymerisation with xanthates

Xanthate **4** (0.281 g, 9.98×10^{-4} mol), AIBN (101.9 mg, 6.21×10^{-5} mol) and vinyl acetate (9.34 g, 1.09×10^{-1} mol) were combined to form a stock solution, of which 5 equal aliquots of 2 mL were transferred to ampoules, degassed with 4 freeze-pump-thaw cycles, and sealed under vacuum. The ampoules were then heated at 60 °C for 1, 2, 4, 8, 16 hrs and subsequently the polymerisations were quenched in liquid nitrogen. Samples of the monomer/polymer mixture were diluted with THF or $CDCl_3$ (for GPC or NMR analysis respectively). Results can be found in Table 4.6.

4.2.11 Large scale polymerisation

RAFT agent **1** (9.07 g, 2.79×10^{-2} mol) and styrene (200 g, 1.92 mol) were transferred to a 500 mL 3 necked round bottomed flask, purged with argon for 3 hours and degassed with 3 vacuum-argon-vacuum cycles and sealed under a slight positive pressure of argon. The mixture was then heated at 110 °C for 24 hours and subsequently the polymerisation was quenched with addition of ~300 mL THF and the polymer was precipitated into 2.5 L of methanol. The polymer was filtered under reduced pressure for 16 hrs and dried in a vacuum oven at 40 °C for 16 hrs. Samples of the monomer/polymer mixture and of the precipitate

were diluted with THF or $CDCl_3$ (for GPC or NMR analysis respectively). Results can be found in Table 4.4.

4.2.12 Hydrazinolysis of α-phthalimidopolystyrene (17&18)

Sufficient ethanol (*ca* 1 mL) was added to a two phase mixture of a solution of the end-functional polystyrene **18** (0.8 g) in THF (10 mL) and hydrazine monohydrate (0.5 mL) to give a homogeneous solution which was then heated under reflux overnight (16 h). The solution was observed to turn yellow after *ca* 2 h due to formation of phthalyl hydrazide. The polystyrene was isolated by precipitation into methanol and filtration and was dried in a vacuum oven for 16h to give a colourless polymer **19**.

4.2.13 Polymer derivatisation with trichloroacetyl isocyanate

The following procedure is typical:[32]

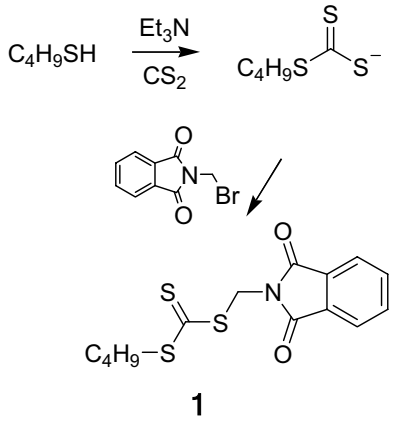
A sample of polystyrene **19** (~40 mg) was dissolved in $CDCl_3$ (0.5 mL) and the solution transferred to a 5 mm NMR tube. An excess of trichloroacetyl isocyanate (10 μL, 6.3 mg, 33.4 μmol) was then added and the ^1H NMR spectrum obtained for **20**. Derivatisation was complete within the time taken to place the tube in the spectrometer (< 10 min).

4.3 Results and discussion

4.3.1 RAFT agent synthesis

The further exploitation of amino functional polymers required an efficient synthesis of phthalimido-functional RAFT agents. Previous work had shown that trithiocarbonates are readily synthesized in high purity and high yield from a thiol, carbon disulfide and an alkylating agent in a one-pot synthetic procedure

(Scheme 4.3). Yields are generally high (>70%) for substitution of primary and secondary alkyl halides, but can be low for tertiary halides (5-40%).[30,33] The trithiocarbonates RAFT agents **1** (>95% yield) and **2** (>95% yield) were synthesized from 1-butanethiol and 1,4-butanedithiol respectively as the thiol and with *N*-(bromomethyl)phthalimide as the alkylating agent. The synthesis of **7** (>95% yield) made use of the same procedure with (1-bromoethyl)benzene as the alkylating agent. The phthalimide derivatives were readily recrystallized from warm ethanol to provide purities exceeding 98%. A large scale synthesis of **1** that made use of unpurified *N*-(bromomethyl)phthalimide, which was later shown to be acidic (pH 4) due to partial hydrolysis, gave a lower yield (~37%) and two main by-products **5** and **6** were obtained in ~25-30% yield each. Small amounts of both **5** and **6** were also observed to form during the long cooling times in the recrystallisation of **1** from hot ethanol.



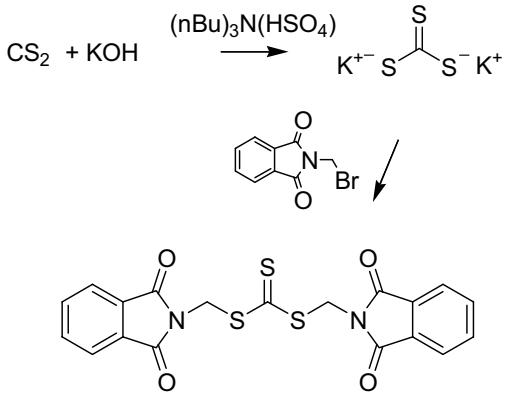
1

Scheme 4.3

The synthesis of **1** was also attempted using *N*-(chloromethyl)phthalimide as the alkylating agent, but more forcing reaction conditions (refluxing for 16 hours in chloroform) were required and provided a substantially lower yield (8.9%) than what was obtained with *N*-(bromomethyl)phthalimide.

RAFT agent **3** was obtained by the procedure described by Leung *et al.* (Scheme 4.4).[31] The isolated yield (43%) was low which can be attributed to the potential sensitivity of the phthalimide to strong bases exasperated by the extended reaction times that are used for the synthesis of these symmetrical

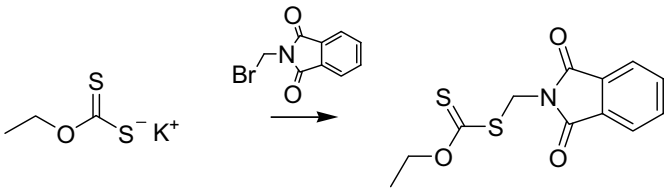
trithiocarbonates. The solubility of the alkylating agent and the RAFT agent in the medium could also be an issue.



3

Scheme 4.4

Xanthate **4** was synthesized in high purity (>98%) and yield (98%) by alkylation of the commercially available potassium *O*-ethyl xanthate with *N*-(bromomethyl)phthalimide (Scheme 4.5).



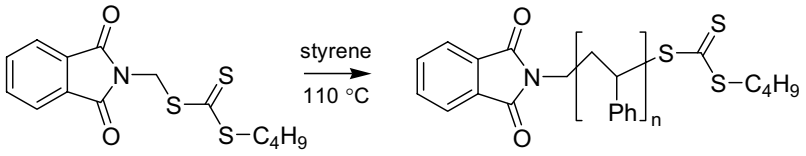
4

Scheme 4.5

4.3.2 Primary phthalimido end-functional polystyrene

The polymerisation using RAFT agent **1** and **2** provided molecular weights close to those expected and narrow polydispersities ($\overline{M}_w / \overline{M}_n$ <1.2 at high conversion, Table 4.2 and Table 4.3). The overall process for synthesis of α-phthalimidomethylpolystyrene using RAFT agent **1** is shown in Scheme 4.6. The RAFT agent **1** is still being consumed up until around ~20% conversion,

forming the polymeric RAFT agent, with polydispersity control increasing to a peak (1.12) at around 60–80% conversion.



Scheme 4.6

The RAFT agent **3** also gave good control over the polymerisation (Table 4.2). However, its use was complicated by its low solubility in styrene at room temperature. Each of the RAFT agents **1**–**3** were soluble in styrene at the polymerisation temperature. Molecular weights, polydispersities and conversions obtained in thermal styrene polymerisations with RAFT agents **1**–**3** are provided in Table 4.2–Table 4.4. Plots showing the evolution of the molecular weight and polydispersity with conversion are shown in Figure 4.1–Figure 4.3. Similar data have been obtained for dibenzyl trithiocarbonate (**13**) and *S*-(1-phenylethyl) *S'*-trithiocarbonate (**7**)[24] which are provided in Figure 4.5 and Figure 4.4, respectively. Generally, they all show a linear increase in molecular weight with conversion, a correspondence between calculated molecular weights ($\overline{M}_{\mathrm{n}}^{\mathrm{Calc}}$) and those measured by GPC ($\overline{M}_{\mathrm{n}}$) and a narrowing of polydispersity (<1.16) at high conversions (60–80%).

Table 4.3 demonstrates that AIBN initiated styrene polymerisation using **1** can also be conducted successfully at 60 °C. However, an unavoidable production of AIBN terminated polymer chains will result in slightly compromised end-group purity.

As expected, **5** showed little RAFT activity, exhibited in minor control over the molecular weight shown in Table 4.2. This can be rationalized in terms of **5** containing two poor R leaving/reinitiating butyl groups. Thiolethers, like impurity **6** (although not tested) generally show very low transfer constants and can be considered inert in the polymerisation.[34]

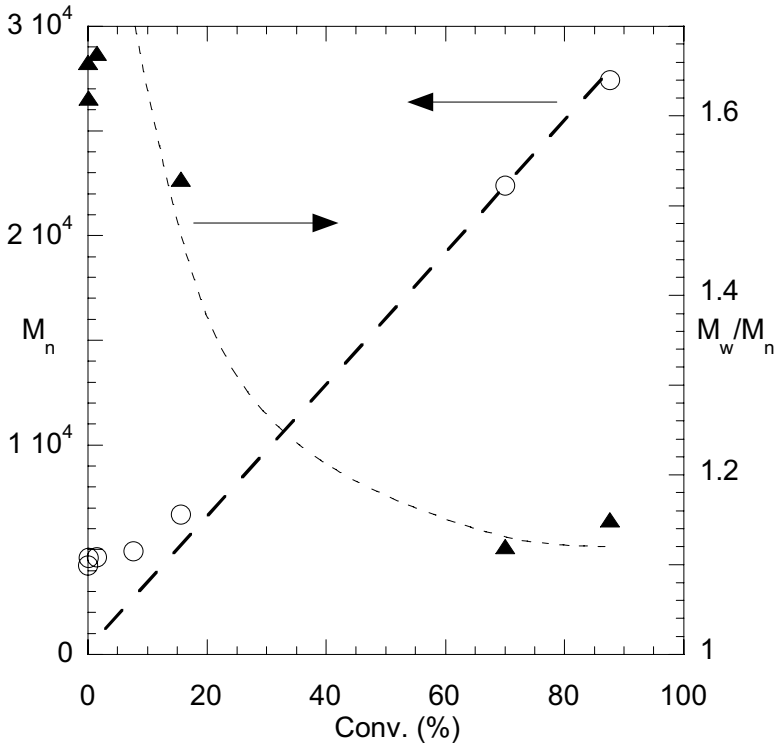


Figure 4.1. Evolution of polydispersity (▲,---) and molecular weight (○) with conversion for bulk thermal styrene polymerisation at 110 °C in the presence of (**1**). Calculated molecular weight by NMR (- - -).

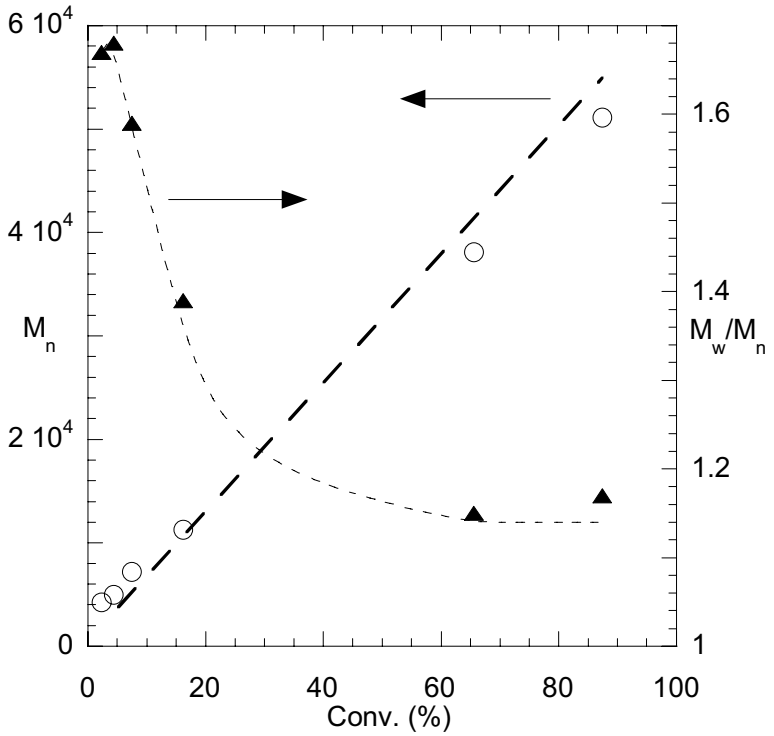


Figure 4.2. Evolution of polydispersity (▲,---) and molecular weight (○) with conversion for bulk thermal styrene polymerisation at 110 °C in the presence of (**2**). Calculated molecular weight by NMR (**- - -**).

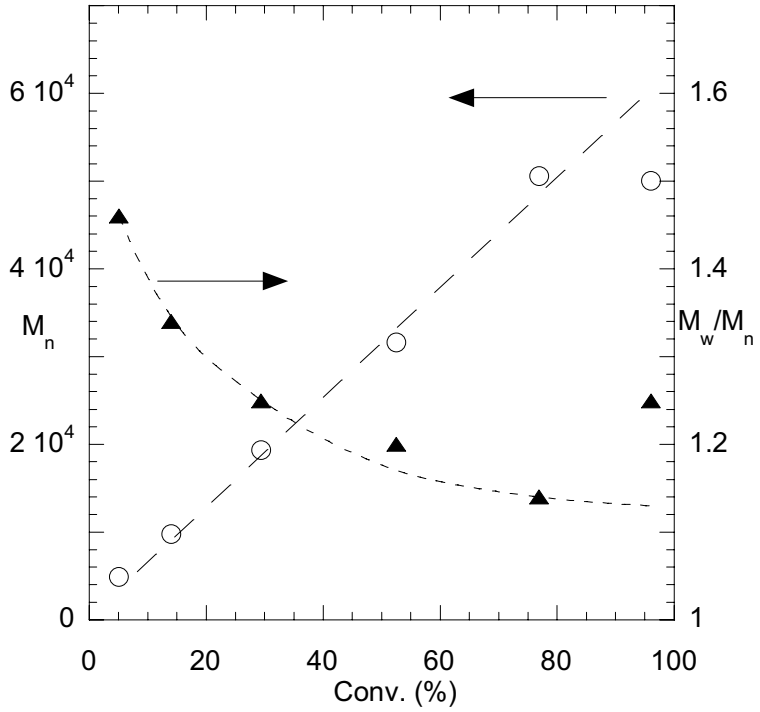


Figure 4.3. Evolution of polydispersity (▲,---) and molecular weight (○) with conversion for bulk thermal styrene polymerisation at 110 °C in the presence of (**3**). Calculated molecular weight by NMR (- - -).

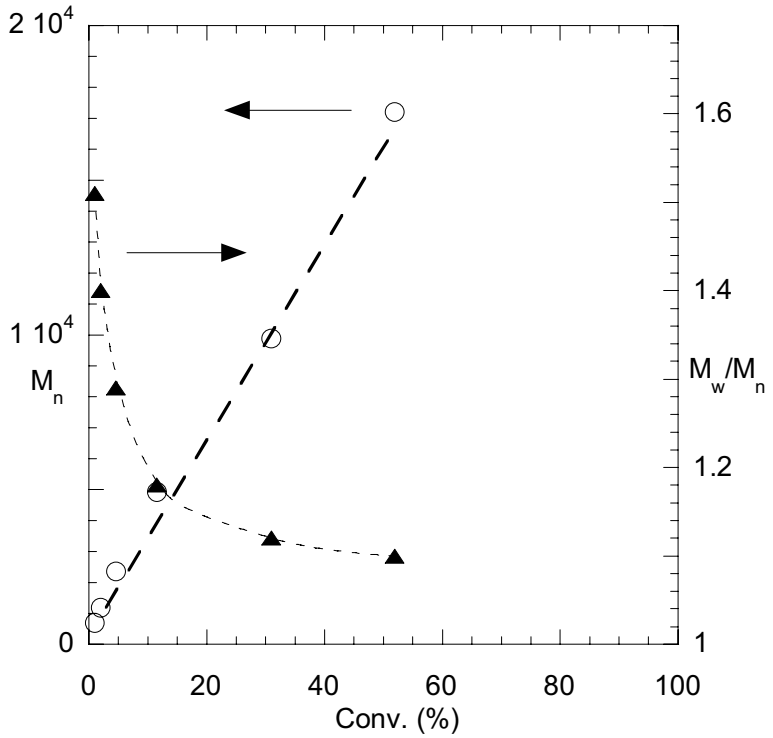


Figure 4.4. Evolution of polydispersity (▲,---) and molecular weight (○) with conversion for bulk thermal styrene polymerisation at 110 °C in the presence of (**7**). Calculated molecular weight by NMR (**- - -**).

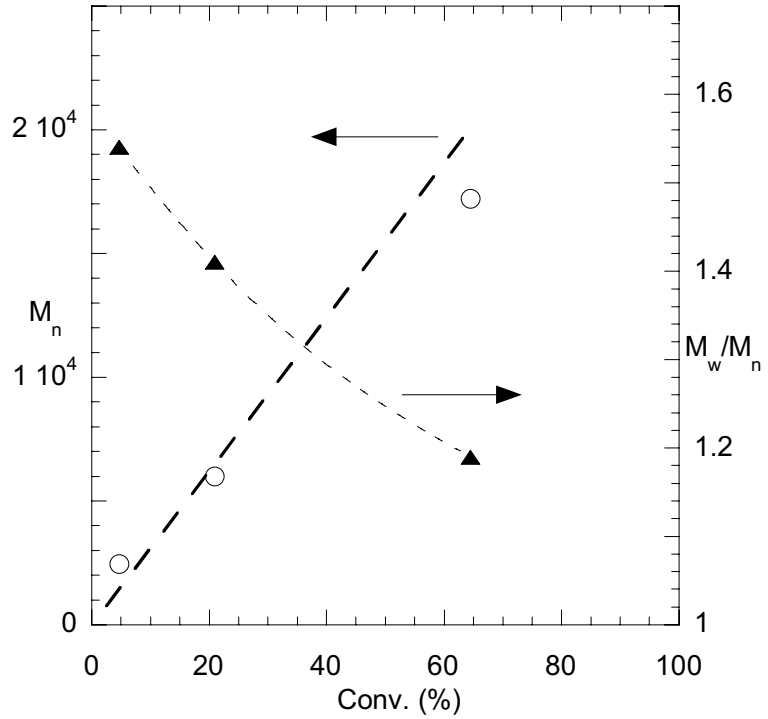
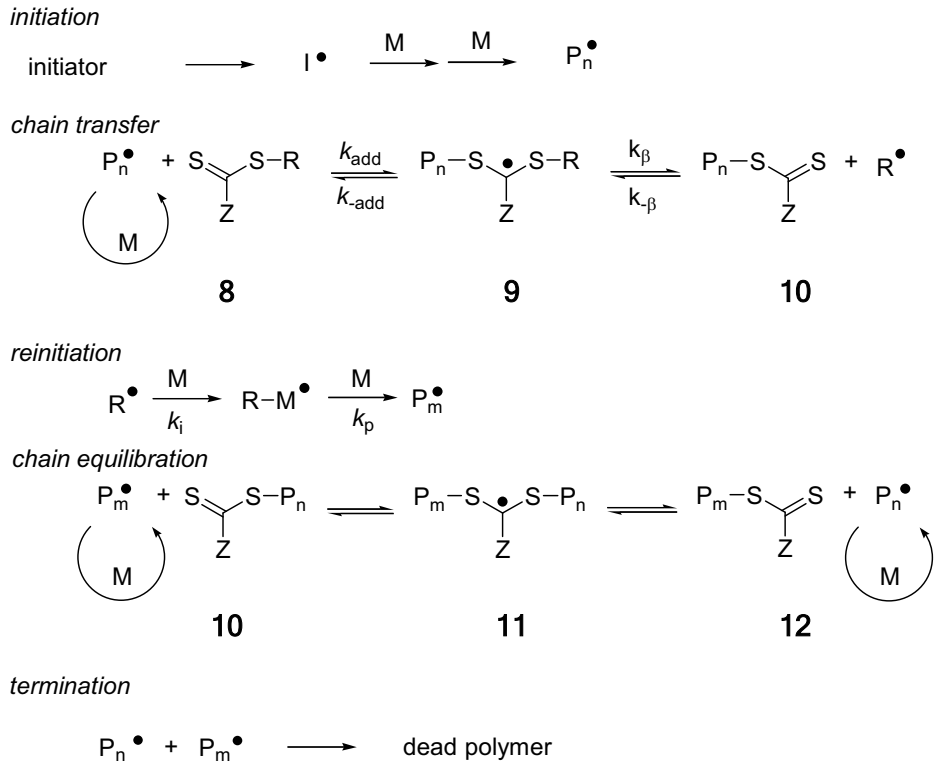


Figure 4.5. Evolution of polydispersity (▲,---) and molecular weight (○) with conversion for bulk thermal styrene polymerisation at 110 °C in the presence of (**13**). Calculated molecular weight by NMR (– – –).Experimental details were obtained and printed with permission.[24]

4.3.3 RAFT agent activity in styrene polymerisation



Scheme 4.7

The apparent transfer constants for the RAFT agents can be calculated using equation (1), referring to RAFT Scheme 4.7.

$$\frac{d[\mathbf{8}]}{d[M]} \approx C_{tr} \frac{[\mathbf{8}]}{[M] + C_{tr}[\mathbf{8}] + C_{-tr}[\mathbf{10}]} \qquad (1)$$

This equation can, in principle, be solved numerically to provide estimates of C_{tr} and C_{-tr}. If the rate of the reverse reaction between R• and the polymeric RAFT agent (**10**) is negligible (low C_{-tr} and/or low [**10**]) and if chains are long (monomer consumed by reaction with R• is small), this expression simplifies to an expression (equation 2) that describes conventional chain transfer and the transfer constant can be evaluated from the slope of a plot of log[**8**] *vs.* log[M].[39]

$$\frac{d[\mathbf{8}]}{d[M]} \approx C_{tr} \frac{[\mathbf{8}]}{[M]} \qquad (2)$$

$$C_{tr} \approx \frac{d\log[\mathbf{8}]}{d\log[M]} \quad (3)$$

Values of C_{tr} reported in this chapter have been calculated using equation (3) and should therefore be considered as apparent transfer coefficients for the given reaction conditions rather than transfer constants and be taken as minimum values pending further investigation over a wider range of RAFT agent concentrations. The linearity of the double log plots (log[**8**] *vs*. log[M]) or Mayo plots is consistent with, but does not prove, that the reaction between R• and the polymeric RAFT agent (**10**) is negligible.

In chain transfer by addition-fragmentation (Scheme 4.7), the rate constant for chain transfer (k_{tr}) is given by the following expression (equation 4).[40]

$$k_{tr} = k_{add} \times \frac{k_{\beta}}{k_{-add} + k_{\beta}} \quad (4)$$

Similarly, the reverse transfer constant (k_{-tr}) is given by equation (5).

$$k_{-tr} = k_{-\beta} \times \frac{k_{-add}}{k_{-add} + k_{\beta}} \quad (5)$$

In this work, the concentration of residual RAFT agent in the reaction mixtures has, where possible, been determined directly by NMR analysis. The ^{1}H NMR resonance associated with the methylene of phthalimido RAFT agents **1**-**3** appears at ~δ 5.64 where there is no interference from other signals.

The signals due to RAFT agents were compared with those due to the residual monomer $([RAFT]/[M])_t$. Thus, since the conversion $([M]_t)$ is known independently,

$$\text{conversion of RAFT agent} = (([RAFT]/[M])_t\,[M]_t)/[RAFT]_o \quad (6)$$

Plots of log[RAFT] *vs*. log[M] for thermal polymerisation of styrene at 110 °C for the RAFT agents **1**-**3** are shown in Figure 4.6. The apparent transfer coefficients are summarized in Table 4.1. The transfer constants are of the

same magnitude as that previously determined for dibenzyl trithiocarbonate (**13**) under similar reaction conditions.[24]

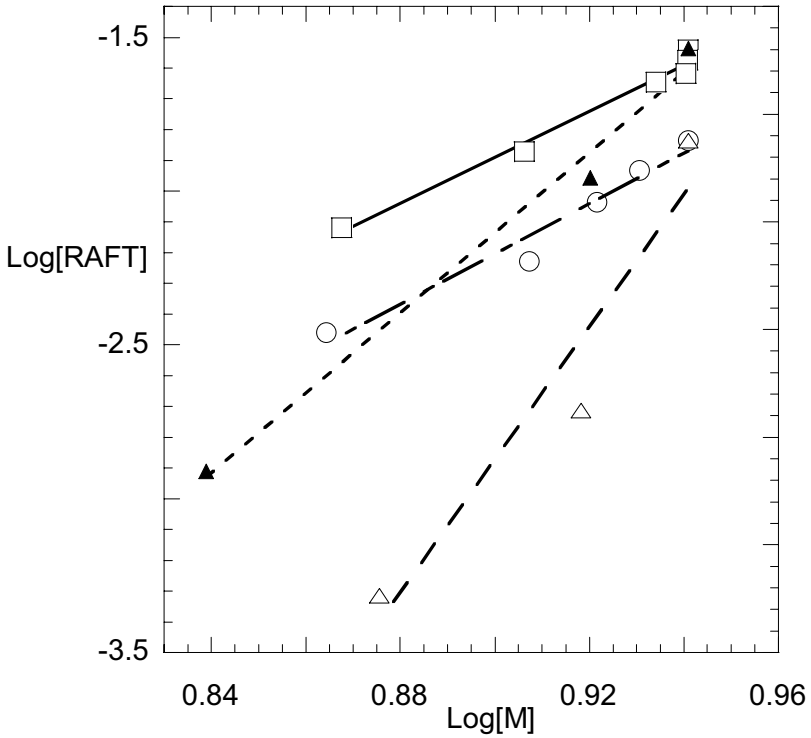


Figure 4.6. Double log plot of [RAFT] *vs* [Styrene] for thermal polymerisations at 110 °C. Residual RAFT agent determined from NMR. RAFT agents **1** (□), **2** (○), **3** (Δ) and **13**(▲). Lines of best fit to molecular weight derived data that provide transfer constants shown in Table 4.1.

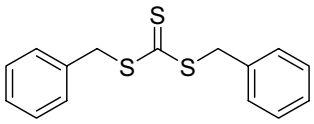


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Table 4.1. Transfer coefficients for RAFT agents in the thermal polymerisation of styrene at 110 °C evaluated from NMR.

RAFT agent	C_{tr}
1	7.5
2	8.2
3	22
13	18[24]

Referring to Figure 4.6, the apparent coefficient for RAFT agent **3** is not linear, in fact it shows two distinct trends, this is also observed with **13**. We believe for **3**, that this is attributed to the polystyryl chain being a better homolytic leaving group, at a certain stage of the polymerisation, than the phthalimidomethyl group of the polymeric RAFT agent. Hence the kinetic change observed during the polymerisation.

Table 4.2. Molecular weights and polydispersities for polystyrene obtained in thermal polymerisations of styrene in the presence of RAFT agents (**1**-**5**) at 110 °C.

RAFT agent	time (h)	$[M]_o/[RAFT]_o$ ($\times 10^2$)	$\overline{M}_n^{Calc}$ [a,b] (g mol^{-1})	$\overline{M}_n$ [a] (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv.[c] (%)
1	2	3.01	2730	4920	1.74	7.7
1	24	0.200	1680	1460	1.21	65
1	24	1.00	7370	6840	1.16	68
1	24	6.04	42700	43200	1.16	67
2	2	5.95	4950	7220	1.59	7.5
2	24	0.200	1520	1470	1.25	57
2	24	1.00	6760	6650	1.14	59
2	24	3.00	19500	19800	1.12	60
2	24	5.94	41100	38100	1.15	66
3	16	5.96	33000	31600	1.20	52
3	32	5.92	47860	50600	1.14	77
control	16	0	-	279000	1.92	58
control	24	0	-	287000	1.95	77
5	24	5.79	54000	265000	1.90	89 [d]
5	24	0.581	4570	174000	1.96	76

[a] All values rounded to three significant figures. [b] $\overline{M}_n^{Calc}$ ~ [M]/[RAFT]$_o$×Conv×104+(molecular weight of RAFT agent). [c] NMR conversion, [d] Gravimetric conversion.

Table 4.3. Molecular weights and polydispersities for polystyrene obtained in polymerisations of styrene in the presence of RAFT agent (**1**), AIBN at 60 °C for 24 hours.

RAFT agent	Time (h)	[M]$_o$/[RAFT]$_o$ (×10^2)	$\overline{M}_n^{Calc}$ [b,c] (g mol^{-1})	$\overline{M}_n$ [b] (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv.[d] (%)
1	24	1.00	4980	4610	1.27	48
1	24	0.200	1740	1850	1.20	84

[a] AIBN concentration = 7.69×10^{-2} mol. [b] Values rounded to three significant figures. [c] $\overline{M}_n^{Calc}$ ~ ([M]/[RAFT]$_o$×Conv×104)+(molecular weight of RAFT agent). [d] NMR conversion.

The scale-up of the polymerisation of styrene using **1** has been investigated for molecular weights ranging from 1k–100k and polymer yields of ~100–300 grams. The results are shown in Table 4.4. Whilst there is some deviation from calculated molecular weight and broadening of molecular weight distribution observed in the samples of the higher molecular weights, the results are satisfactory for our objectives. These results may in part be attributed to the increased scale of the polymerisations which may coincide in some compromises to reaction conditions (thorough degassing, adequate temperature control). Furthermore, the polymerisation was conducted with >90% pure RAFT agent **1** (from the scaled synthesis), although the main impurities, **5** and **6**, being relatively inert.

Table 4.4. Molecular weights and polydispersities for polystyrene obtained in large scale thermal polymerisations of styrene in the presence of RAFT agent (**1**) at 110 °C for 24 hours.

RAFT agent	$[M]_o/[RAFT]_o$ ($\times 10^2$)	$\overline{M}_n^{Calc}$ [a,b] (g mol^{-1})	$\overline{M}_n$ [a] (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv.[c] (%)	Polymer (g)
1	0.208	1610	1370	1.18	49	133.1
1	0.689	5560	4770	1.17	66	142.1
1	3.02	16800	13600	1.24	44	218.0
1	6.00	43200	35200	1.23	66	313.9
1	30.3	169000	124000	1.37	68	276.3

[a] Values rounded to three significant figures. [b] $\overline{M}_n^{Calc}$ ~ $[M]/[RAFT]_o \times Conv \times 104 +$(molecular weight of RAFT agent). [c] NMR conversion.

4.3.4 RAFT agent activity in *n*-butyl acrylate, *N*-isopropylacrylamide and *N*-vinyl pyrrolidinone polymerisation

Acrylates can be controlled with a wider range of RAFT agents as their polymerisation is characterised by propagating radicals that show relatively low steric bulk and high reactivity, facilitating both the addition of the propagating radical to the C=S double bond and the fragmentation of the R group. Figure 4.7, showing the evolution of the molecular weight and polydispersity with conversion of *n*-butyl acrylate with RAFT agent **1** at 60 °C is in agreement with a living system. It is particularly noteworthy that the polydispersity for the generated poly (*n*-butyl acrylate) starts off low and remains low, even at high conversion (> 80%). This would indicate that the phthalimido substituent of **1** must be a good homolytic leaving group relative to the attacking *n*-butyl acrylate P_n• radical. This data is also contained in Table 4.5.

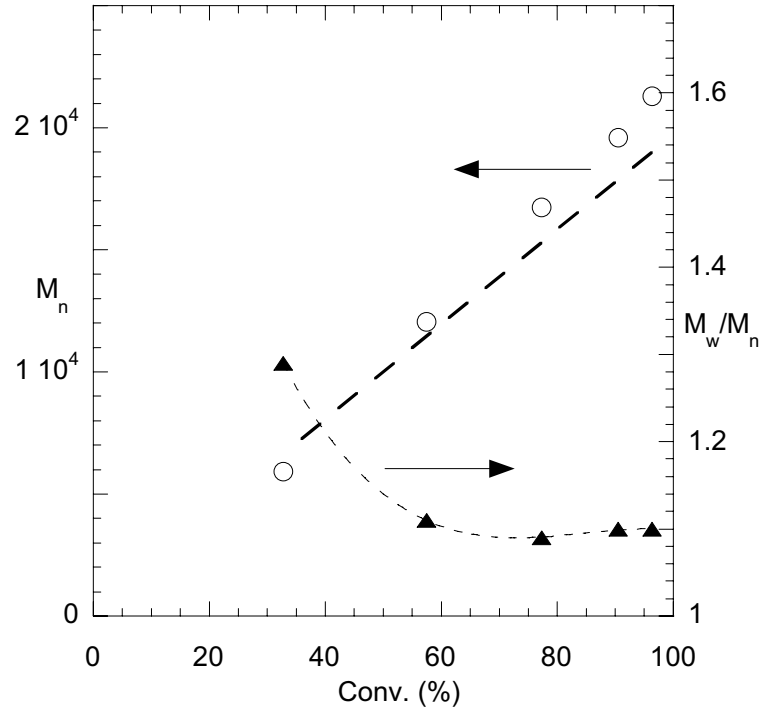


Figure 4.7. Evolution of polydispersity (▲,---) and molecular weight (○) with conversion for bulk *n*-butyl acrylate polymerisation at 60 °C in the presence of (**1**) and AIBN. Calculated molecular weight by NMR (- - -). For experimental details, see Table 4.5.

However, in the polymerisation of acrylic monomers to high conversions bimodal distributions have been reported.[35] This behaviour was also observed for the polymerisation of *n*-butyl acrylate in the presence of **1**, as is illustrated with the GPC traces in Figure 4.8. The origin of the high molecular weight shoulder, evident at higher conversions, has not been fully elucidated in these and other acrylate polymerisations, although some initial attempts have been made.[36] For the examples shown, the high molecular weight shoulders are too large to be only explained by radical coupling processes involving the propagating species (P_n•, P_m•) and/or the adducts (**9**, **11**) (Scheme 4.7). Analysis by GPC with UV detection (Figure 4.8) shows that the higher molecular polymer has retained its thiocarbonylthio chromophore (Figure 4.9) and must be substantially alive. This finding also argues against radical coupling. Note that at 305 nm there is no poly(*n*-butyl acrylate) absorption and only chains with the trithiocarbonate end are detectable and observed, equally at 220 nm only

phthalimide absorbs. The high molecular weight shoulder can appear smaller for UV detection because the intensity is proportional to $\overline{M}_n$ (*vs.* $\overline{M}_n{}^2$ for RI detection). The size of the peak depends on the molecular weight of the polymer and the conversion, as expected from what has been reported.[36] However, in our case the most pronounced shoulder is for $\overline{M}_n$ =16700 g mol^{-1}, 4 hr, 77% conversion, the shoulder reducing somewhat for the higher molecular weight/conversion samples.

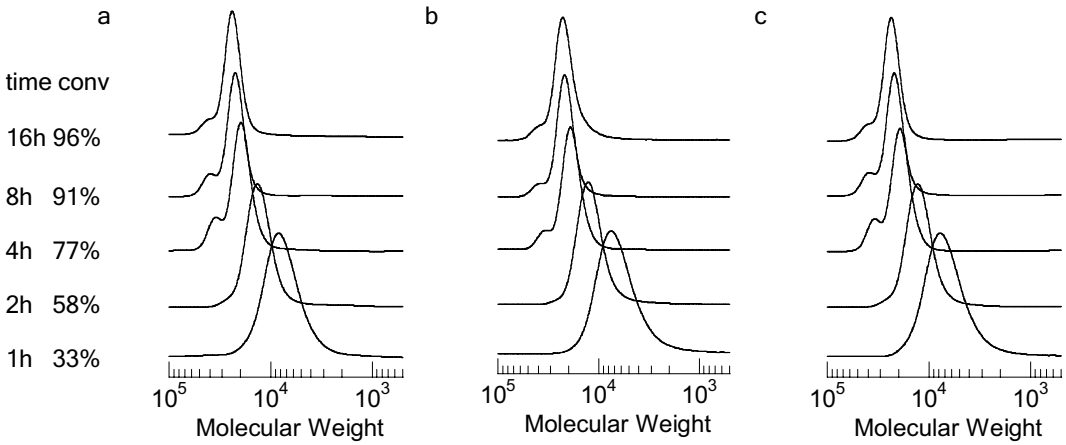


Figure 4.8. Normalised GPC traces at various reaction times/conversions for polymerisation of *n*-butyl acrylate in presence of **1**, (a) RI detection, (b) UV detection at 305 nm and (c) UV detection at 220 nm.

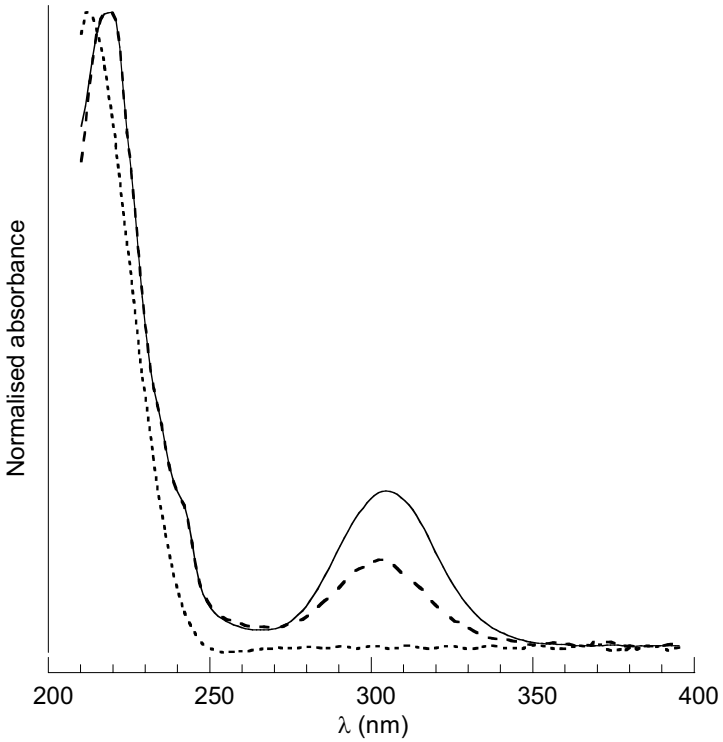


Figure 4.9. Normalised UV spectra of poly(*n*-butyl acrylate) (4hr, 77% conv., Figure 4.8): the main peak (—) and the high molecular weight shoulder (---) compared to a standard poly(*n*-butyl acrylate) sample (····). Thiocarbonylthio absorption maximum at 305 nm, phthalimide absorption maximum at 220 nm.

The polymer polydispersity can also play a part in hiding the high molecular weight shoulder. A relatively narrow polydispersity of ~1.2 can still be sufficiently broad to obscure or completely hide bimodality. And a polydispersity of <1.1 can actually be what is required to fully reveal the bimodality (Figure 4.10).[36]

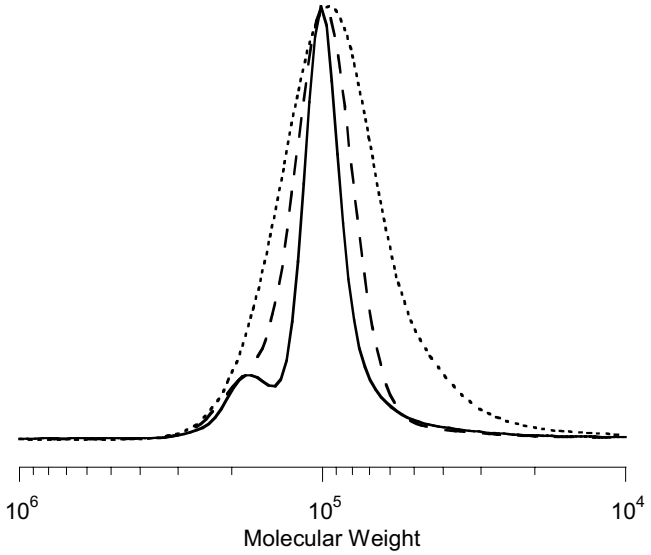


Figure 4.10. GPC traces of high conversion poly (methyl acrylate) prepared in the presence of various RAFT agents. $\overline{M}_w / \overline{M}_n$ =1.19 (····), completely hiding the shoulder; $\overline{M}_w / \overline{M}_n$ =1.10 (- - -), partially hiding the shoulder and $\overline{M}_w / \overline{M}_n$ =1.08 (—), revealing the bimodality. Reprinted with permission.[36]

Long chain branching caused by intermolecular transfer to polymer may be one of the major contributing causes to the formation of multimodal distributions. In this case, such bimodal distributions should not only be independent of RAFT agent, they should also be observed in other living radical polymerisations (ATRP, NMP) carried to high conversion.

Table 4.5. Molecular weights and polydispersities for PBA, PNIPAAm and PNVP obtained in polymerisations of BA, NIPAAm and NVP in the presence of RAFT agent (**1**) and AIBN at 60 °C.

Monomer	time (h)	$[M]_o/[RAFT]_o$ ($\times 10^2$)	$\overline{M}_n^{Calc}$ [a,b] (g mol^{-1})	$\overline{M}_n$ [a,c] (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv.[d] (%)
BA	1	1.51	6670	5910	1.29	33
	2	(1.16×10^{-3})	11500	12100	1.11	58
	4		15300	16700	1.09	77
	8		17900	19600	1.10	91
	16		19000	21300	1.10	96
NIPAAm	16	0.50 (6.81×10^{-3})	5500	2580	1.38	~80[g]
				10600[e]	1.07	
				(6000)[f]		
NVP	1	1.51	2400	oligomer	-	11
	2	(3.08×10^{-3})	3090	oligomer	-	14
	4		3100	oligomer	-	14
	8		5130	22600[e]	1.48	25
	16		9540	26700[e]	1.61	48

[a] Values rounded to three significant figures. [b] $\overline{M}_n^{Calc}$ ~ $[M]/[RAFT]_o \times Conv \times 104$+(molecular weight of RAFT agent). [c] PS equivalent THF GPC. [d] NMR conversion. [e] DMAc GPC. [f] ^{1}H NMR phthalimide signal to polymer NH signal at 170°C in DMSO-d_6. [g] Precipitated conversion. AIBN concentration in brackets in column 3.

Non exhaustive polymerisation experiments of other monomers were carried out for the purpose of comparison and to further extend the scope of RAFT agent **1**. As the polymerisations of styrenic (styrene) and acrylic (*n*-butyl acrylate) monomers were successful, an acrylamide (NIPAAm) and a vinyl monomer (NVP) were also briefly investigated in order to observe the compatibility of **1**, these results are shown in Table 4.5.

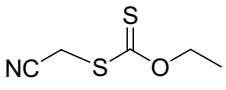
Acrylamides, like acrylates, are also characterised by propagating radicals of low steric bulk and high reactivity, thus RAFT agent **1** should be sufficient to control their polymerisation. NIPAAm was polymerised with **1** under the conditions described by Schilli *et al.*[37] and the results are shown in Table 4.5. Promising results were observed with NIPAAm, with a narrow polydispersity of 1.07, $\overline{M}_n$ =10600 g mol^{-1} (polystyrene equivalents). However, thorough analysis of the polymer was hampered due to the particular nature of the polymer.

NVP polymerisation with **1** showed a long retardation time (with a corresponding decolourisation of the polymerising mixture) as the RAFT agent was being consumed. The polymerisation then commenced to form uncontrolled high molecular weight polymer. This highlights a limitation of the use of trithiocarbonate RAFT agent **1** with vinyl monomers, as their propagating radicals are poorly stabilised, of low steric bulk and thus both highly reactive and poor as homolytic leaving groups. The initial inhibition time is likely to be due to the slow fragmentation of the intermediate radical **11**, when P_m and P_n are PNVP chains. Vinyl monomers are best controlled with less reactive RAFT agents like dithiocarbamates and *O*-alkyl xanthates. This is further investigated with vinyl acetate in section 4.3.5.

4.3.5 Xanthate RAFT agent activity in vinyl acetate polymerisation

Poly(vinyl acetate) (PVA) is one of the largest water soluble polymers produced commercially and is important industrially for the production of adhesives and paints. PVA is also the precursor in hydrolysis for the synthesis of poly(vinyl alcohol) (PVAL) which has applications as a non-toxic, easily processed bio-

adhesive and, if crosslinked to a hydrogel or as a star polymer,[38] it can be used as a diffusive drug delivery system. PVAL also exhibits good gas barrier properties either alone (under low humidity conditions) or as a ethylene-vinyl alcohol copolymer.[39] Controlled radical polymerisation of vinyl acetate has been problematic and techniques like ATRP and nitroxide mediated polymerisation (NMP) are generally not effective in PVA polymerisation.[40-42] This has been overcome by controlling the polymerisation of vinyl acetate (VA) polymerisation with xanthate[35,43,44] and dithiocarbamate RAFT agents.[43] The use of xanthates is sometimes also called MADIX (macromolecular design by interchange of xanthate).[45]



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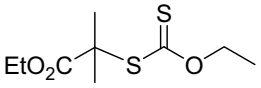

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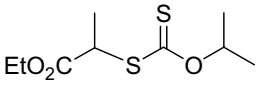

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Previous work has indicated that RAFT polymerisation mediated by xanthates exhibits variable inhibition periods and moderate rate retardation which is dependent on the *O*-alkyl[46] group. However it was later indicated that retardation might be also be attributed to the presence of impurities (oxygen) or by-products left over from the RAFT agent synthesis.[47]

The phthalimido xanthate RAFT agent **4** gave a better degree of control of vinyl acetate polymerisation at 60 °C than at 100 °C (Table 4.6). This contrasts with the earlier finding with other xanthates (**14**–**16**) and dithiocarbamates that better control was obtained at higher temperatures,[35] though different reaction conditions were used in those experiments. The polydispersities obtained ($\overline{M}_w / \overline{M}_n$=1.20–1.35) are comparable with those obtained in the earlier work.[35] Conversions after 16 h were lower than those obtained in the control (without **4**). However, there was no inhibition period evident. The apparent transfer coefficient of RAFT agent **4** in VA polymerisation at 60 °C was evaluated using the methods described above and found to be ~6.8.

The phthalimido xanthate RAFT agent **4** appears to be an effective RAFT agent in vinyl acetate polymerisation to yield phthalimido functional poly(vinyl acetate).

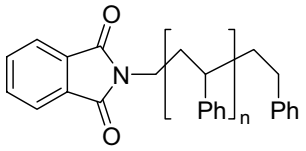
Table 4.6. Molecular weights and polydispersities for poly(vinyl acetate) obtained in polymerisations of vinyl acetate in the presence of *S*-butyl-*S*′-phthalimidomethyl dithiocarbonate (**4**)[a]

Temp. (°C)	time (h)	$[M]_o/[\mathbf{4}]_o$ ($\times 10^2$)	$\overline{M}_n^{Calc}$ [b,c] (g mol^{-1})	$\overline{M}_n$ [b] (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Conv.[d] (%)
60	16	control		59700	4.27	98
60	1	1.09	600	425	1.35	2.7
	2		1500	854	1.35	8.5
	4		3400	2300	1.24	23
	8		6600	5010	1.23	46
	16		10900	8800	1.31	77
100	16	control		93700	4.07	78
100	1	1.08	7700	5470	1.49	53
	2		10800	8340	1.54	76
	4		11500	9590	1.71	81
	8		11600	10190	1.70	81
	16		12500	10970	1.65	88

[a] AIBN (6.20×10^{-3} M) at 60 °C and Vazo 88™ (8.42×10^{-4} M) at 100 °C. [b] Values rounded to three significant figures. [c] $\overline{M}_n^{Calc}$ = $[M]/[\mathbf{4}]_o \times Conv \times 104$+(molecular weight of RAFT agent). [d] Conversion from integration of ^{1}H NMR spectrum.

4.3.6 Primary amino end-functional polystyrene

As mentioned before the RAFT process is not compatible with unprotected primary amine functionalities. The thiocarbonylthio group reacts rapidly with primary (and secondary) amines to form a thiol and a dithiocarbamate derivative. It was therefore necessary to protect the amine group during the RAFT polymerisation and in the present work this was done using the phthalimidomethyl protecting strategy. Furthermore, the removal of the RAFT moiety, which is dealt in the next chapter, needed to be carried out prior to amine deprotection. The deprotection was therefore carried out on polymers, like **17** or **18**, which had the thiocarbonylthio group already removed.



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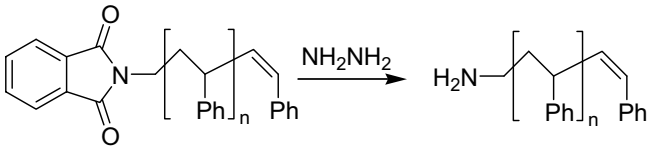
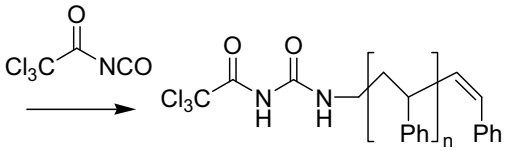
Hydrazinolysis of the phthalimido end-group group in α-phthalimidopolystyrene **18** afforded polystyrene with the desired α-monoamino functionality (**19**) (Scheme 4.8). The deprotection step was realized by treatment with hydrazine either in dimethylformamide (DMF) at 80 °C for 12 hours or in refluxing tetrahydrofuran (THF)/ethanol for 2 hours.[48] The advantage of using DMF is that it dissolves well both the hydrazine monohydrate and polystyrene, however, it complicates isolation of the polymer product and is difficult to remove. This problem can be largely overcome by using THF, however it warrants the addition of the optimum amount of ethanol to dissolve the hydrazine monohydrate and at the same time maintain the polymer in solution.

The presence of the primary amino group was confirmed by derivatisation with trichloroacetyl isocyanate (TAI) (Scheme 4.8) and ^{1}H NMR.[32] The amidic and imidic hydrogens of (**20**) are diagnostic and appear in a clear region of the ^{1}H NMR spectrum at δ 7.5 (multiplet) and 8.2 (broad “doublet”). The results tabulated in Table 4.7 are from Chapter 6, where this topic is further explored and applied.



18 19



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Scheme 4.8

Table 4.7. GPC and NMR analysis of α-phthalimidomethyl, α-aminomethyl and TAI derivatised α-aminomethylpolystyrene.

Entry	$\overline{M}_n^{Calc}$ [a]	$\overline{M}_n^{GPC}$ [b]			[NH_2][c]	f_n [d]
		Phthalimido	Amino	TAI	(μeq/g)	
1	1380	1320	-[e]	1660	5.5823	1.06
2	5020	4870	900	4990	1.2871	0.97
3	13300	14400	6020	13800	0.5681	0.99
4	38700	37000	26800	35000	0.1872	0.90
5	159000	121000	108000	114000	0.0369	0.48

[a] Expected molecular weight based on the polymerisation conditions and the concentrations of RAFT agent used, experiments in Table 4.4. [b] GPC determined molecular weight for polystyrenes. [c] [NH_2] is the concentration of amine functionality in microequivalents per gram determined by equation (7), where *m* is the molar mass of the monomer unit

$$[NH_2] = \frac{\frac{1}{\overline{M}_n^{NMR}}}{m} 10^6 \qquad (7)$$

[d] f_n (number of functional groups per chain) was estimated using equation (8), where $\overline{M}_n^{GPC}$ is the molecular weight of the polymer determined by GPC (phthalimido or TAI), and $\overline{M}_n^{NMR}$ is the apparent molecular weight determined by comparing the integral of the TAI resonance with that for the backbone ArH.

$$fn = \frac{\overline{M}_n^{GPC}}{\overline{M}_n^{NMR}} \quad (8)$$

[e] Low molecular weight broad bimodal distribution.

4.4 Conclusions

In this chapter we have shown that several phthalimide RAFT agents can be synthesized practically. The polymerisations using the RAFT agents exhibited great control and yielded polymers with narrow polydispersity and controlled molecular weight. Analysis of the polymers formed elucidated the mechanism of their RAFT activities. Phthalimide hydrazinolysis of polystyrene resulted in the synthesis of the desired α- primary amino end-groups.

In the next chapter thiocarbonylthio removal techniques were investigated and a method was developed and applied to polystyrene and poly(*n*-butyl acrylate). The development of such methods clarified and expanded an understanding of the RAFT mechanism and the activities of the phthalimido RAFT agents.

4.5 References

1. Förch, R.; Zhang, Z.; Knoll, W. *Plasma Process. Polym.* **2005**, *2*, 351-372.
2. Kingshott, P.; Thissen, H.; Griesser, H. J. *Biomaterials* **2002**, *23*, 2043-2056.
3. Chung, M. T. C. *Functionalization of Polyolefins;* 1st ed. Academic Press: London, 2002.
4. Wicks, Z. W. Jr.; Jones, F. N.; Pappas, S. P. *Organic Coatings: Science and Technology;* John Wiley & Sons: New York, 1994.

5. Matyjaszewski, K.; Nakagawa, Y.; Gaynor, S. G. *Macromol. Rapid Commun.* **1997**, *18*, 1057-1066.
6. Sadhu, V. B.; Pionteck, J.; Voigt, D.; Komber, H.; Voit, B. *Macromol. Symp.* **2004**, *210*, 147-155.
7. Coessens, V.; Nakagawa, Y.; Matyjaszewski, K. *Polymer Bulletin* **1998**, *40*, 135-142.
8. Haddleton, D. M.; Waterson, C. *Macromolecules* **1999**, *32*, 8732-8739.
9. Lecolley, F.; Waterson, C.; Carmichael, A. J.; Mantovani, G.; Harrisson, S.; Chappell, H.; Limer, A.; Williams, P.; Ohno, K.; Haddleton, D. M. *J. Mater. Chem.* **2003**, *13*, 2689-2695.
10. Summers, G. J.; Ndawuni, P. M.; Summers, C. A. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2058-2067.
11. Summers, G. J.; Ndawuni, M. P.; Summers, C. A. *Polym. Int.* **2003**, *52*, 158-163.
12. Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939-945.
13. Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; Desimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.
14. Kukula, H.; Schlaad, H.; Falkenhagen, J.; Kruger, R. P. *Macromolecules* **2002**, *35*, 7157-7160.
15. Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206-1212.
16. Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1998**, *31*, 3759-3763.
17. Meijs, G. F.; Morton, T. C.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1991**, *24*, 3689-3695.
18. Pierson, R. M.; Costanza, A. J.; Weinstein, A. H. *J. Polym. Sci.* **1955**, *17*, 221-246.
19. Clouet, G.; Juhl, H. J. *Macromol. Chem. Phys.* **1994**, *195*, 243-251.
20. Konter, W.; Bömer, B.; Köhler, K. H.; Heitz, W. *Makromol. Chem.* **1981**, *182*, 2619-2632.
21. Serre, B.; Rubio, S.; Sledz, J.; Shue, F.; Chapelet-Letourneux, G. *Polymer* **1981**, *22*, 513-518.
22. Rizzardo, E.; Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 297-307.

23. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379-410.
24. Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273-2283.
25. Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993-1001.
26. Chong, B. Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256-2272.
27. Moad, G.; Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromol. Symp.* **2002**, *182*, 65-80.
28. Ing, H. R.; Manske, R. H. F. *J. Chem. Soc.* **1926**, 2348-2351.
29. Postma, A.; Moad, G.; O'Shea, M. S.; Davis, T. P. *React. Funct. Polym.* **2006**, *66*, 137-147
30. Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tet. Lett.* **2002**, *43*, 6811-6814.
31. Leung, M. K.; Hsieh, D. T.; Lee, K. H.; Liou, J. C. *J. Chem. Research-S* **1995**, *11*, 478-479.
32. Postma, A.; Donovan, A. R.; Moad, G.; Mulder, R.; O'Shea, M. S.; Davis, T. P. *Polymer* **2005**, submitted.
33. Moad, G.; Simon, G. P.; Dean, K. M.; Li, G.; Mayadunne, R. T. A.; Rizzardo, E.; Evans, R. A.; Wermter, H.; Pfaendner, R. Int. Pat. 04113436, 2004; *Chem. Abstr. 142*, 75401r.
34. Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization;* Pergamon, Elsevier Science Ltd: Oxford, U.K., 1995.
35. Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *ACS Symposium Series*ACS: 2000; Vol. 768, Chapter Ch. 20, pp 278-296.
36. Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. *ACS Symp. Ser.* **2003**, *854*, 520-535.
37. Schilli, C.; Lanzendorfer, M. G.; Muller, A. H. E. *Macromolecules* **2002**, *35*, 6819-6827.
38. Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Chem. Commun.* **2004**, 1546-1547.
39. Ketels, H. H. T. M. Ph.D. Synthesis, Characterization and Applications of Ethylene Vinylalcohol Copolymers, Scheikundige Technologie, Technische Universiteit Eindhoven, Eindhoven, 1989.

40. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
41. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689-3745.
42. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.
43. Destarac, M.; Charmot, D.; Franck, X.; Zard, S. Z. *Macromol. Rapid. Commun.* **2000**, *21*, 1035-1039.
44. Stenzel, M. H.; Cummins, L.; Roberts, G. E.; Davis, T. P.; Vana, P.; Barner-Kowollik, C. *Macromol. Chem. Phys.* **2003**, *204*, 1160-1168.
45. Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol. Symp.* **2000**, *150*, 23-32.
46. Destarac, M.; Bzducha, W.; Taton, D.; Gauthier-Gillaizeau, I.; Zard, S. Z. *Macromol. Rapid. Commun.* **2002**, *23*, 1049-1054.
47. Favier, A.; Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Macromol. Chem. Phys.* **2004**, *205* , 925-936.
48. Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955-970.

"We had to destroy the village in order to save it."

- Peter Arnett attributed the quote to an unidentified Army officer

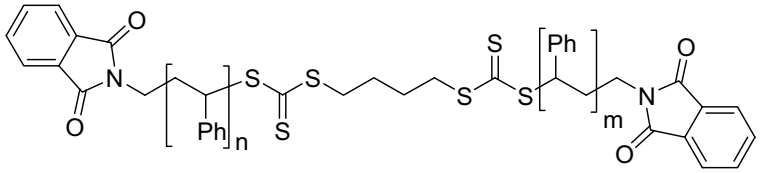
5 Investigations into the Efficient Removal of the RAFT Moiety

5.1 Introduction

Radical polymerisation with thiocarbonylthio RAFT (reversible addition-fragmentation chain transfer) agents[1-4] is arguably one of the most versatile processes for living free radical polymerisation displaying superior flexibility with respect to monomers and reaction conditions. A key feature of RAFT polymerisation is that the thiocarbonylthio group(s), present in the initial RAFT agent, is (are) retained in the polymeric product(s). The retention of these groups is responsible for the polymers' living character. The presence of the thiocarbonylthio groups, however, also means that the polymers are usually coloured. The polymers may also, in some cases, be odorous or release an odour over time due to decomposition of the thiocarbonylthio groups and the evolution of volatile sulfur containing compounds. The presence of such colour and odour can be disadvantageous in some applications. Even though some of these issues may be largely mitigated or overcome by more appropriate selection of the initial RAFT agent, this might not be a viable option in all cases. This has prompted efforts to develop effective methods for treatment of RAFT-made polymers to cleave the thiocarbonylthio end-groups postpolymerisation.

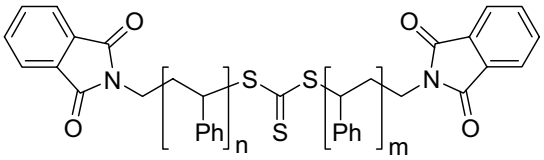
A variety of methods for removing the thiocarbonylthio groups have been reported. These include radical-induced reduction (to provide a hydrocarbon end-group),[5,6] radical exchange,[7,8] reaction with nucleophiles (e.g., amine,[1,6,9-13] hydroxide,[14,15] borohydride[16,17] -to provide a thiol end-group), treatment with oxidizing agents (e.g., NaOCl,[1] H_2O_2,[1] tBuOOH[18]) and UV irradiation.[19-21] Of these existing processes, only the radical-induced reactions are known to provide desulphurisation by complete end-group removal/transfer. These

processes require additional reagents and can be complicated by difficult-to-remove byproducts.



1 RAFT agent (n,m=0)

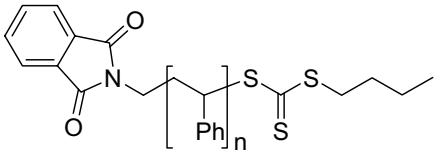
2 Polymer (n,m>0)



3 RAFT agent (n,m=0)

4 Polymer (n=0, m>0)

5 Polymer (n,m>0)



6 RAFT agent (n=0)

7 Polymer (n>0)

In seeking to develop a method for the synthesis of primary amino-functional polymers by way of phthalimido-functional trithiocarbonate RAFT agents (**1**, **3**, **6**),[6] we required a convenient method for trithiocarbonate removal to provide an inert end-group. Since primary and secondary amines are known to react with thiocarbonylthio groups, it was important that we removed the RAFT functionality prior to deprotection of the phthalimido functionality. The results of phthalimido deprotection were however presented in the previous chapter since its focus was principally on the primary α-amino end-functionality. Whilst it is not presented in the chronological order, this chapter focuses on the important development of an effective method for treatment of phthalimido polystyrene

and *n*-butyl acrylate RAFT-made polymers to cleave the thiocarbonylthio end-groups postpolymerisation.

It was proposed that it would be possible to monitor the success of the method by utilizing a range of analytical methods. For example, for lower molecular weight polymers, the end-group transformations can be conveniently followed by ^{1}H NMR. The polystyryl methine hydrogen adjacent to the thiocarbonylthio appears as a broad 'doublet' at δ 4.7 in the ^{1}H NMR spectrum of the polystyrenes formed with **1**, **3** and **6**. However, for the case of the polymers formed with the bis-RAFT agents (**2**, **4**, **5**), it is also possible to follow the process by GPC since removal of the trithiocarbonate functionality should cleave the polymer in half. Additionally, UV detection used with GPC allows for the analysis of both the thiocarbonylthio and phthalimide end-groups within the polymer distributions at 305 nm and 292 nm, respectively. These approaches were further expanded upon in this chapter with a view to also clarify some of the RAFT mechanisms investigated chapter 4.

5.2 Experimental Section

5.2.1 General

Solvents were of AR grade and were distilled before use. All chemicals and were purchased from Aldrich unless stated. ^{1}H NMR spectra were obtained with a Bruker Advance DRX500, Bruker Av400 or a Bruker AC200 spectrometer on samples dissolved in deuterochloroform, unless stated. Chemical shifts are reported in ppm from external tetramethylsilane. $\overline{M}_n$ ^{NMR}= number average molecular weight by ^{1}H NMR by integration of the signals attributable to the phthalimido end-group (δ 7.6–8.0) relative to those for the polystyrene aromatics (δ 6.3–7.4) or, for the case of poly(*n*-butyl acrylate), the polymer -OC**H**$_2$CH$_2$CH$_2$CH$_3$ (δ 3.8–4.4). Electrospray ionization (ESI) mass spectra were acquired with a Micromass Q-TOF II spectrometer. Gel permeation chromatography (GPC) was performed with a system comprising a Waters 515 HPLC pump and Waters 717 Plus Autosampler equipped with Waters 2414

refractive index detector and 3×Mixed C and 1 mixed E PLgel column (each 7.5 mm×30 mm) (1 × 10^2-2 × 10^6) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22±2 °C. GPC with UV detection was performed with a Waters 2695 Separations Module equipped with Waters 2414 refractive index detector and Waters 2996 photodiode array detector and similar set of columns. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 30±2 °C. In each case, the columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) ranging from 600 to 7.5 × 10^6 g mol^{-1}. A third order polynomial was used to fit the $\log_{10}$M *vs* time calibration curve, which was approximately linear across the molecular weight range 2 × 10^2-2 × 10^6 g mol^{-1}.

5.2.2 Reduction of polystyrene trithiocarbonate (2) with tri-*n*-butylstannane

Polystyrene (**2**) (51 mg, $\overline{M}_n$ =51100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17), tri-*n*-butylstannane (11.7 mg, 4.02×10^{-5} mol), AIBN (0.3 mg, 1.83×10^{-6} mol) and benzene (1 mL) were placed in an argon flushed ampoule. The contents were degassed by three freeze-evacuate-thaw cycles, sealed and heated in a constant temperature bath at 70 °C for 3h. Solution was observed to change from yellow to colourless. The product had $\overline{M}_n$ =30000 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.11 (**8**). The GPC of the product (**8**) and the precursor polystyrene (**2**) are shown in Figure 5.2a.

Reduction with tris(trimethylsilyl)silane was performed under similar conditions: Polystyrene (**2**) (51 mg, $\overline{M}_n$ =51100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17), tris(trimethylsilyl)silane (13.3 mg, 5.35×10^{-5} mol), AIBN (1.1 mg, 6.70×10^{-6} mol) and benzene (1 mL) resulted in incomplete trithiocarbonate group removal (Figure 5.2b).

5.2.3 Aminolysis with piperidine of polystyrene trithiocarbonate (2)

Polystyrene (**2**) (50 mg, $\overline{M}_n$ =51100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17) was dissolved in dry THF (10 mL) in a 25 mL round bottomed flask. The solution was flushed with argon for 10 minutes and an excess of piperidine (1 mL) was added. The stirred reaction mixture was heated to reflux for 1h during which time the initially yellow solution became colourless. The product had $\overline{M}_n$ =29700 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.24. The GPC of the product and the precursor polystyrene is shown in Figure 5.4c.

The above polystyrene (51 mg) was redissolved in THF (3 mL) and the solution flushed with argon for 10 min. Glacial acetic acid (1 mL) and zinc powder (0.5 g) were added and the stirred reaction mixture was warmed to 40 °C and maintained at that temperature, under argon, for 12 h. The product had $\overline{M}_n$ =27800 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.28 (**9** & **10**). The GPC of the product is shown in Figure 5.4c.

5.2.4 Small scale dynamic thermolysis of polystyrene trithiocarbonate (7)

The following procedure is typical:

Small scale dynamic thermolysis was carried out using a Mettler Toledo TGA/SDTA521 thermogravimetric balance equipped with a TSO 801RO sample robot. Polystyrene **7** ($\overline{M}_n$ =1850 g mol^{-1}) and polydispersity ($\overline{M}_w / \overline{M}_n$ =1.20) was heated dynamically at 2 °C/min under nitrogen in an alumina crucible from 50–700 °C (shown in Figure 5.5). The mass loss step between 200–270 °C corresponds to 7.5% of total mass (9.0% expected for $C_5H_{10}S_3$).

5.2.5 Small scale isothermal thermolysis of polystyrene trithiocarbonate (2 & 7)

The following procedure is typical:

Small scale isothermal thermolysis was carried out using a Mettler Toledo TGA/SDTA521 thermogravimetric balance equipped with a TSO 801RO sample robot. Thermolysis of pale yellow polystyrene (**2**) (22.3 mg, $\overline{M}_n$ =51100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17) was weighed into an alumina crucible and placed in the sample furnace of the thermogravimetric balance. The sample was heated isothermally under nitrogen at 210 °C for 3 h to provide a colourless product (**11**) ($\overline{M}_n$ =27100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17). The colourless residue was dissolved in chloroform and analyzed directly by ^{1}H NMR and GPC.

Copper mediated thermolysis was performed under similar conditions: polystyrene (**7**) (10.0 mg, $\overline{M}_n$ =1850 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.20) and copper powder (9.88 mg, 1.55×10^{-4} mol) were mixed and placed into an alumina crucible and placed in the sample furnace of the thermogravimetric balance. The sample was heated isothermally under nitrogen at 165 °C for 3 h to provide a product ($\overline{M}_n$ =2339 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.36). The residue was dissolved in chloroform and analyzed directly by ^{1}H NMR and GPC.

5.2.6 Large scale thermolysis of polystyrene trithiocarbonate (7) in Kugelrohr

Large scale thermolysis was conducted on 130 g of **7** ($\overline{M}_n$ =1370 g mol^{-1}) placed in a 1 L flask of a large scale Aldrich Kugelrohr operating at 220 °C under vacuum for 3.5 hrs. 115 g of **11** ($\overline{M}_n$ =1300 g mol^{-1}) was recovered and purified by dissolving in chloroform (150 mL) and precipitating into methanol (1.5L) and filtering to dryness as a colourless product.

5.2.7 Large scale thermolysis of polystyrene trithiocarbonate (7) in Extruder

Extrusion was performed on a Prism TSE Eurolab 16 TC:24:16mm co-rotating segmented twin screw extruder of L/D 24:1 manufactured by Thermo Haake. The extruder consisted of 6 temperature controlled barrel sections and a heated die. The feedthroat was maintained under a under nitrogen blanket while the polymer **7** was fed at 0.625, 1.36 and 2.73 g/min and extruded at 190, 250, 280 and 300 °C, with a constant screw speed of 100 rpm. The first barrel section was water cooled to prevent premature melting of the polymer. A vent port was fitted to barrel section five for the removal of the volatile cleaved products. The vent was open to atmosphere. The extruder was operated in a fume hood to isolate the operators from the fumes produced from the thermolysis reaction. The segmented screw consisted of mixing, conveying and reversing screw elements to facilitate the thermolysis. A diagram of the screw profile used is shown in Figure 5.1

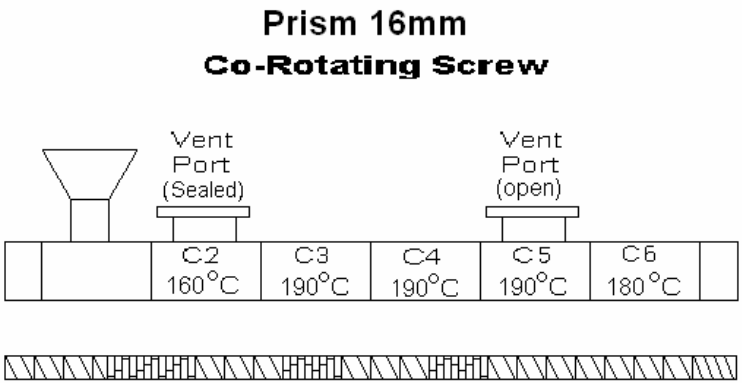


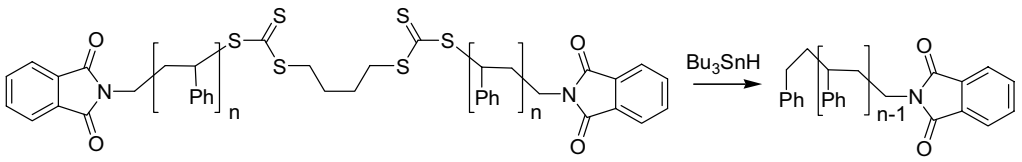
Figure 5.1 Screw and barrel profile of the Prism TSE Eurolab 16 twin-screw extruder employed scaled thermolysis.

5.3 Results and discussion

5.3.1 Radical reduction

Chen *et al.*[5,22] have shown that tri-*n*-butylstannane reduces dithiobenzoate end-groups. It is also possible to cleave trithiocarbonate groups quantitatively from polystyrene (*i.e.*, **2**, $\overline{M}_n$ =51100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17) by reduction with tri-*n*-butylstannane and it appeared to cleanly cleave the polymer in half (**8**, $\overline{M}_n$ =30000 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.11) (Figure 5.2a). This experiment also shows the two polystyrene chains of (**2**) are equivalent *(i.e.*, *n*~*m*) and therefore that that the two trithiocarbonate groups of the bis-RAFT agent (**1**) have reacted equally during polymerisation. This finding was further elucidated by similar results obtained using thermolysis (5.3.3). It is noteworthy that little evidence of coupling of polymer chains was observed in the GPC trace. The ^{1}H NMR spectrum demonstrates the removal of the thiocarbonylthio group and the retention of the phthalimido end-group group (Figure 5.3). The data is consistent with reduction providing a α-phthalimidopolystyrene (**8**) as shown in Scheme 5.1. Removal of excess tri-*n*-butylstannane and derived by-products from the reduction proved, however, problematic.

Radical induced reduction with tris(trimethyl silyl)silane (TTSS) was also investigated by GPC (Figure 5.2b). TTSS was a less effective radical reduction agent and didn't go to completion (evident by a high molecular weight shoulder in the GPC trace), however adding more initiator and using longer reaction times more than likely would have resulted in a more efficient reduction. It is also possible that some coupling occurs, which would also explain the high molecular weight impurity. TTSS and its by-products, however, are more readily removed from the polymer.



2 **8**

Scheme 5.1

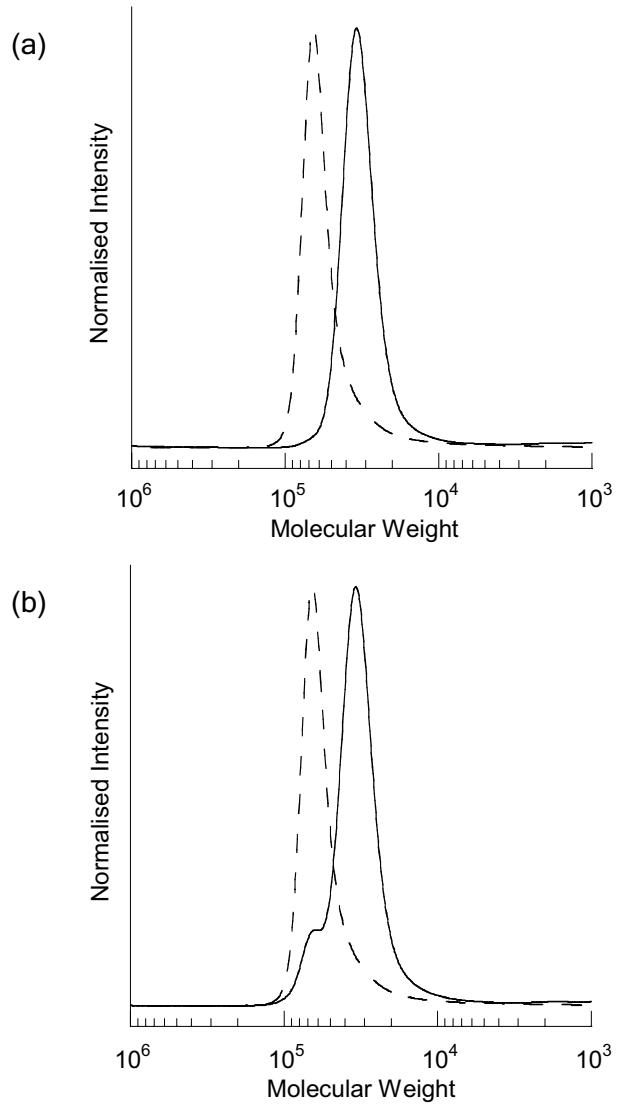


Figure 5.2. GPC traces for the precursor bis-polystyrene trithiocarbonate **2** (- - -) and reaction products **8** (—) which arise from the radical-induced reduction with (a) tri-*n*-butylstannane (Scheme 5.1), (b) tris (trimethylsilyl) silane. For details see Experimental.

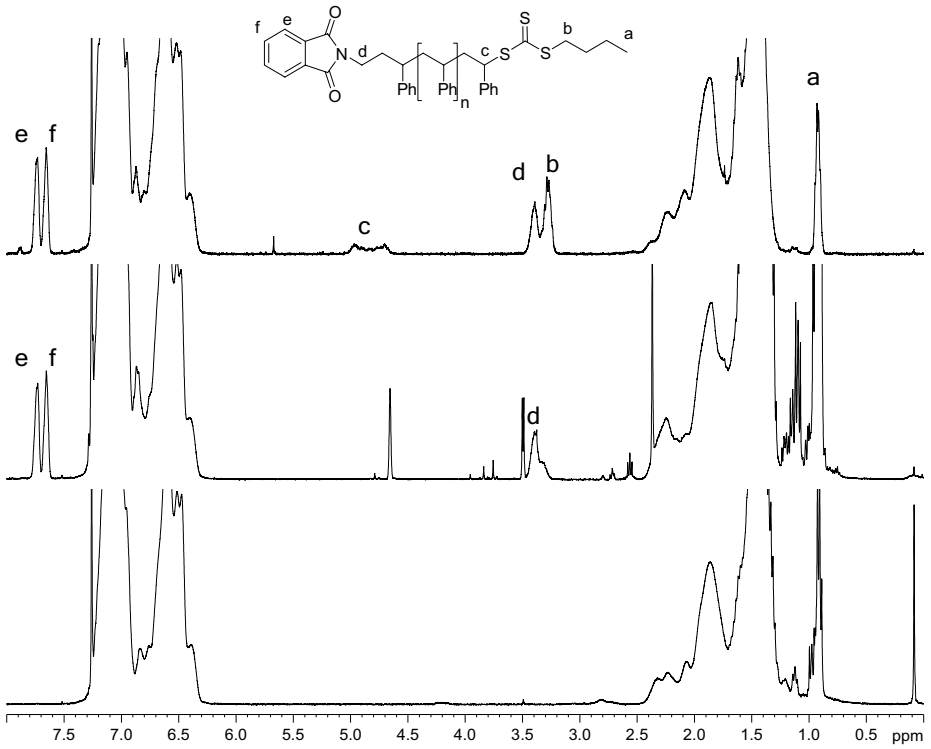


Figure 5.3. ^{1}H NMR spectra of phthalimide terminal RAFT polymer **7** (upper), Radical reduction of RAFT group with tri *n*-butylstannane (middle), reduction of terminal phthalimide with hydrazine monohydrate (lower).

5.3.2 Aminolysis

Reactions of (**2**) with ethylenediamine, *n*-butylamine and piperidine were examined. These reactions were expected to produce polystyrene with a thiol chain end (**9**) (Scheme 5.2). Even though the products were colourless, indicating removal of the thiocarbonylthio end-group, the reaction products had a bimodal distributions (Figure 5.4). Potential pathways that lead to the formation of higher molecular weight impurity should be considered:

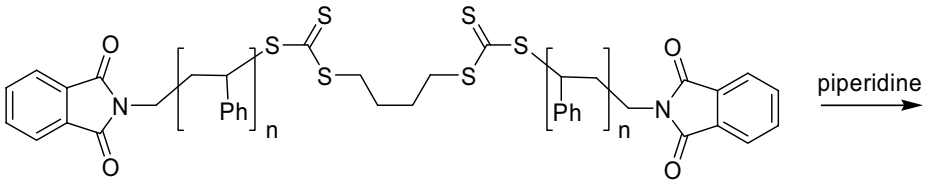
(a) One known side-reaction, if air is not completely excluded from the reaction, is that the initially formed thiol may undergo oxidative coupling to give a disulfide (**10**)[23,24].

(b) It has also been observed that under certain conditions primary amines have the ability to open phthalimides,[25] this would allow the freed amine to enter the RAFT-aminolysis reaction, providing another mechanism for chain-chain coupling (Scheme 5.3).

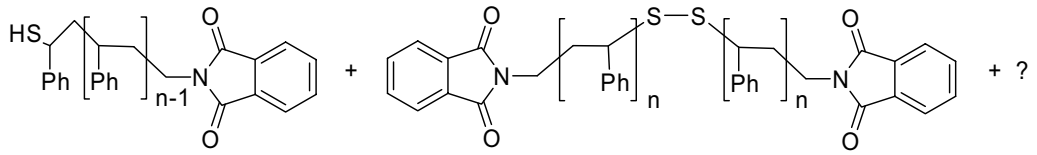
Incomplete reaction of the amine forming the stable dithiocarbamate derivative can also contribute to the formation of coupled impurities (Scheme 5.3).

Further treatment of the product with Zn/acetic acid,[24] which should reduce any disulfide by-product formed by pathway (a), diminished but did not eliminate the high molecular weight shoulder in the molecular weight distribution (of the piperidine cleaved polystyrene - Figure 5.4c).

Ethylenediamine was also observed to give a product with $\overline{M}_{\mathrm{p}}$=96400, as well as $\overline{M}_{\mathrm{p}}$=32500, which is half that of the initial polymer **2** ($\overline{M}_{\mathrm{p}}$=65500). The formation of the higher molecular weight product has not yet been fully explored and is under further investigation.[26]

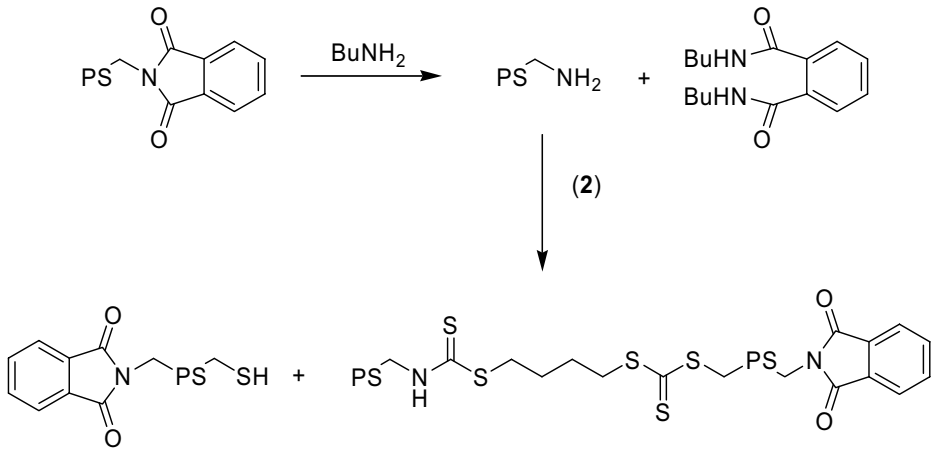


2



9 **10**

Scheme 5.2



Scheme 5.3

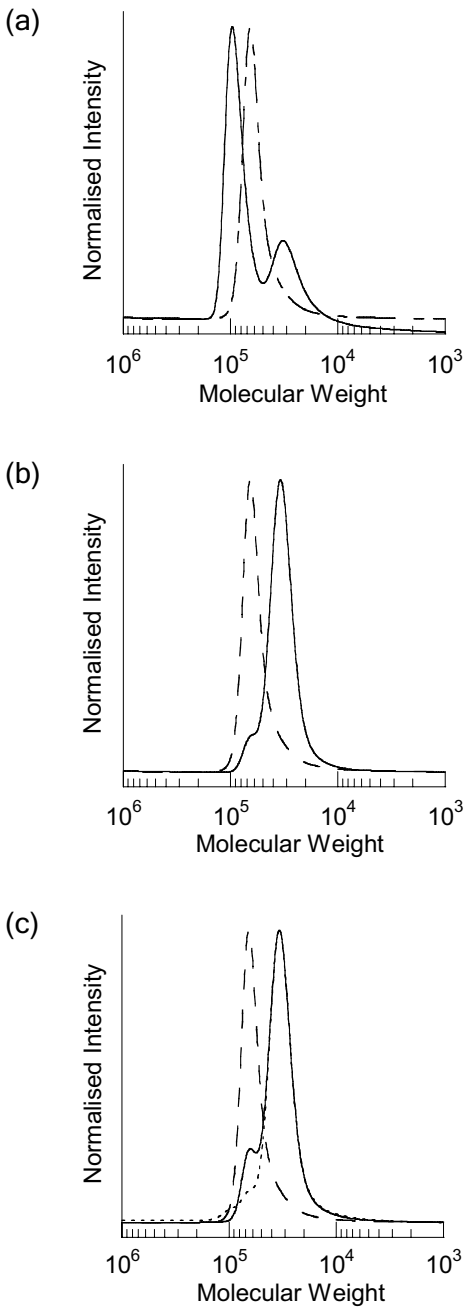
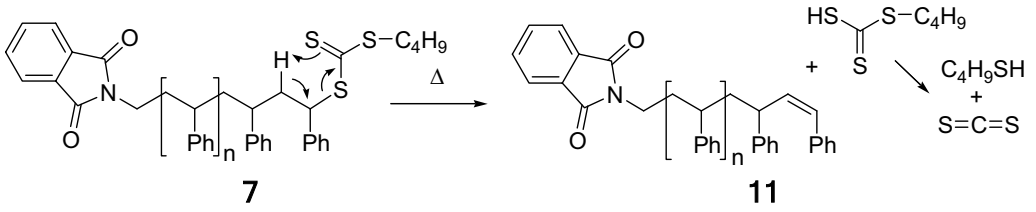


Figure 5.4. GPC traces for the precursor bis-polystyrene trithiocarbonate **2** (- - -) and reaction products **9** and **10** (—) which arise from the treatment with (a) ethylenediamine, (b) *n*-butylamine, (c) piperidine (Scheme 5.2), (—) and Zn/CH_3COOH reduction (·····). For details see Experimental.

5.3.3 Thermolysis

Our continuing efforts to develop a convenient method for trithiocarbonate removal prompted us to investigate thermolysis. Thermolysis as a means of cleaving thiocarbonylthio compounds has some precedent in ester[27] and xanthate pyrolysis (the Chugaev reaction for synthesizing olefins from alcohols)[28] and has the clear advantage over the methods mentioned above in that no chemical treatment is required. It does, however, require that the polymer and any desired functionality are stable to the thermolysis conditions.



7 **11**

Scheme 5.4

Initially, small-scale thermolysis was carried out using a thermogravimetric balance. Thermolysis of pale yellow polystyrene **7** at 210-250 °C cleanly cleaves the *S*-butyl trithiocarbonate group to provide a colourless product (**11**). The thermolysis product was characterised by ^{1}H NMR and GPC. In the thermogram shown in Figure 5.5a, the mass loss step between 200 and 270 °C corresponds to 7.5% of total mass (9.0% expected for $C_5H_{10}S_3$).

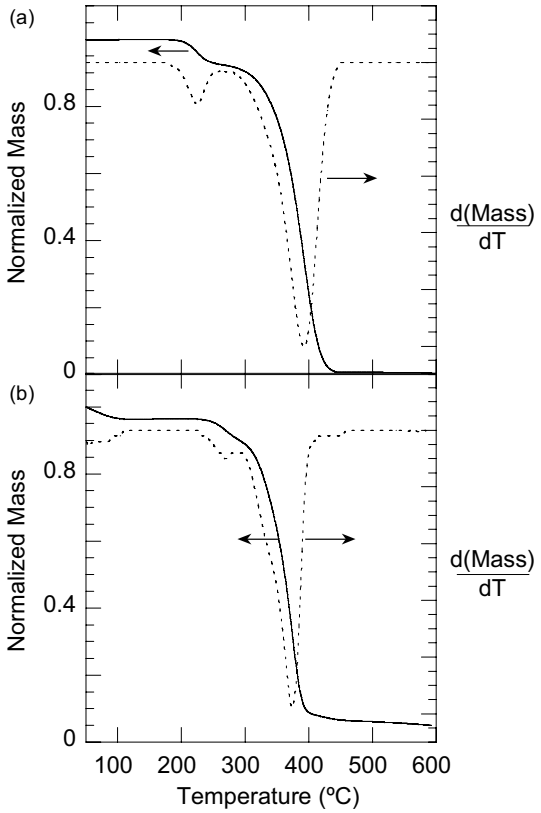


Figure 5.5. Normalised mass loss (—) and first derivative of mass loss (arbitrary units) (----) (a) for polystyrene **7** with number-average molecular weight ($\overline{M}_n$) 1850 g mol^{-1} and polydispersity ($\overline{M}_w / \overline{M}_n$ =1.20) and (b) for poly(*n*-butyl acrylate) **12** with $\overline{M}_n$ =6830 g mol^{-1} and $\overline{M}_w / \overline{M}_n$ =1.17. Experimental details in 5.2.5.

The ^{1}H NMR spectrum of the product of thermolysis of **7** demonstrates the quantitative disappearance of the trithiocarbonate group (the methine hydrogen adjacent to the trithiocarbonate appears as a broad "doublet" at δ 4.7), the formation of a 1,3-diphenylpropenyl end-group (signals at δ 3.1 and 6.1),[2,29-32] and retention of the phthalimido end-group (α-methylene at δ 3.4 and aromatics at δ 7.65 and 7.75) (Figure 5.6). Signals were also observed at δ 5.3 and 5.6 which may be attributed to the (E) 1,3-diphenylpropenyl end-group,[29] however this is still under investigation.

A sample of polystyrene **7** thermolysed in the presence of copper powder provided a polymer with both 1,3-diphenylpropenyl and a macromonomer end-group (signals at δ 4.8 and 5.1).[32,33] The macromonomer product was identified by comparison with an authentic sample and is analogous to that observed from poly(*n*-butyl acrylate) thermolysis (**15**, Scheme 5.6). The onset temperature for degradation was found to be lowered to 165 °C. It appears the addition of copper promotes loss of the trithiocarbonate end by homolysis. This could account for the significant amount of coupled product and oligomers observed in the GPC trace. This effect could possibly be enhanced by the solubilisation of the copper in the polystyrene melt, through the correct selection of thermally stable ligands, this may provide a route to relatively narrow polydispersity polystyrene macromonomers. The presence of the phthalimido resonances provides a reference peak to simplify end-group quantitation.

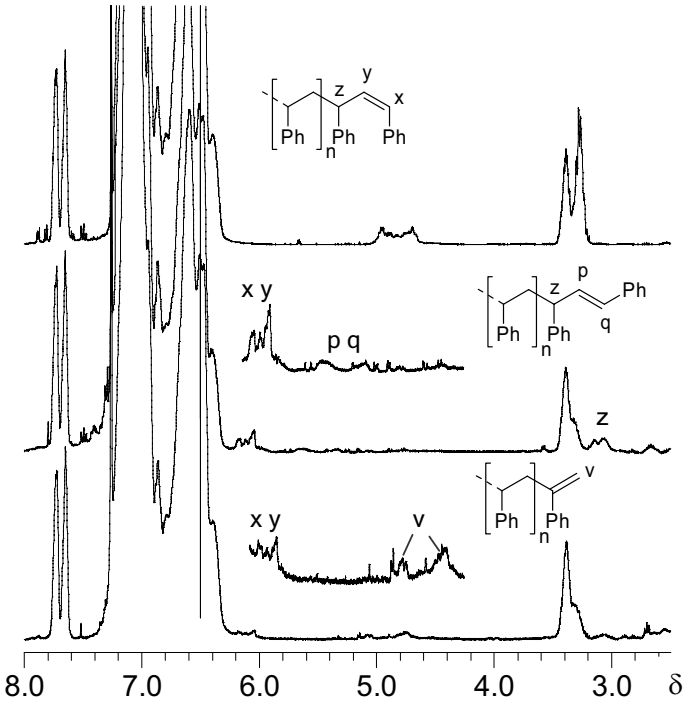


Figure 5.6. ^{1}H NMR spectrum of polystyrene **7** with $\overline{M}_n$=1850 g mol^{-1} ($\overline{M}_n$ ^{NMR}=1950 g mol^{-1}), $\overline{M}_w / \overline{M}_n$=1.20 (upper) and thermolysis product **11** with $\overline{M}_n$=1740 g mol^{-1} ($\overline{M}_n$ ^{NMR}=1860 g mol^{-1}), $\overline{M}_w / \overline{M}_n$=1.18 (middle) and the copper mediated thermolysis product with $\overline{M}_n$=2339 g mol^{-1} ($\overline{M}_n$ ^{NMR}=1990 g

mol^{-1}), $\overline{M}_w / \overline{M}_n$ =1.36 (lower). Insets show expansion of region δ 4.6-6.2 showing olefinic resonances. See spectral assignments of polystyrene **7** in Figure 5.3.

The electrospray ionization mass spectrum (Figure 5.7) shows a series of peaks at *n* × 104.06(styrene) + 160.04(phthalimidomethyl) + 103.05(end-group) + 22.99(Na^+) in accord with the proposed structure **11**. The GPC chromatogram shows the molecular weight distribution to be essentially unchanged (Figure 5.8a).

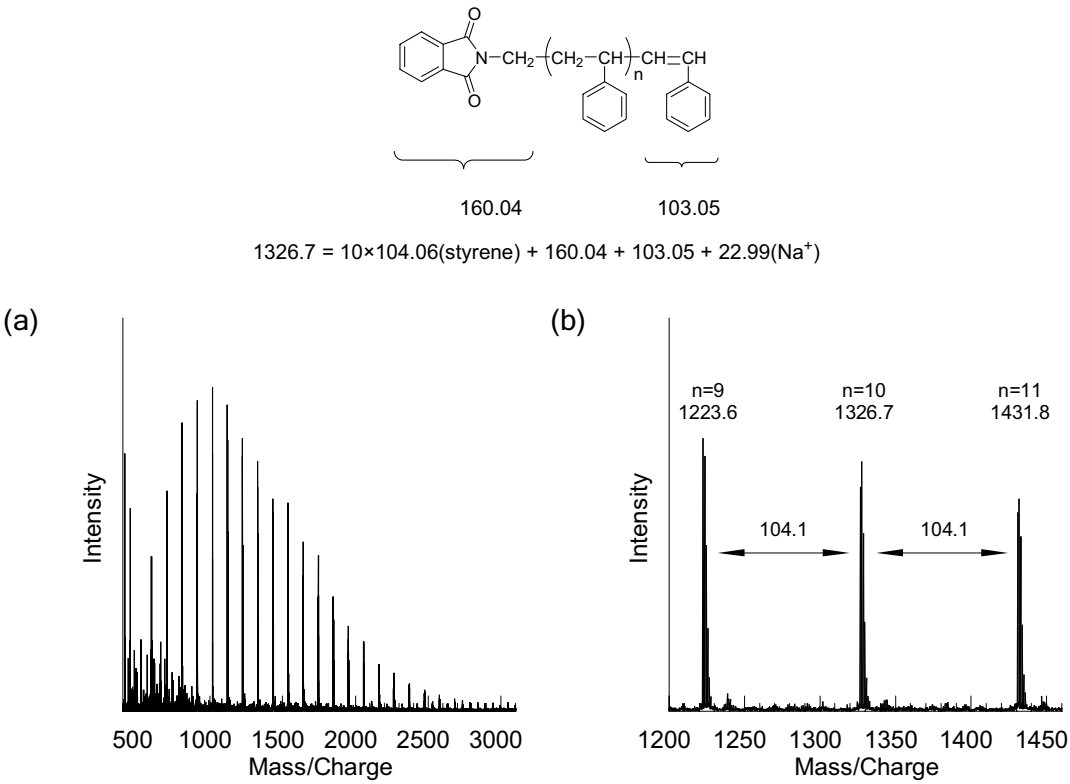


Figure 5.7. (a) Electrospray ionization (ESI) mass spectrum of **11** ($\overline{M}_n$ =1740 g mol^{-1} ($\overline{M}_n{}^{NMR}$=1860 g mol^{-1}), $\overline{M}_w / \overline{M}_n$ =1.18) and (b) expanded region of spectrum. The major peaks are labelled with their measured molecular weights and the number of repeat units (*n*). The interpeak distance corresponding to the mass of the styrene repeat unit.

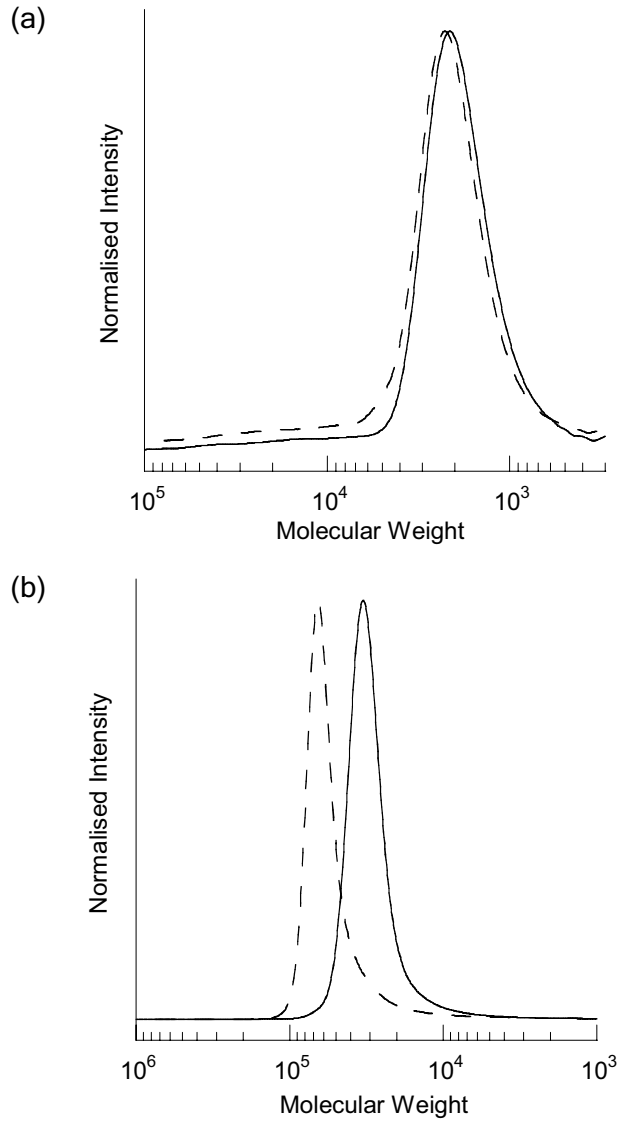
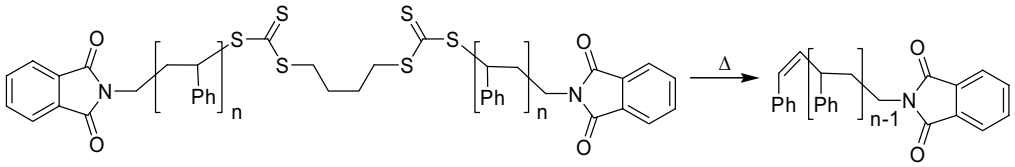


Figure 5.8. GPC traces for the precursor polymer (- - -) and reaction products (——) which arise from thermolysis: (a) monopolystyrene trithiocarbonate **7** (precursor $\overline{M}_n$ =1850 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.20; product $\overline{M}_n$ =1740 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17), (b) bis(polystyrene) trithiocarbonate **2** (precursor $\overline{M}_n$ =52900 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.13; product $\overline{M}_n$ =27100 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.17).

As mentioned previously, chain cleavage and GPC analysis can provide useful information regarding the mechanism of RAFT polymerisation. For the thermolysis of polystyrene **2** (Scheme 5.5) which is prepared from the bis-trithiocarbonate **1**, the TGA weight loss curve is more complex (not shown) and

the ^{1}H NMR spectrum of the colourless thermolysis product is similar. However, GPC analysis clearly showed that thermolysis cleanly cleaves the polymer in half (Figure 5.8b) and confirms a decrease in molecular weight of 50% for both low and high molecular weight/conversion samples. This futher implicates that the two polystyrene chains of **2** are equivalent (*i.e.*, *n*~*m*) and therefore that the two trithiocarbonate groups of the bis-RAFT agent (**1**) have equal reactivity during polymerisation. Chain length analysis of thermalized bis-polystyrene trithiocarbonate (**2**), before and after thermolysis, shown in Figure 5.9, further illustrates the RAFT mechanism for the bis-RAFT agent (**1**). In the early stages of the polymerisation the ratios of the initial chain lengths to the final chain lengths after thermolysis ($\overline{M}_{\mathrm{p}}^{\mathrm{i}} / \overline{M}_{\mathrm{p}}^{\mathrm{f}}$) is close to 1 but rapidly increases at ~20% conversion to 1.5 and plateaus off to just <2 at ~60% conversion. $\overline{M}_{\mathrm{p}}$ and $\overline{M}_{\mathrm{w}}$ were chosen for representative analysis of the chain lengths since they were found to be more stable parameters, more so than $\overline{M}_{\mathrm{n}}$ which is more sensitive to baseline inconsistencies, especially for low molecular weight samples.



2 **11**

Scheme 5.5

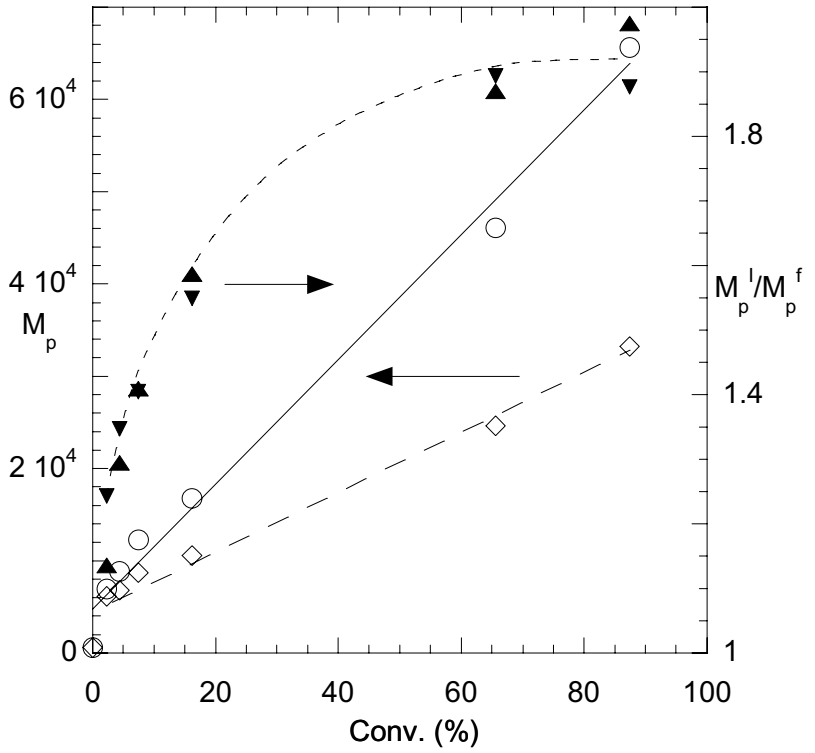


Figure 5.9. Chain length analysis of thermalized bis-polystyrene trithiocarbonate (**2**), $\overline{M}_p$ before ($\overline{M}_p^i$)(○,—) and after ($\overline{M}_p^f$)(◇,- - -) thermolysis. Ratios of initial (i) and final (f) polymer chain lengths (----), $\overline{M}_p^i/\overline{M}_p^f$ (▲) and $\overline{M}_w^i/\overline{M}_w^f$ (▼).

In contrast low-conversion polystyrenes synthesized with RAFT agent **3**, show little change in molecular weight (*n*«*m*) or molecular weight distribution on thermolysis, and only high-conversion samples show the expected ~50% reduction in molecular weight (5.1% conversion, $\overline{M}_n$=4900 g mol^{-1}, $\overline{M}_w/\overline{M}_n$=1.46, after thermolysis $\overline{M}_n$=4630 g mol^{-1}, $\overline{M}_w/\overline{M}_n$=1.36; 96% conversion, $\overline{M}_n$=50100 g mol^{-1}, $\overline{M}_w/\overline{M}_n$=1.25; after thermolysis $\overline{M}_n$=31200 g mol^{-1}, $\overline{M}_w/\overline{M}_n$=1.18). At higher-conversion (above 20%) samples showed the expected reduction in molecular weight, indicated by the chain length of thermalized polystyrene, before and after thermolysis becoming significantly different (Figure 5.10). This is attributed to the polystyryl chain, at a certain point in the polymerisation, being a better homolytic leaving group than the phthalimidomethyl group in the polymeric RAFT agent **4**. Our thermolysis

methodology has very recently been applied in characterisation of poly(styrene-*alt*-maleic anhydride)-*block*-styrene ABA triblocks prepared by RAFT polymerisation.[34]

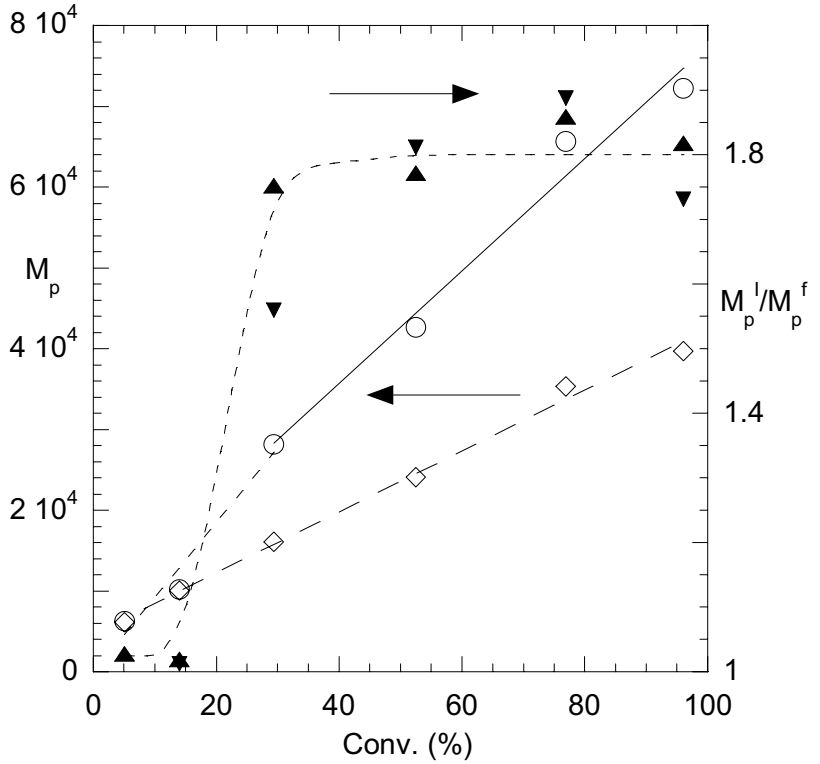


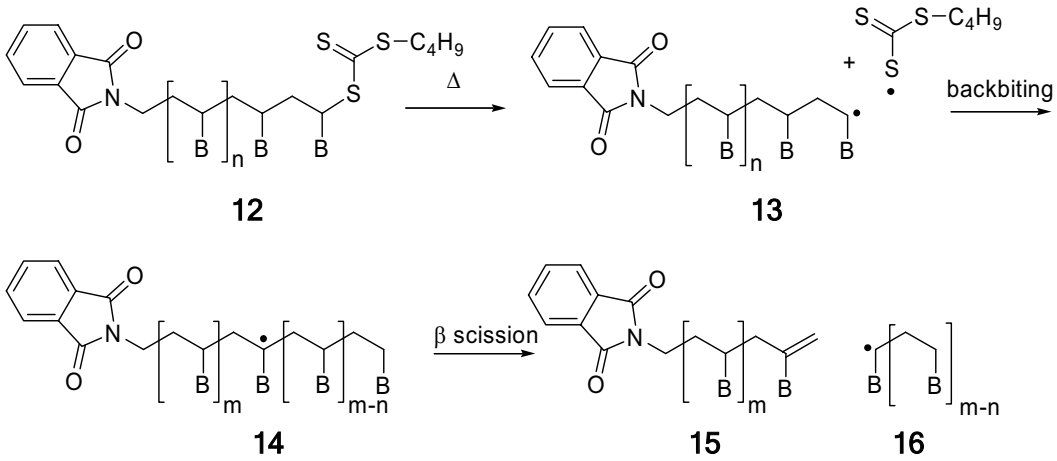
Figure 5.10. Chain length analysis of thermalized polystyrene, synthesized by RAFT agent **3**, $\overline{M}_{\mathrm{p}}$ before ($\overline{M}_{\mathrm{p}}^{\mathrm{i}}$) (○,—) and after ($\overline{M}_{\mathrm{p}}^{\mathrm{f}}$)(◇,- - -) thermolysis. Ratios of initial (i) and final (f) polymer chain lengths (----), $\overline{M}_{\mathrm{p}}^{\mathrm{i}}/\overline{M}_{\mathrm{p}}^{\mathrm{f}}$ (▲) and $\overline{M}_{\mathrm{w}}^{\mathrm{i}}/\overline{M}_{\mathrm{w}}^{\mathrm{f}}$ (▼).

Poly(*n*-butyl acrylate) (**12**) synthesized with RAFT agent **6** shows quite different thermolysis behavior from the analogous polystyrene samples (Figure 5.5b). The ^{1}H NMR spectrum (Figure 5.11) shows no signals for the direct elimination product but rather signals at δ 5.55 and 6.1, which are characteristic of a methacrylate end-group **15** (Scheme 5.6). The corresponding ^{13}C NMR signals appear at δ 127 and 138. Two-dimensional NMR (HMBC, HSQC) proved the assignments. The ratio of phthalimide chain ends to unsaturated chain ends was estimated by integration of the ^{1}H NMR as ~10:6. The product is similar to

that formed by backbiting β-scission during high-temperature polymerisation of *n*-butyl acrylate[33] or by copolymerisation of butyl acrylate in the presence of a methacrylate and a catalytic chain transfer agent.[2,32,35] The GPC trace for a low molecular weight sample indicates some broadening of the molecular weight distribution and the formation of oligomeric products (Figure 5.12a). Thermolysis of a higher molecular weight poly(*n*-butyl acrylate) sample ($\overline{M}_n$ =23900 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.07) gave a relatively unchanged molecular weight yet with some oligomer formation evident (overall $\overline{M}_n$ =20890 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.09, with the major component $\overline{M}_n$ =20900 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.08 and oligomer component $\overline{M}_n$ =1320 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.20) (Figure 5.12e) The intermediate samples (Figure 5.12b-d) show a similar trend in insignificant reduction of molecular weight of the main peak and the formation of an oligomer fraction (~$\overline{M}_n$ =1000 g mol^{-1}). Chain length analysis (Figure 5.13) shows insignificant change in molecular weight of chains before and after thermolysis, over the range of conversions, as is expected from poly(*n*-butyl acrylate) **12** forming **15** and **16**.

A proposed mechanism for poly(*n*-butyl acrylate) thermolysis is shown in Scheme 5.6. The C-S bond undergoes homolysis to a poly(*n*-butyl acrylate) propagating radical which decays by intramolecular (or, to a lesser degree, intermolecular) transfer and β-scission. Intramolecular backbiting is strongly favoured over intermolecular abstraction at very high temperatures where depolymerisation occurs by sequential backbiting β-scission[36-38] and under lower temperature polymerisation conditions during polymerisation of acrylate esters.[33] It seems reasonable to expect the intramolecular process will also dominate under our thermolysis conditions. Thermal degradation of poly(*n*-butyl acrylate) and other polyacrylates usually occurs at significantly higher temperatures (304-370 °C).[36-38] β-Scission following backbiting is known[33] to strongly favour formation of the polymeric macromonomer (**15**) and "dimer" radical (**16**, *m*-*n* = 1). If β-scission takes the alternate pathway, the polymeric product will be a new radical **13** with chain length shortened by 3 units which can then decay by the same path. On the basis of this mechanism, we predict

good end-group purity and found it to be between 65-90%. Thermolysis of RAFT-made poly(*n*-butyl acrylate) may provide a route to relatively narrow polydispersity macromonomers.



Scheme 5.6. (B= $CO_2C_4H_9$).

The normalised 292 nm UV GPC trace of the poly(*n*-butyl acrylate) thermolysis product **15**, is equivalent to its corresponding refractive index (RI) GPC trace, showing that the phthalimidomethyl end-group is not distributed evenly over the full molecular weight range (Figure 5.14). The high molecular weight shoulder has *ca*. twice the phthalimide groups of the main peak. This is consistent with the mechanism suggested in the previous chapter. The oligomer fraction, which is attributed to **16**, does not show UV absorption at 292 nm, consistent with there being no phthalimide functionality (Figure 5.15). This provides additional supporting evidence for the proposed mechanism.

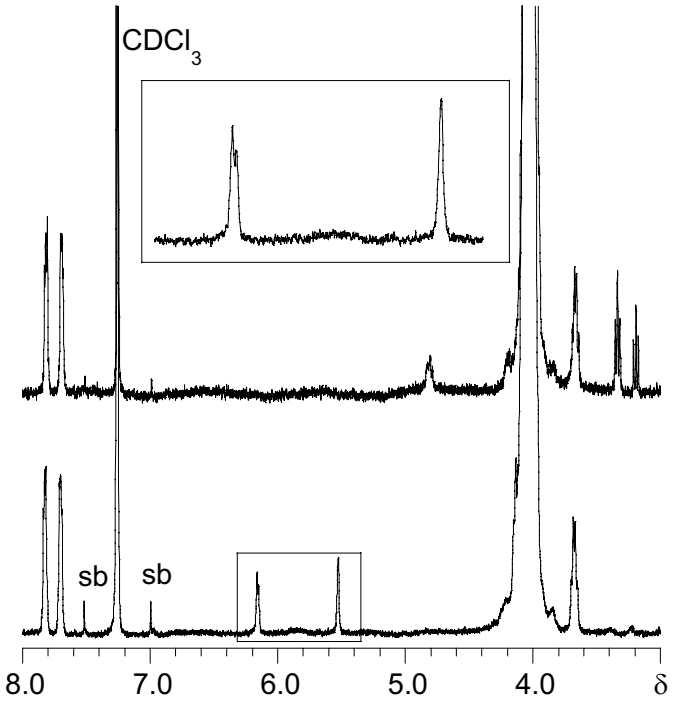


Figure 5.11. ^{1}H NMR spectrum of poly(*n*-butyl acrylate) **12** with $\overline{M}_n$=6830 g mol^{-1} ($\overline{M}_n{}^{NMR}$=6220 g mol^{-1}), $\overline{M}_w / \overline{M}_n$=1.17 (upper) and thermolysis products (**15 16**) with $\overline{M}_n$=4500 g mol^{-1} ($\overline{M}_n{}^{NMR}$=6160 g mol^{-1}), $\overline{M}_w / \overline{M}_n$=1.67 (lower), prepared under isothermal conditions. Inset shows expansion of region δ 5.4-6.2 showing olefinic resonances of the macromonomer end-group of **15**.

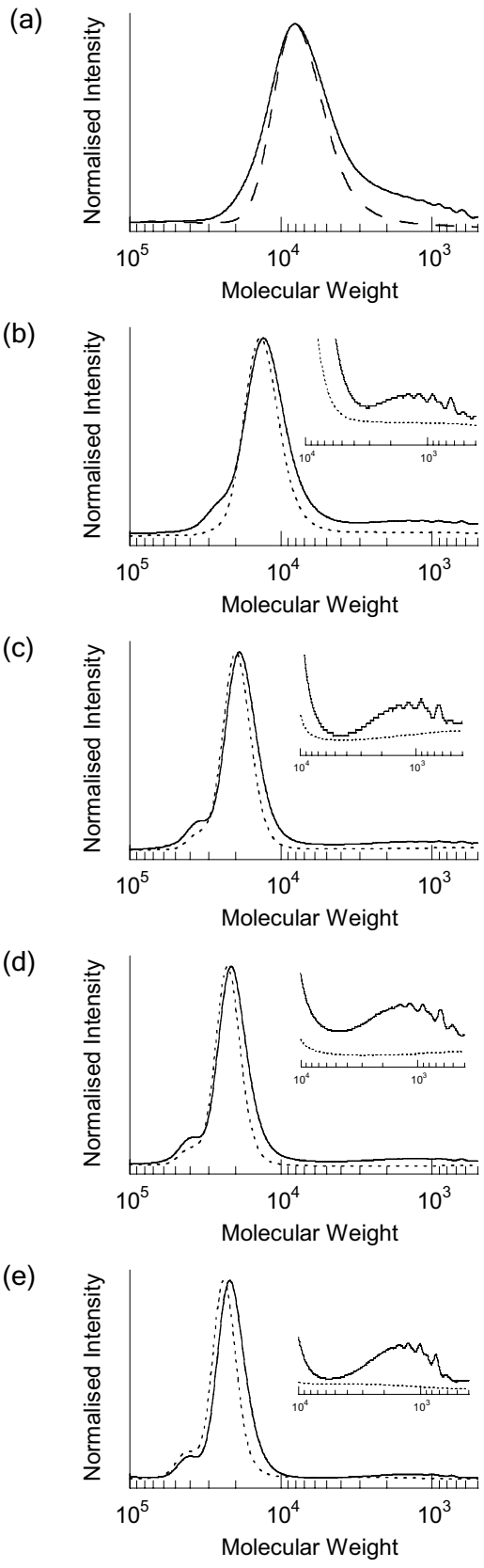

(a)
Normalised Intensity
10^5
10^4
10^3
Molecular Weight
(b)
Normalised Intensity
10^5
10^4
10^3
Molecular Weight
(c)
Normalised Intensity
10^5
10^4
10^3
Molecular Weight
(d)
Normalised Intensity
10^5
10^4
10^3
Molecular Weight
(e)
Normalised Intensity
10^5
10^4
10^3
Molecular Weight

Figure 5.12. GPC traces (a-e) for the precursor polymer **12** (- - -) and reaction products **15** and **16** (—) which arise from the thermolysis of mono-poly(*n*-butyl acrylate) trithiocarbonate **12** (Scheme 5.6). Oligomer fraction is attributed to **16**.

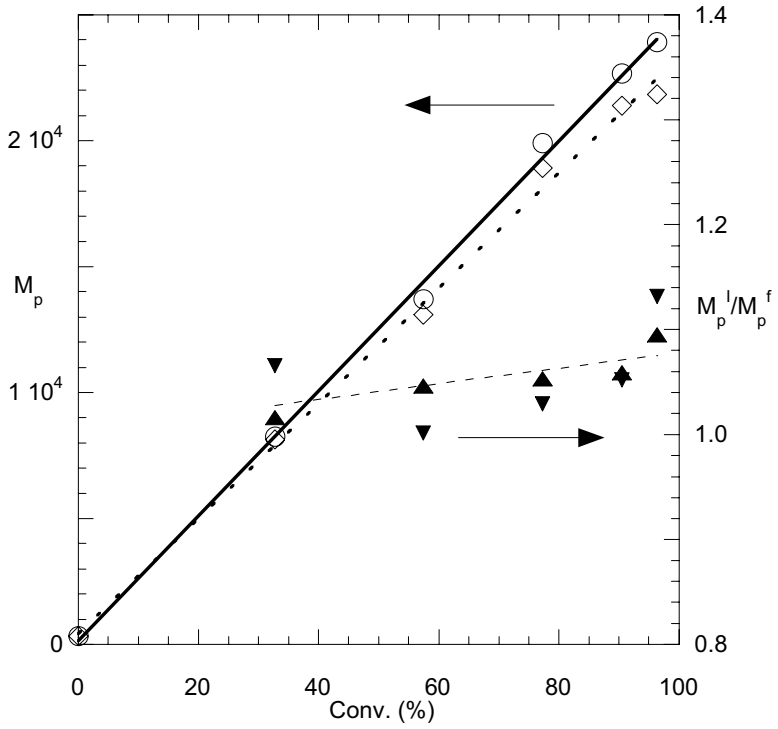


Figure 5.13. Comparison of peak molecular weights of poly(*n*-butyl acrylate) **12**, before ($\overline{M}_{\mathrm{p}}^{\mathrm{i}}$)(○,—) and after ($\overline{M}_{\mathrm{p}}^{\mathrm{f}}$)(◇,- - -) thermolysis. Ratios of initial (i) and final (f) polymer chain lengths (----), $\overline{M}_{\mathrm{p}}^{\mathrm{i}}/\overline{M}_{\mathrm{p}}^{\mathrm{f}}$ (▲) and $\overline{M}_{\mathrm{w}}^{\mathrm{i}}/\overline{M}_{\mathrm{w}}^{\mathrm{f}}$ (▼).

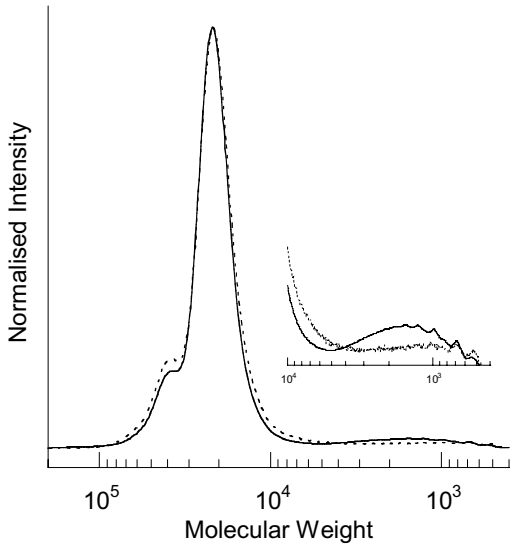


Figure 5.14. Normalised GPC traces of the poly(*n*-butyl acrylate) thermolysis product **15**: RI trace (—) and UV trace (·····) at 292 nm. Inset shows oligomer fraction, which is attributed to **16.**

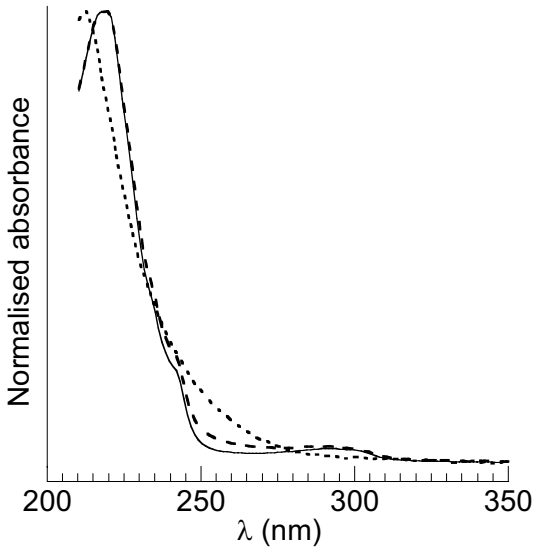


Figure 5.15. Normalised UV spectra of thermalized poly(*n*-butyl acrylate) (**15**, 4hr, 77% conversion); the main peak (—), high molecular weight shoulder (----) and the oligomer peak **16** (·····). Phthalimide absorption maximum at 220 nm (secondary absorption at 292 nm).

Thermolysis of polystyrene **7** was successfully scaled to ~300 g by conducting the thermolysis in a large scale Kugelrohr operating at 220 °C under vacuum. The thermolysed polymer mixtures all retained a yellow colour that was removed by precipitation. The filtrate was found to contain some of *S*,*S*′-bis(*n*-butyl) trithiocarbonate, either from the impurity in the large scale synthesis of RAFT agent **6** (section 4.2.5) used in the bulk polymerisation, or from thiol exchange involving butanethiol thermolysis byproduct and the thiocarbonylthio group on the polymer. The thermolysis treated polymers all showed RAFT removal and exhibited molecular weights that did not differ significantly from the respective precursor polymers.

Some preliminary experiments were also carried out to explore the use of an extruder in chain end thermolysis. A higher molecular weight polystyrene **7** ($\overline{M}_n$ =120000 g mol^{-1}) sample was used. The polymer obtained post extrusion at 190 °C was found to retain the thiocarbonylthio moiety. Samples collected at 250–300 °C were odorous and ^{1}H NMR showed loss of the thiocarbonylthio group and the retention of the phthalimidomethyl functionality. However, it was difficult to analyse quantitatively the efficiency of the thiocarbonylthio removal by NMR due to the polymer molecular weight being high. Molecular weight of the polymer samples obtained were found to be slightly lower ($\overline{M}_n$ =100000 g mol^{-1}) and showed some low molecular weight tailing. This might be attributed to shear scissioning of the polymer chains under the extrusion conditions. Future investigations will be directed at carrying out experiments using longer residence times with lower temperatures; less intensive mixing during extrusion as well as vacuum venting of volatiles.

We anticipate that thermolysis should also be appropriate for removing other forms of RAFT agent residues such as dithioester and xanthate chain ends. Similarly, the method may be applied to other polymers, the only proviso being that the polymer and any desired functionality are stable to the conditions used for thermolysis. However, temperature required may vary according to the specific structure of the polymer and the RAFT agent used.

5.4 Conclusions

Of the methods investigated for thiocarbonylthio removal, thermolysis provides a simple and efficient way of removing trithiocarbonate group from polystyrene and poly(*n*-butyl acrylate) to provide, in the case of our intended application, an inert ω end-group. The process was successfully scaled up and is anticipated to be compatible with applications which exploit primary amino functional polymers.

5.5 References

1. Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559-5562.
2. Chiefari, J.; Rizzardo, E. *Handbook of Radical Polymerization*; Matyjaszewski, K.; Davis, T. P., Editor; John Wiley & Sons, Inc.: Hoboken, USA, 2002; pp 629-690.
3. Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273-2283.
4. Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365-375.
5. Chen, M.; Ghiggino, K. P.; Smith, T. A.; Thang, S. H.; Wilson, G. J. *Aust. J. Chem.* **2004**, *57*, 1175-1177.
6. Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458-8468.
7. Perrier, S.; Takolpuckdee, P.; Mars, C. A. *Macromolecules* **2005**, *38*, 2033-2036.
8. Chong, B. Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256-2272.
9. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243-245.
10. Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505-1513.

11. Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y. *Macromolecules* **2003**, *36*, 7446-7452.
12. Thomas, D. B.; Convertine, A. J.; Hester, R. D.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2004**, *37*, 1735-1741.
13. Favier, A.; Ladaviere, C.; Charreyre, M.-T.; Pichot, C. *Macromolecules* **2004**, *37*, 2026-2034.
14. Schilli, C.; Lanzendorfer, M. G.; Muller, A. H. E. *Macromolecules* **2002**, *35*, 6819-6827.
15. Llauro, M.-F.; Loiseau, J.; Boisson, F.; Delolme, F.; Ladavière, C.; Claverie, J. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5439-5462.
16. Sumerlin, B. S.; Lowe, A. B.; Stroud, P. A.; Zhang, P.; Urban, M. W.; McCormick, C. L. *Langmuir* **2003**, *19*, 5559-5562.
17. McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312-325.
18. Vana, P.; Albertin, L.; Barner, L.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4032-4037.
19. Rizzardo, E.; Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 297-307.
20. Quinn, J. F.; Barner, L.; Barner-Kowollik, C.; Rizzardo, E.; Davis, T. P. *Macromolecules* **2002**, *35*, 7620-7627.
21. de Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3596-3603.
22. Chen, M.; Ghiggino, K. P.; White, J.; Thang, S. H.; Wilson, G. J. *J. Org. Chem.* **2005**, *70*, 1844-1852.
23. Lima, V.; Jiang, X.; Brokken-Zijp, J.; Schoenmakers, P. J.; Klumperman, B.; van der Linde, R. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 959-973.
24. Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y. *Macromolecules* **2003**, *36*, 7446-7452.
25. Clouet, G.; Juhl, H. J. *Macromol. Chem. Phys.* **1994**, *195*, 243-251.
26. Skidmore, M. unpublished results.
27. Krstina, J.; Moad, G.; Solomon, D. H. *Eur. Polym. J.* **1989**, *25*, 767-777.
28. Chugaev (Tschugaeff), L. *Ber.* **1899**, *32*, 3332.
29. Schreck, V. A.; Serelis, A. K.; Solomon, D. *Aust. J. Chem.* **1989**, *42*, 375-

393.

30. Yoshikawa, C.; Goto, A.; Fukuda Takeshi *e-Polymers* **2002** (013), 1-12.
31. Lutz, J.-F.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 897-910.
32. Chiefari, J.; Jeffery, J.; Krstina, J.; Moad, C. L.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2005**, *38*, 9037-9054.
33. Chiefari, J.; Jeffery, J.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 7700-7702.
34. Harrisson, S.; Wooley, K. L. *Chem. Commun.* **2005**, *26*, 3259-3261.
35. Pierik, S. C. J.; van Herk, A. M. *Macromol. Chem. Phys.* **2003**, *204*, 1406-1418.
36. Hu, Y.-H.; Chen, C.-Y.; Wang, C.-C. *Polym. Degrad. Stab.* **2004**, *84*, 505-514.
37. Lehrle, R. S.; Place, E. J. *Polym. Degrad. Stab.* **1997**, *56*, 215-219.
38. Lehrle, R. S.; Place, E. J. *Polym. Degrad. Stab.* **1997**, *56*, 221-226.

6 A Simple Method for Determining Protic End-Groups of Synthetic Polymers by ^{1}H NMR Spectroscopy

6.1 Introduction

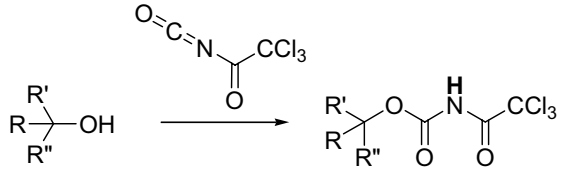
This chapter investigates the scope of an efficient method for characterisation and determination of a wide range of protic (hydroxy, carboxy, amino) end-groups in synthetic polymers.

In order to fully characterise polymers and their reactions, it is important to have a precise knowledge of the polymer end-groups. This is particularly important for the synthesis and applications of specific end-functional polymers. The various methods described in the literature include techniques based on the use of classical titration,[1,2] mass spectrometry (MALDI-TOF, ESI),[3-6] various chromatographic techniques,[7,8] FTIR,[9-11] NMR,[12-16] UV[17] and fluorescence.[18] All of the methods described to date suffer from some limitations with respect to sensitivity and/or versatility.

NMR is one of the most used methods for polymer end-group determination. In ^{1}H NMR spectra, the exchangeable protons of functional groups such as hydroxy, amino and carboxy often produce signals that are broad and which integrate poorly. Even in polymers of modest molecular weight, there is the additional problem of the end-group signals being easily overwhelmed. Consequently, they can be difficult to resolve when they appear in close proximity of the much larger signals for protons associated with the polymer repeat units. Where the groups (X) are attached to primary or secondary carbon (*i.e.* -CH_2-X, >CH-X), the presence of protons adjacent to the functionality may permit identification and quantification. However, the same limitations with respect to the need for sufficient resolution from signals due to the polymer

repeat unit apply, and when the functional groups are aryl or tertiary (*i.e.* ≡C-X, Ar-X) this option is not available. The use of selective labeling, special pulse sequences or multidimensional NMR may alleviate the requirement that signals appear in a clear region of the NMR spectrum in some cases, though precise quantitation remains problematic.

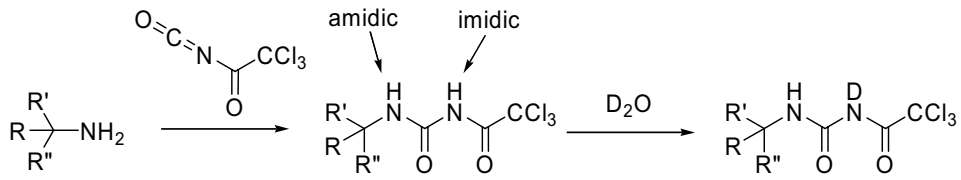
In small molecule chemistry, derivatisation strategies are often employed to simplify the characterisation of functional groups and to overcome problems with direct NMR analysis. A simple technique for determining alcohols and glycols was devised by Goodlett *et al.*[19] who utilized trichloroacetyl isocyanate (TAI) as an in situ derivatisation reagent. The derivatisation was found to be both rapid and quantitative (Scheme 6.1). Their work[19] focused on observing the change in chemical shift of α-carbamate hydrogens for compounds **1** where R' and/or R"=H. Subsequent work by other groups observed and/or quantified TAI-derivatised alcohols,[20,21] phenols,[20] amines[20,21] and hydroxy acids[22] by ^{13}C and ^{1}H NMR. In this work, while the presence of imidic hydrogen signals has sometimes been noted,[20,21,23] only a few have used these signals for quantitation.[24]



1

Scheme 6.1

Buděšínský *et al.*[21] examined the reaction of primary, secondary and tertiary amines and amino alcohols with TAI (Scheme 6.2) and noted that while the chemical shift and appearance of the imidic hydrogen resonance (-NH-C(O)-NH-$COCCl_3$) of the derivative **2** was concentration dependent, the amidic hydrogen resonance (-NH-C(O)-NH-$COCCl_3$) showed no such dependence. The more acidic imidic hydrogen of **2** was also found to undergo H-D exchange upon the addition of deuterium oxide (this can be an aid in distinguishing the fickle imidic hydrogen from the constant amidic hydrogen, amongst complex polymer end-group signals – see later discussion).



2

Scheme 6.2

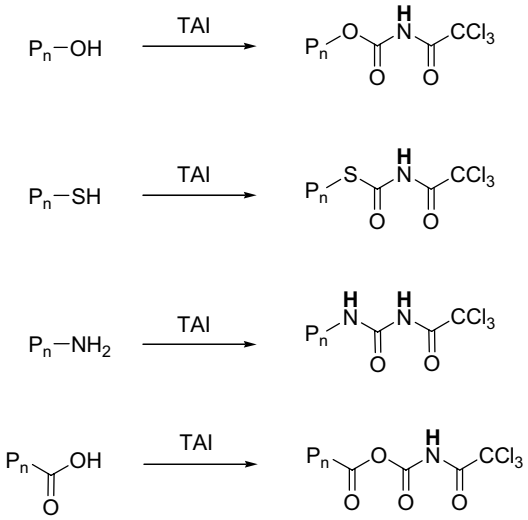
There are some previous reports of the use of derivatisation strategies in analysing polymer end groups by NMR.[1,13,25-28]

Most recently derivatisation with reagents containing fluorine or phosphorus has been recommended. These methods have the advantage that most polymers do not themselves contain fluorine or phosphorus so the issue of resolving end group signals from polymer backbone signals does not arise. Efficient derivatisation/^{19}F NMR strategies applicable to hydroxyl,[28-30] carboxy[29,31] and amine chain ends[13] have been described. However, several of the methods require product isolation and relatively long reaction times. Moreover, different reagents are required for different end groups. The ^{19}F NMR analysis also requires precise addition of a suitable internal standard for quantitative analysis. Strategies for derivatisation of hydroxy and carboxy end groups with phosphorus based reagents with subsequent ^{31}P NMR analysis have been devised.[32,33] These methods face the same issues as the ^{19}F NMR-based techniques.

TAI derivatisation and ^{1}H NMR has also been applied to polymer end-group analysis.[1,25-27] Ronda *et al.*[27] characterised the TAI derivatives of hydroxy end-functional polymers based on phenyl glycidyl esters. Analysis of the signals for the α-carbamate hydrogens allowed the proportion of primary and secondary hydroxy end groups to be estimated. The signals for the imidic hydrogens (-O-C(O)-N**H**-COCCl$_3$) of the derivatised primary and secondary hydroxy end-groups were not sufficiently resolved to allow precise quantitation. Vinyl ethers prepared by living cationic polymerisation initiated by 1-trimethylsiloxy-4-iodo-3-oxabutane in the presence of tetrabutylammonium triflate, yields a polymer with a trimethylsilyloxy end-group.[25] The hydroxy-terminated poly(vinyl ether) formed by end-group hydrolysis was characterised by ^{1}H NMR of the TAI

derivative. Commercial polyethylene glycols (PEG), their monomethyl ethers[26] and propylene glycol (PPG) copolymers have been investigated using TAI end-group analysis. Fallais *et al.*[1] studied the preparation of end functional polystyrenes by anionic polymerisation. Primary amino and hydroxy end-groups were determined with the aid of TAI derivatisation. In each of these studies, quantitation relied on determination of signals for protons adjacent to the end-group. In our laboratories we have recently demonstrated that the TAI derivatisation method can be applied to quantitatively determine both the carboxy and hydroxy end-groups of carious polyesters including commercial polyethylene terephthalate (PET).[34]

In this chapter it was shown that the TAI derivatisation method is a reliable method for the determination of a wide range of protic (hydroxy, carboxy, amino) end-groups in synthetic polymers. The proposed products from the reaction of various polymer end-groups with TAI are shown in Scheme 6.3.



Scheme 6.3

The method has subsequently been further applied in the ongoing work on synthesis of end-functional polymers by various living radical techniques[35-37] including reversible addition-fragmentation chain transfer (RAFT),[38,39] atom transfer radical polymerisation (ATRP),[40-42] and nitroxide-mediated polymerisation (NMP).[43] In particular, as part of this thesis it can be invaluable for the characterisation of amino-end functional polymers synthesized for use in

the production of segmented grafted copolymers. Furthermore it was envisaged that such a technique could be used to determine the level of functionality imparted by the polymerisation process. In this chapter the method was extended to characterise polymers and block copolymers based on poly(ethylene oxide) PEO which have potential application as dispersants/intercalants/dispersants in polymer nanocomposites.[44]

6.2 Experimental

6.2.1 NMR

400 MHz Proton Nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a Bruker Av400 spectrometer at 298K. Spectra were recorded for samples dissolved in deuterochloroform ($CDCl_3$) and chemical shifts are reported as ppm from external tetramethylsilane unless stated otherwise.

6.2.2 Two dimensional NMR

^{1}H and ^{13}C NMR spectra of a TAI derivatised α-aminomethylpolystyrene (**4**) were recorded in $CDCl_3$ (referenced to δ_H 7.26 and δ_C 77.03) at 25 °C/298K using a Bruker DRX500 spectrometer at 500.13 MHz for ^{1}H and 125.6 MHz for ^{13}C. For ^{1}H spectra, 32K data points were collected for the FID, over a sweep width of 7500 Hz (0.23 Hz/pt). For ^{13}C spectra, 64K data points were collected for the FID over a sweep width of 30300 Hz (0.46 Hz/pt). The 2D experiments used standard Bruker library sequences with the following parameters: **COSY** (cosygpqf45) 4096 FID data points, 5000 Hz sweep width, 0.41 s acquisition time, 1.0 s relaxation delay, 512 experiments, multiplied by an unshifted sine function in both dimensions and Fourier transformed over 2048 × 1024 points; **HSQC** (hsqcetgpsisp.2) 2048 FID data points, 5000 Hz sweep width, 0.20 s acquisition time, 1.0 s relaxation delay, $^1J_{CH}$ = 145 Hz, 512 experiments, multiplied by an π/2-shifted sine-squared function in both dimensions and Fourier transformed over 2048 × 1024 points; **HMBC** (hmbcgplpndqf) 4098 FID

data points, 5000 Hz sweep width, 0.58 s acquisition time, 0.7 s relaxation delay, 512 experiments, 3.44 ms low-pass *J*-filter ($^1J_{CH}$ = 145 Hz), 62.5 ms delay for evolution of long-range coupling ($^nJ_{CH}$ = 8 Hz), multiplied by an $\pi/2$-shifted sine function in both dimensions and Fourier transformed over 2048 × 1024 points.

A portion of the COSY spectra of a TAI derivatised α-aminomethylpolystyrene (**4**) is shown in Figure 6.2.

6.2.3 Gel permeation chromatography

Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with differential refractometer and 3×Mixed C and 1 mixed E PLgel column (each 7.5 mm×30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22±2 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories). A third order polynomial was used to fit the $\log_{10}$M *vs* time calibration curve, which appeared to be linear across the molecular weight range 2×10^2–2×10^6.

6.2.4 Materials

Trichloroacetyl isocyanate (96%) and model compounds were obtained from Aldrich and were used without further purification. Polyethylene glycol (PEO), α-methoxy-poly(ethylene oxide-*co*-propylene oxide)-propan-2-amine (PEO-*co*-PPO, tradename JEFFAMINE® M-2070) were obtained from Aldrich and Huntsman respectively. The synthesis of end-functional polymers (**4**)[36] and (**8**)[37,45] are described in Chapter 4., polymer (**11**)[37,45] in Chapter 3 and (**18**)[37] is described elsewhere.

6.2.5 α-Carboxy, ω-hydroxypolystyrene (20)

4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (0.64 g, 3.72×10^{-3} mol), azobis(4-cyanovaleric acid) (1.02 g, 3.64×10^{-3} mol) and styrene (40 mL, 0.35 mol) were transferred to a flask and which was purged with argon for 30 min then heated at 135 °C under argon for 45 min. A sample (2 mL) was withdrawn, cooled, and purified by precipitation into methanol. The gravimetric monomer conversion was 40%, GPC analysis showed $\overline{M}_n$ =2824 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.40.

6.2.6 α-Ethylhydroxypolystyrene (22)

This material was obtained from Bronwyn Fox: Water (1040 g) which was purged with nitrogen for 20 min and styrene (40 mL) were transferred to a flask and azobis(4-cyanovaleric acid) (2.16 g in 64 g water), sodium dodecyl sulphate (12 g in 120 g water) and sodium bicarbonate (2 g in 40 g water) were added and the mixture purged for a further 30 min. The reaction mixture was then heated to 80 °C with stirring (270 rpm) and styrene (320 g) and a solution of 2-mercaptoethanol (10.8 mL of 10% v/v in water) was added. A further 16.2 mL of degassed mercaptoethanol solution were added at a rate of 0.09 mL/min (~180 min) by syringe pump. The reaction mixture was maintained at 80 °C for a further 30 min and then allowed to cool. The gravimetric monomer conversion was 94.8%, GPC analysis showed a bimodal molecular weight distribution $\overline{M}_n$ =10300 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =6.85.

6.2.7 Polyethylene-block-poly(ethylene oxide) (24)

The polyethylene-*block*-poly(ethylene oxide) (PE-*block*-PEO) **24a-d** were obtained from Aldrich Chemical Co. The low molecular weight PE-*block*-PEO (**24e**), was supplied by Ciba Specialty Chemicals. The compositions and molecular weights of **24** are summarized in Table 6.1.

Table 6.1. Average Composition of PE-block-PEO non-ionic surfactants.

Additive	$\overline{M}_n$ [a]	Av. n[b]	Av. m[b]	Av. n[b,c] (NMR^{TAI})	Av. m[b,c] (NMR^{TAI})
24a PE-*block*-PEO	1400	25	16	24.9	18.6
24b PE-*block*-PEO	920	15	10	22.8	15.9
24c PE-*block*-PEO	875	25	4	24.3	5.2
24d PE-*block*-PEO	575	16.4	2.6	20.9	3.4
24e PE-*block*-PEO	406	9	2	10.6	2.1

[a] Nominal number average molecular weight ($\overline{M}_n$) and composition based on information provided by supplier. [b] Average degree of polymerisation; n= number of repeat units of PE block, m= number of repeat units of PEO block. [c] Determined by integration of NMR spectrum of TAI derivative (see text in Section 6.3.5).

Derivatisation of the PE-block-PEO samples was executed by Guoxin Li.

6.2.8 Derivatisation and ^{1}H NMR analysis for model compounds

The following procedures are typical:

A sample of 1-phenylethylamine (10 mg, 82.5 μmol) was dissolved in $CDCl_3$ (0.5 mL), after dissolution the mixture was transferred to an NMR tube and an excess of trichloroacetyl isocyanate (30 μL, 47.4 mg, 0.25 mmol) was added and the ^{1}H NMR spectrum recorded. ^{1}H NMR ($CDCl_3$): δ 1.57 (d, *J* = 6.94 Hz, 3H, PhCHC**H**$_3$,), 5.06 (p, *J* = 6.94 Hz, 1H, PhC**H**), 7.35 (m, 5H, Ar), 8.26 (d, *J* = 6.94 Hz, 1H,), 8.96 (s, 1H, CON**H**CO).

An excess of D_2O (10 μL, 11.1 mg, 0.55 mmol) was added to the TAI derivatised 1-phenylethylamine prepared above in the NMR tube and the ^1H NMR spectrum was recorded. ^1H NMR ($CDCl_3$): δ 1.57 (d, *J* = 6.94 Hz, 3H, PhCHC**H**$_3$,), 4.82 (br s, 1H, **H**DO), 5.05 (p, *J* = 6.94 Hz, 1H, PhC**H**), 7.35 (m, 5H, Ar), 8.23 (d, *J* = 6.94 Hz, 1H, CON**H**CO).

6.2.9 Derivatisation and ^1H NMR analysis for end-functional polymers

The following procedures are typical:

A sample of ω-aminopolystyrene (**11**) (40 mg, $\overline{M}_n$ =1230 g mol^{-1}, $\overline{M}_w / \overline{M}_n$ =1.10) was dissolved in $CDCl_3$ (0.5 mL), after dissolution the mixture was transferred to an NMR tube and an excess of trichloroacetyl isocyanate (10 μL, 15.8 mg, 83.9 μmol) was added and the ^1H NMR spectrum of (**12**) was recorded. ^1H NMR ($CDCl_3$): δ 1.25-2.50 (br m, backbone C**H**, C**H**$_2$), 4.52 (m, 1H, -C**H**NHCO-), 6.25-7.40 (br m, ArH), 7.73 + 7.91 (br d, 1H, -CHN**H**C(O)-), 8.26 (tr, 1H, -C(O)N**H**C(O)-).

An excess of D_2O (10 μL, 11.1 mg, 0.55 mmol) was added to the TAI derivatised ω-aminopolystyrene (**12**) prepared above in the NMR tube and the ^1H NMR spectrum of (**13**) was recorded. ^1H NMR ($CDCl_3$): δ 1.25-2.50 (br m, backbone C**H**, C**H**$_2$), 4.52 (m, 1H, C**H**), 4.75 (br s, 1H, **H**DO), 6.25-7.40 (br m, ArH), 7.73 + 7.91 (br d, 1H, CHN**H**CO).

6.3 Results and discussion

6.3.1 Derivatisation procedure

The analytical procedure is the same as what has been reported previously[34] and involves dissolving a sample of the polymer (typically 5-10 mg) in a suitable aprotic solvent such as $CDCl_3$ or C_6D_6 directly in an NMR tube, adding a drop (10 μL) of TAI and recording the ^1H NMR spectrum. The reaction is essentially

instantaneous being complete within the *ca* 10 minutes taken to place the sample in the spectrometer. Excess TAI, being aprotic, causes no additional signals in the spectrum. While it is desirable that the samples and solvent are dry, reaction with extraneous water yields carbon dioxide and trichloroacetamide, neither of which give signals that interfere in the region of interest *i.e.* δ 8-11.5. The main by-product, trichloroacetamide exhibits two broad singlets that appear at *ca* δ 6.0 and 6.7. It is important to store TAI under anhydrous conditions. It has been observed that use of aged TAI, stored under less appropriate conditions, can give rise to unidentified by-products that provide extraneous peaks in the spectra.

6.3.2 TAI derivatisation of model compounds

In order to establish the ^{1}H NMR chemical shifts of the TAI end-group, the NMR spectra of a series of model compounds containing amino, carboxy, hydroxy and sulfanyl groups were examined. The chemical shifts of the imidic and amidic, in the case of amines, (δ NH) and α-hydrogens (δ H_α) are reported in Table 6.2. In accord with literature report,[21] the imidic hydrogens were found to be exchangeable such that the corresponding signals vanish on addition of D_2O. For the case of amines, signals attributable to the amidic hydrogens did not exchange and remained on addition of D_2O. Discussion of specific features of the spectra of the model compounds appear in the appropriate section of this chapter.

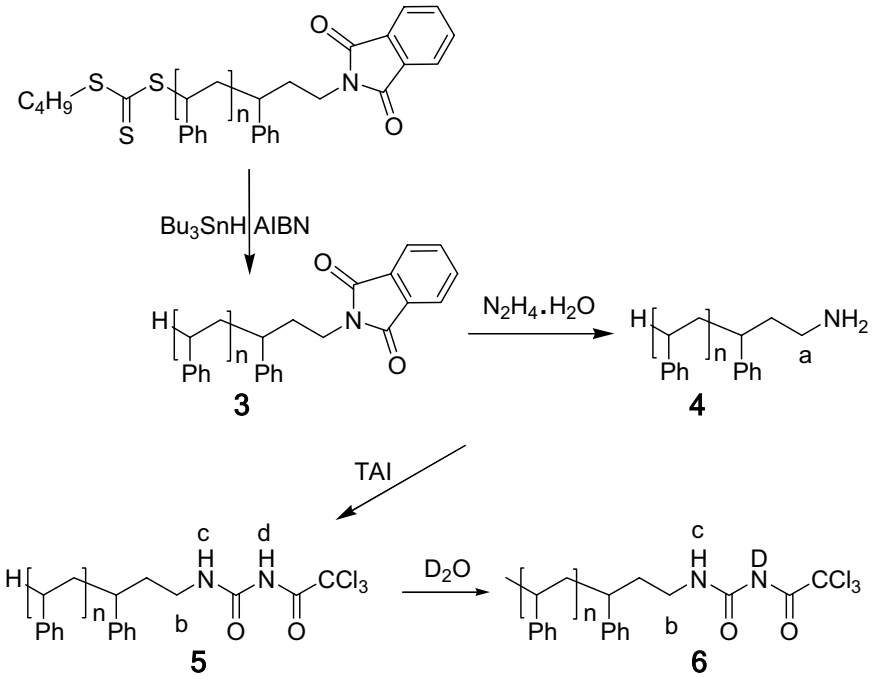
Table 6.2. Chemical shifts for imidic, amidic (δ NH) and adjacent hydrogens (δ H_α) for trichloroacetyl isocyanate-derivatised model compounds with amino, sulfanyl or hydroxy end-groups.

Model Compound	Functionality	δ C**H**$_\alpha$[a]	δ N**H**[a]	
			amidic	imidic[c]
1-phenylethylamine	-CH(Ph)NH_2	5.06 (p)	8.26 (d)	8.96 (s)
2-phenylethylamine	-CH_2NH_2	3.60 (q)	7.91 (br tr)	8.96 (s)
n-butylamine	-CH_2NH_2	3.33 (q)	7.90 (tr)	9.41 (s)
benzylmercaptan	CH_2(Ph)SH	4.22 (s)	-	9.14 (s)
n-butylmercaptan	-CH_2SH	2.98 (t)	-	8.92 (s)
n-butylmercaptan	-CH_2SH	2.63 (t)	-	8.78 (s)[b]
2-mercaptoethanol[d]	-CH_2SH	4.49 (t)	-	8.99 (s)
2-mercaptoethanol[e]	-CH_2OH	4.39 (t)	-	8.46 (s)
2-mercaptoethanol[d]	-CH_2OH	3.32 (t)	-	8.42 (s)
ethanol	-CH_2OH	4.32 (q)	-	8.40 (s)
2-methoxyethanol	-CH_2OH	4.36 (t)	-	8.89 (s)

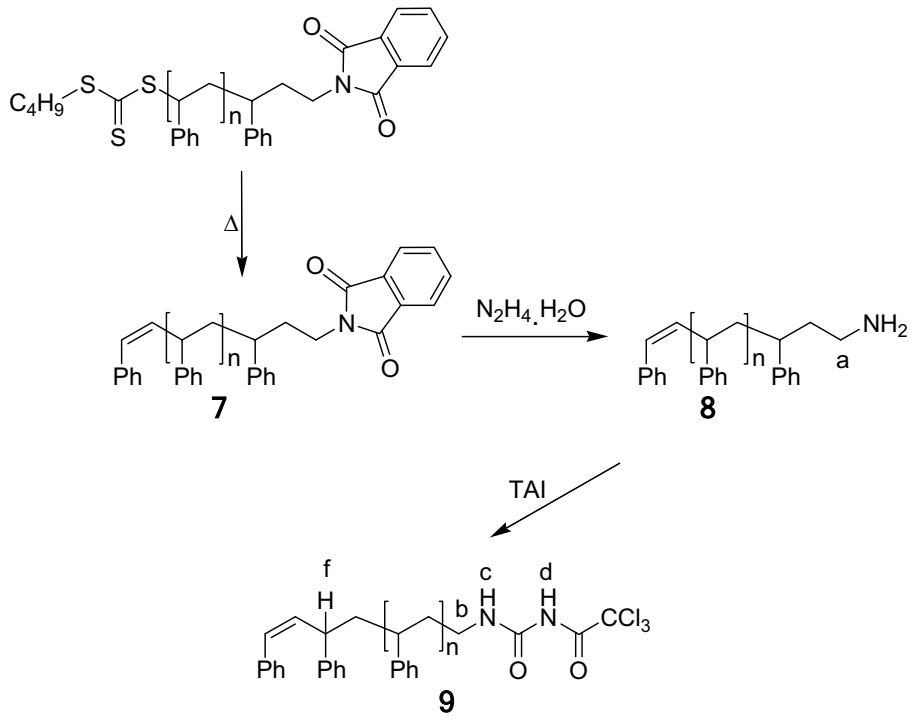
[a] Solvent $CDCl_3$. [b] Solvent C_6D_6. [c] Precise chemical shifts show some concentration dependence (±0.05 ppm). [d] Both -SH and -OH groups derivatised. [e] -OH only derivatised.

6.3.3 TAI derivatisation of amino end-functional polymers

In this thesis the synthesis of amine end-functional polystyrenes by hydrazinolysis of phthalimido end-functional polystyrenes synthesized by ATRP[36] and RAFT[37] has already been described. RAFT-synthesized α-phthalimidomethylpolystyrenes were converted to α-aminomethylpolystyrenes either as shown in Scheme 6.4[37,45] or Scheme 6.5.[37,46] Full details of the syntheses are presented elsewhere[36,37,45] as well as in Chapters 3 to 5.



Scheme 6.4



Scheme 6.5

Portions of the ^{1}H NMR spectrum of the TAI derivative of α-aminomethylpolystyrene (**4**) are shown in Figure 6.1. The amidic hydrogen (c) for the derivative **5** appears as a 'doublet' at δ 7.50 reflecting the fact that the chain end is a mixture of diastereomers. The signal (e) is extraneous and is only observed when a large excess of TAI is used. This signal (e) disappears on addition of D_2O, while the signal for imidic hydrogen (d) for derivative **5** at δ 8.21 remains, indicating that the exchange to form (**6**) is slow for this example. The signal for the α-methylene shifted from δ 2.3 to a clear region of the spectrum at δ 2.9-3.1 on TAI derivatisation. The signals (d), (c) and (b) were in the expected 1:1:2 ratio.

For the TAI derivative of the model compound, 2-phenylethylamine, the imidic and amidic hydrogens give rise to a singlet at δ 8.96 a broad triplet at 7.91 respectively at significantly lower field than the corresponding end group signals. The signal for imidic hydrogen for the model compound was removed by D_2O exchange.

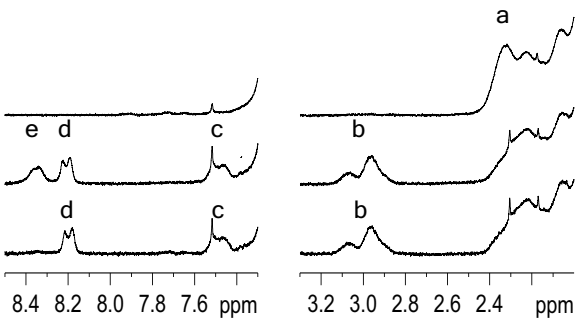


Figure 6.1. Portions of the ^{1}H NMR spectra of (from top to bottom) α-aminomethylpolystyrene (**4**) and derivative (**5**) before and after D_2O exchange. The sample corresponds to entry 2 in Table 6.4. Signal assignments are: (a) -C**H**$_2$-NH$_2$ (**4**), (b) -C**H**$_2$-NH-C(O)- (**5**), (c) amidic -NH signal -CH$_2$-N**H**-C(O)- (**5**), (d) imidic -NH signal -CH$_2$-NH-C(O)-N**H**-COCCl$_3$ (**5**), (e) extraneous peak.

Two-dimensional spectra NMR (HMBC, HSQC and COSY) for the TAI derivative (**9**) of the similar α-aminomethyl styrene polymer (**8**) were obtained to confirm the amidic and imidic signal assignments. A correlation was observed in the HMBC between the carbamate carbonyl at δ_C 150.6 and the α-methylene δ_H 3.1. A further correlation was found between the trichloroacetyl carbonyl δ_C 161.5 and the imidic hydrogen at δ_H 8.2. The COSY spectrum (Figure 6.2) shows a correlation between the signal for the amidic hydrogen at δ 7.5 and that for the α-methylene at δ 2.9-3.1. In this polystyrene, the α-methylene signal at δ 2.9-3.1 overlaps with that for the aliphatic methine of the ω-(1,3-diphenylpropenyl) chain end at δ 3.1. The imidic signal at δ_H 8.2 shows no cross peaks. A correlation (not shown) was also seen between the olefinic hydrogens at δ 6.1-6.3 and the methine of the ω-(1,3-diphenylpropenyl) δ 3.1.[46] The overlap of the signals for the α-methylene and the methine of the ω-(1,3-diphenylpropenyl) means that integration of the amidic or imidic hydrogens provides for more reliable end group quantification.

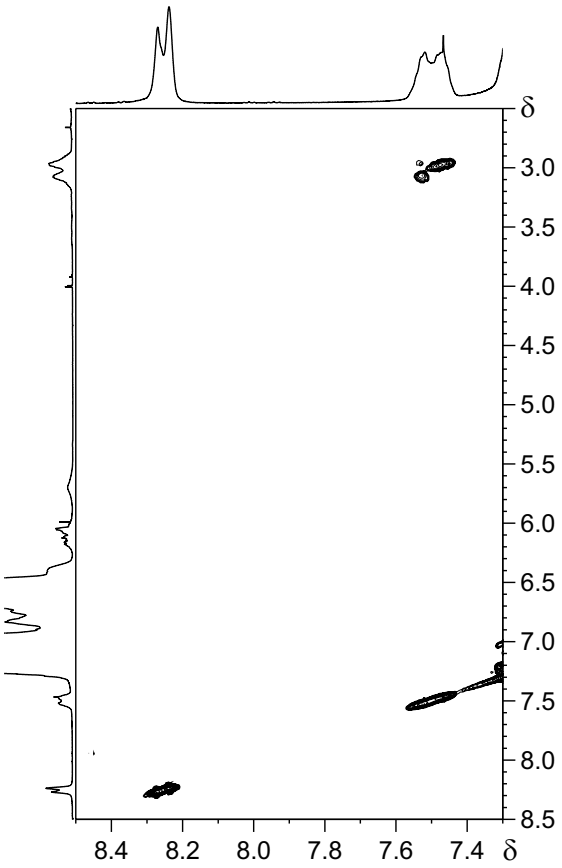
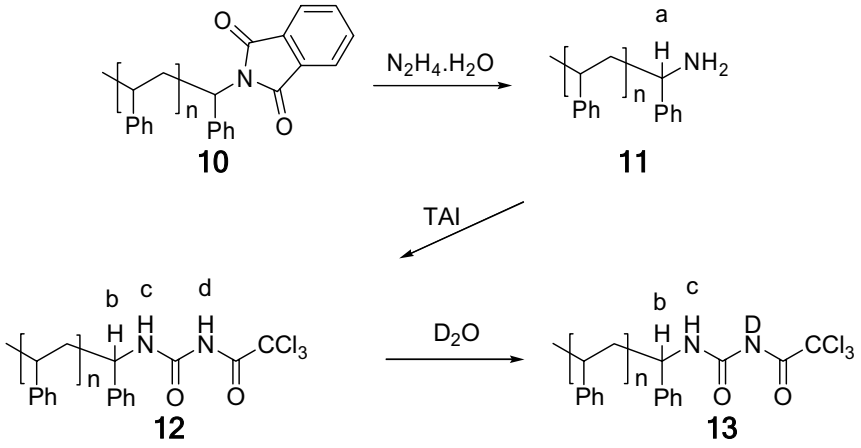


Figure 6.2. Portion of the COSY spectrum of TAI derivative of polystyrene (**8**) showing connectivities between the amidic and α-methylene hydrogens. Spectrum recorded in $CDCl_3$ at 298 K using a Bruker DRX500 spectrometer at (see 6.2.2 and text for further experimental details and assignments).

The ^1H NMR spectrum of a low molecular weight ATRP-synthesized ω-aminopolystyrene (**11**, Scheme 6.6)[36] and its TAI derivative (**12**) before and after D_2O exchange are shown in Figure 6.3. The signals attributed to the -C**H**(Ph)NH_2 methine proton show complexity which is attributed to the influence of the tacticity of the polystyrene chain. This influence is also evident in the appearance of signals for the amidic (at δ 7.7-8.0) and imidic hydrogens (δ 8.2-8.4) (Figure 6.3). These signals appear at significantly higher field than those for the model compound 1-phenylethylamine where the amidic hydrogen is a singlet at δ 8.26 while the imidic hydrogen appears as a doublet at δ 8.96.

The signal for the more acidic imidic hydrogen disappears from the spectrum with D_2O exchange (Scheme 6.6). This is also observed for amine terminated PEO/PPO and for the model compounds. The result provides confirmation for the signal assignments.



Scheme 6.6

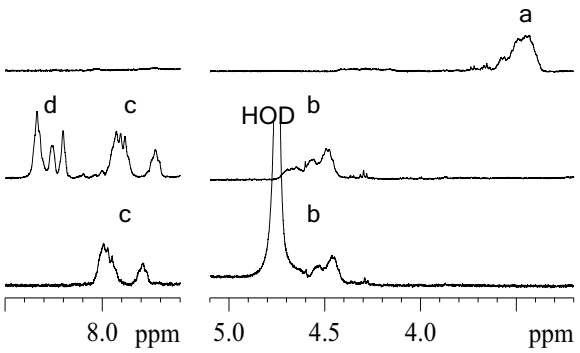


Figure 6.3. Portions of the ^{1}H NMR spectra of (from top to bottom) ω-amino polystyrene (**11**), TAI derivative (**12**) and product of D_2O exchange (**13**). Sample corresponds to first entry of Table 6.4 – refer Scheme 6.4. The regions showing the polymer backbone signals have been removed for clarity. Signal assignments are as follows (a) -C**H**(Ph)NH_2 (for **11**), (b) -C**H**(Ph)NH-C(O)- (for **12** or **13**), (c) -CH(Ph)N**H**-C(O)-NH-$COCCl_3$ (**12** or **13**), (d) -CH(Ph)NH-C(O)-N**H**-$COCCl_3$ (**12**), f_n = 0.95, [NH_2] = 2.70 μeq/g.

In order to test the quantitative power of the technique, it was applied to determine the end groups of RAFT-synthesized polymers where it was important to determine how the fraction of amine chain ends depended on the

reaction conditions used in synthesis. Molecular weights of the polymers were determined by GPC in THF and these are tabulated in Table 6.3 for the amino-functional polystyrene (**8**), its precursor, the phthalimido-functional polystyrene (**7**) and its TAI derivative (**9**). It was found that polar amine end-group interfered with the GPC molecular weight determination by causing the peak to appear at longer retention times. Substantial band broadening was also observed. The effect was most significant for lower molecular weight polystyrenes. The GPC molecular weights for the TAI derivatives are very similar to those of the corresponding α-phthalimidopolystyrene. It appears TAI derivatisation can be an aid in achieving more reliable GPC molecular weight data for amine functional polystyrenes, and possibly other polymers subject to similar effects.

For polymers with molecular weight <40k the end group purity is high (>90%). However, for the highest molecular weight sample only *ca* half of the chains possess the desired end groups. The low functionality can be attributed to the relative importance of radical-radical termination in RAFT polymerisation under the reaction conditions when low concentrations of RAFT agent are used. The derivatisation experiments with TAI indicate that the efficiency of conversion of the phthalimido group to the amino group is quantitative within experimental error. These and similar results will be further explored in detail as part of future experiments and publications arising from this work.

Table 6.3. GPC and NMR analysis of α-phthalimidomethyl, α-aminomethyl and TAI derivatised α-aminomethylpolystyrene.

Entry	$\overline{M}_n^{Calc}$ [a]	$\overline{M}_n^{GPC}$ [b]			$[NH_2]$[c]	f_n[d]
		Phthalimido (**7**)	Amino (**8**)	TAI (**9**)	μeq/g	
1	1380	1320	-e	1660	5.5823	1.06
2	5020	4870	900	4990	1.2871	0.97
3	13300	14400	6020	13800	0.5681	0.99
4	38700	37000	26800	35000	0.1872	0.90
5	159000	121000	108000	114000	0.0369	0.48

[a] Expected molecular weight based on the polymerisation conditions and the concentrations of RAFT agent used. Phthalimido end-functional polystyrenes (**7**) were prepared by thermal polymerisation of styrene at 110 °C for 24 hours under nitrogen in the presence of the RAFT agent *S*-butyl *S*'-phthalimidomethyl trithiocarbonate and subsequently transformed to amino end-functional polystyrene (**8**) and derivatised with TAI as indicated in Scheme 6.5. Entries 1-5 correspond to experiments with $[styrene]_0/[RAFT\ agent]_0$= 0.208, 0.689, 3.02, 6.00 and 30.3 respectively, also reported in Table 4.4, Chapter 4.

[b] GPC determined molecular weight for polystyrenes (**7**, **8**, **9** – refer Scheme 6.5) with end group indicated.

[c] $[NH_2]$ is the concentration of amine functionality in microequivalents per gram determined by eq. 1, where *m* is the molar mass of the monomer unit

$$[NH_2] = \frac{\frac{1}{\overline{M}_n^{NMR}}}{m} 10^6 \qquad (1)$$

[d] f_n (number of functional groups per chain) was estimated using eq 2, where $\overline{M}_n^{GPC}$ is the molecular weight of the polymer determined by GPC (phthalimido

or TAI), and $\overline{M}_n^{NMR}$ is the apparent molecular weight determined by comparing the integral of the TAI resonance with that for the backbone ArH.

$$fn = \frac{\overline{M}_n^{GPC}}{\overline{M}_n^{NMR}} \quad (2)$$

[e] Low molecular weight broad bimodal distribution.

Table 6.4. Imidic and amidic ^{1}H NMR signals of end-groups on various polymer TAI derivatives and of protons α to the derivatised groups (H_α), in deuterochloroform.

Polymer	End-functionality	δ H_α	δ NH		$\overline{M}_n^{GPC}$
			amidic	imidic	(g mol^{-1})
PS[a] (**11**)	-CH(Ph)NH_2	4.57	7.83	8.27	1230
PS[b] (**4**)	-CH_2NH_2	3.00	7.50	8.29	1280
PS[b] (**8**)	-CH_2NH_2	3.00	7.50	8.29	1320
PS[b] (**8**)	-CH_2NH_2	3.00	7.49	8.18	4870
PS[b] (**8**)	-CH_2NH_2	3.00	7.50	8.20	9150
PS[b] (**8**)	-CH_2NH_2	3.00	7.49	8.21	14400
PS[b] (**8**)	-CH_2NH_2	3.00	7.50	8.20	32100
PS[b] (**8**)	-CH_2NH_2	3.00	7.49	8.20	37000
PS[b] (**8**)	-CH_2NH_2	3.00	7.48	8.16	121000
PS[c] (**22**)	-S$(CH_2)_2$OH	4.17		8.31	10300[d]
PS[e] (**18**)	(-$CH_2)_2$CHOH	5.03		8.29	2820

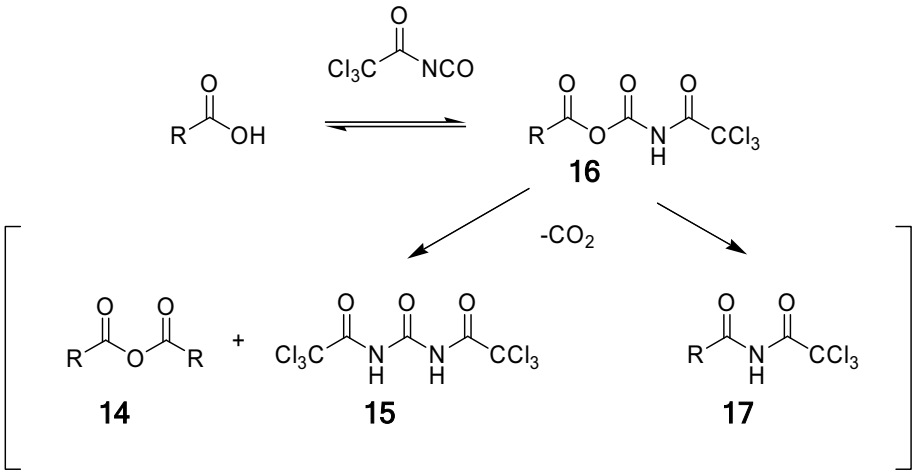
PS[e] (**18**)	-CH_2COOH	[f]		9.38 & 9.85	2820
PMMA[g] (**20**)	-CH_2COOH	2.77		9.34	2620
PEO/PPO[h]	-$CH_2CH(CH_3)$ NH_2	3.99	7.95	8.70	2000
PEO	-$O(CH_2)_2OH$	4.38		8.80	300
PEO	-$O(CH_2)_2OH$	4.40		8.64	1000
ME[i] [47]	-$O(CH_2)_2OH$	-		8.76	-
PET [34]	-$O(CH_2)_2OH$	-		8.22 - 8.65	-
PET [34]	-ArCOOH	-		10.1 - 10.4	-
oligoester [34]	-OH	-		8.08 - 8.81	-
oligoester [34]	-COOH	-		10.3 - 11.4	-
PPGE[j] [27]	-OH	-		8.5	-

[a] Polystyrene synthesised by ATRP[36] (Chapter 3). [b] Polystyrene synthesised by RAFT polymerisation[37] (Chapter 4). [c] Polystyrene synthesized by emulsion polymerisation with mercaptoethanol as a chain transfer agent. (see Experimental). [d] Bimodal distribution. [e] Polystyrene by nitroxide medated polymerisation with 4-hydroxy TEMPO and 4,4'-azobis(4-cyanovaleric acid) (see Experimental). [f] Peak obscured by polymer backbone signal. [g] PMMA synthesised by RAFT polymerisation.[37] [h] JEFFAMINE® M-2070, molecular weight from Huntsman product information sheet. [i] ME = ethoxylated linoleic acid. [j] PPGE = poly(phenyl glycidyl ether).

6.3.4 TAI derivatisation of carboxy functional polymers

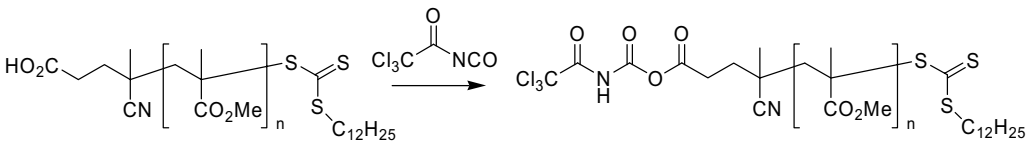
Derivatisation of carboxylic acid functional groups on the model compounds gave rise to complex sets of peaks spanning the region upfield from 10 ppm. It has been reported that the products (**16**) of the reaction between isocyanates

and low molecular weight carboxylic acids are unstable and decarboxylate to form the corresponding anhydride (**14**) and the 1,3-bis(trichloroacetyl)urea (**15**), or the trichloroacetyl amide (**17**) (Scheme 6.7).[48-50] Our observations for benzoic acid and acetic acid support these findings. However, the reaction products from the polymer acid end-groups were found to be stable for >16 h. It was recently reported on the quantitative determination of carboxylic acid and hydroxy end-groups of PET and various polyesters by TAI derivatisation.[34]



Scheme 6.7

For the RAFT-synthesized poly(methyl methacrylate) with carboxy end-groups (**18**), derivatisation with trichloroacetyl isocyanate results in two signals at δ 9.3 (narrow) and 9.4 (broad) in the ^{1}H NMR spectrum (Figure 6.4). These were attributed to the diastereotopic imidic hydrogens of (**19**). No signals attributable to decomposition products were apparent and the signal intensity was consistent with the GPC-determined molecular weight.



Scheme 6.8

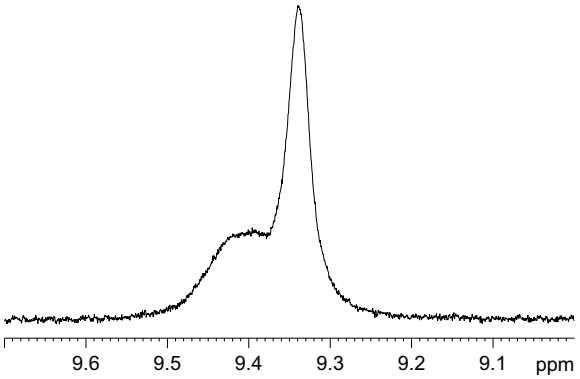
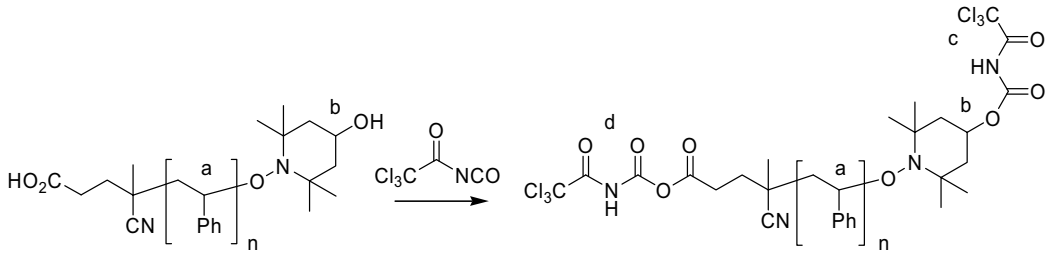


Figure 6.4. Region of ^{1}H NMR Spectrum of TAI derivative (**19**) of poly(methyl methacrylate) (**18**) showing signals attributed to imidic hydrogen of the end group. f_n = 0.90, [COOH] = 2.41 μeq/g.

The α-carboxy, ω-hydroxypolystyrene (**20**) was obtained by nitroxide mediated polymerisation. TAI derivatisation enabled quantitative determination of both the hydroxy- and carboxy- functionalities. The NMR spectra for the polymer (**20**) and its TAI derivative (**21**) are shown in Figure 6.5. The signals for α-methylenes for both the carboxy and the derivatised carboxy group were obscured by polymer backbone signals. The quantitation of the carboxy end-group thus had to solely rely on the signals (d). The signals for the imidic hydrogens of the diastereomeric carboxy (d) the hydroxy (c) and other end-group signals (a) and (b) appeared in a (0.675+0.336)^{d}:1.03^{c}:1.08^{b}:0.98^{a} ratio consistent with structure (**21**).



20 **21**

Scheme 6.9

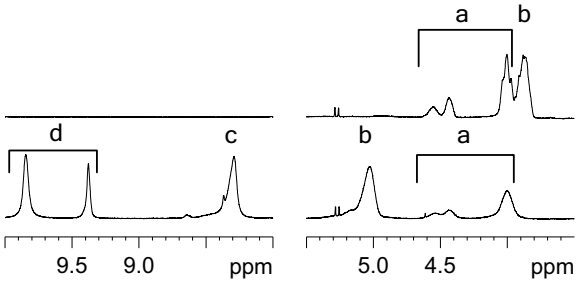
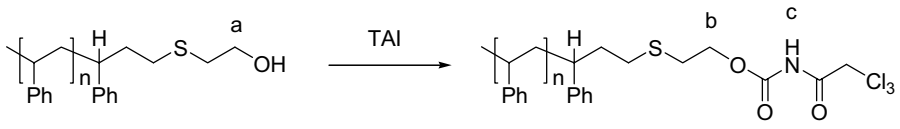


Figure 6.5. Regions of ^{1}H NMR polystyrene (**20**, upper spectrum) and TAI derivative (**21**, lower spectrum) showing signals attributable to the end-groups. Signal assignments as follows (refer Scheme 6.9) (a) -CH_2C**H**(Ph)O- (b) -$CH_2)_2$C**H**O-, (c) -CH_2-O-C(O)-N**H**-$COCCl_3$ (**21**), f_n = 0.64, [OH] = 2.12 μeq/g. (d) -CH_2-C(O)O-C(O)-N**H**-$COCCl_3$ (**21**), f_n = 0.64, [COOH] = 2.07 μeq/g.

6.3.5 TAI derivatisation of hydroxy-functional polymers

Hydroxy groups in model compounds (Table 6.2) and polymers (Table 6.4) were readily derivatised and the end groups quantified by ^{1}H NMR. The imidic hydrogens have chemical shifts in the range δ 8.2-8.8 depending on the specific structure.



22 **23**

Scheme 6.10

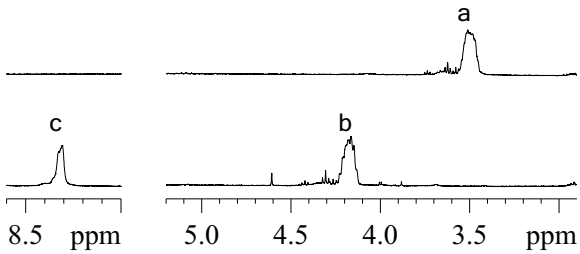
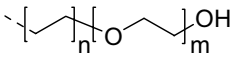


Figure 6.6. TAI derivatisation of α-ethylhydroxypolystyrene (**22**) followed by ^{1}H NMR (from top to bottom). Polymer backbone signals have been removed for clarity. (a) -S-CH_2-C**H**$_2$-OH (**22**), (b) -S-CH_2-C**H**$_2$-O-C(O)- (**23**), (c) imidic signal -CH_2-O-C(O)-N**H**-$COCCl_3$ (**23**), f_n = 0.92, [OH] = 0.86 μeq/g.

A α-hydroxyethylpolystyrene (**22**), synthesised by emulsion polymerisation of styrene with mercaptoethanol as a chain transfer agent, underwent quantitative derivatisation to show a clear end group signal in the NMR (Figure 6.6). The intensity of the signals attributed to -S-CH_2-C**H**$_2$-OH (**22**), -S-CH_2-C**H**$_2$-O-C(O)- (**23**) or -CH_2-O-C(O)-N**H**-$COCCl_3$ (**23**) were consistent with 0.92 hydroxy end-groups per molecule.



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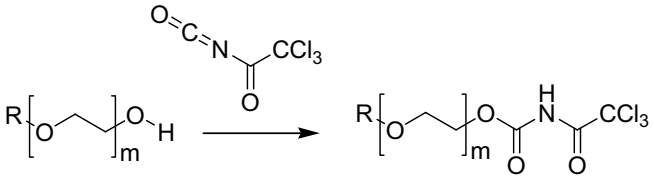
For a review on the determination of hydroxy groups in polymers see Boiko *et al.*[51] Methods for characterisation of polymers containing PEO segments (ethoxylates) have been reviewed by Zalipsky.[52] The purity and average composition of the PEO surfactants can be determined directly by ^{1}H NMR analysis. However peak resolution is such that ^{1}H NMR does not directly provide information on the homogeneity of ethoxylates. The analysis of **24a-d** was aided by derivatisation of the hydroxy end group with TAI (Refer to table 6.1, Experimental Section 6.2.7). The use ^{1}H NMR and TAI derivatisation has been previously used in end group characterisation of PEO[53] and PEO monomethyl ethers.[26] However, those studies[26,53] focused on polymers with higher molecular weight PEO segments and the sensitivity of the chemical shift of the imidic hydrogen to the PEO block length was not recognized. It has also been also reported that ^{13}C NMR can resolve signals for individual ethoxylates with $n \leq 5$.[54]

The TAI derivatisation procedure involves addition of a slight excess of TAI to the sample in $CDCl_3$ in an NMR tube. The PE-*block*-PEO are only partially soluble in $CDCl_3$ at room temperature but completely dissolve at 50 °C.



Scheme 6.11

The ^{1}H NMR chemical shift of the imidic hydrogen of TAI derivatised PE-*block*-PEO shows remarkably sensitivity to the number of PEO units (*m,* see Scheme 6.11). Thus the imidic hydrogens of R(PEO)$_m$O(CO)N**H**(CO)CCl$_3$ with m=0,1,2,3 and ≥4 are at least partially resolved in the 400 MHz NMR (Figure 6.7). There is also some sensitivity to the chemical shift of the imidic hydrogens to the length and type of alkyl chain. Chemical shifts are reported in Table 6.5.

The method was also tested in the analysis of a series of oligo(ethylene glycol) monomethyl ethers. For these examples there is less chemical shift dispersion, nonetheless, the imidic hydrogens CH$_3$(EO)$_m$O(CO)N**H**(CO)CCl$_3$ are resolved for m=1, 2, and ≥3 (Table 6.5).

The average chain lengths estimated from NMR for the PEO blocks of the various ethoxylates are consistent with specifications provided by the suppliers (Table 6.5) and the molecular weight distributions (Figure 6.7) are consistent with that expected from application of a conventional ethoxylation processes.[54]

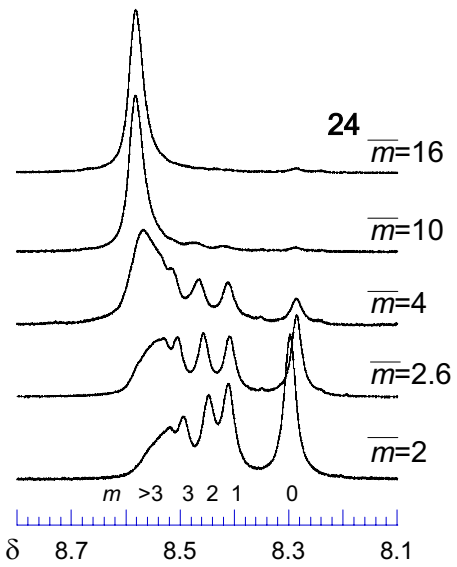


Figure 6.7. Region δ 8.1-8.8 of 400 MHz ^{1}H NMR spectra (CDCl$_3$, 50 °C) of trichloroacetyl isocyanate derivatised PE-*block*-PEO **24a-e** showing peaks attributed to the imidic hydrogens [R(EO)$_m$O(CO)N**H**(CO)CCl$_3$]. Value of average chain length ($\overline{m}$) shown is nominal value indicated by the supplier.

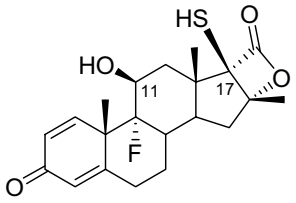
Table 6.5. ^{1}H NMR chemical shifts ($CDCl_3$, 50 °C) of imidic hydrogens in TAI derivatised $R(EO)_mH$ block copolymers.

Compound	$R(EO)_mO(CO)N\mathbf{H}(CO)CCl_3$					
	Chemical Shift (δ) 50 °C ($CDCl_3$) for m=					
	0	1	2	3	4	>4
CH_3	[a]	8.48	8.51	8.58	8.58	[a]
dodecanol	8.30	[a]	[a]	[a]	[a]	[a]
PE (**24e**)	8.30	8.41	8.45	8.49	[b]	[b]
PE (**24d**)	8.28	8.41	8.45	8,50	[b]	[b]
PE (**24c**)	8.28	8.41	8.46	8.51	[b]	8.58
PE (**24b**)	8.28	8.41	8.47	[b]	[b]	8.58
PE (**24a**)	8.28	[a]	[a]	[a]	[b]	8.58

[a] Not determined or not applicable. [b] Not sufficiently resolved (see Figure 6.7).

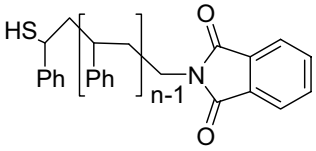
6.3.6 TAI derivatisation of sulfanyl-functional polymers

The only literature report on TAI derivatisation of a thiol relates to the compound **25**. This compound contains both a thiol and a hydroxy group. The 11β hydroxy of **25** was observed to react rapidly, however, the 17β thiol reacted only slowly taking up to 3 days for complete conversion.[55] Singlets for imidic hydrogens were observed at δ 9.02 and 9.66, but were not specifically assigned.



25

In this chapter the TAI derivatisation of several thiol model compounds were examined. These gave clear signals in the region δ 8.7 to 9.2 (Table 6.2) that can be attributed to the imidic hydrogen (-S-C(O)-**NH**-CO-CCl_3). The reactions with simple thiols were rapid (complete within 30 min) and appeared quantitative. In the case of 2-mercaptoethanol a spectrum after *ca* 10 minutes showed that while the hydroxy was completely converted, the thiol had only partly reacted. Conversion of the thiol was complete after 2 hours.



26

Application of the method to polymer samples proved more problematic. A sample of ω-sulfanylpolystyrene (**26**) which was synthesized by aminolysis of a RAFT-synthesized polymer with *n*-butylamine,[37] (Chapter 5) showed a weak signal (<10% of expected intensity) at δ 8.8 that might be attributed to an imidic hydrogen. The signal intensity did not increase after 24 hours. Some difficulties in aminolysis of RAFT-made polymers have been reported in the literature[56] as well as in Chapter 5. However, a tetrahydrofuran solution of the polymer (**26**) gave a positive test to Ellman's reagent (5,5'-Dithio-bis-[2-nitrobenzoic acid]) demonstrating the presence to thiol groups. After treatment with TAI the polymer gave a negative test with Ellman's reagent.[57] Several commercial samples of thiol-terminated PEO (precise end group structure unknown) were also examined. Again, signal intensities were substantially lower than expected on the basis of the known molecular weights. The results suggest that the thiol end-groups are subject to an as yet unidentified side reaction which prevents their quantitative conversion to the required derivative.

6.4 Conclusion

Trichloroacetyl isocyanate reacts rapidly with amine, hydroxy and carboxyl chain ends to form derivatives which can be readily determined and characterised by ^{1}H NMR spectroscopy. The experimental procedure does not require product isolation or sample purification and is conveniently carried out *in situ* in an NMR tube. The signals for the imidic (and in the case of amines amidic) hydrogens appear in a usually clear region of the NMR spectrum (δ 7.5-11) and are characteristic of the particular end-group. No additional internal standards are required. The method has been successfully applied in the characterisation of polymer end groups formed in conventional and living radical polymerisation (RAFT, ATRP, NMP) and to end functional poly(ethylene oxide).

6.5 References

1. Fallais, I.; Devaux, J.; Jérôme, R. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1618-1629.
2. Brzezinska, K.; Deming, T. J. *Macromolecules* **2001**, *34*, 4348-4354.
3. Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Polymer* **2004**, *45*, 7791-7805.
4. Räder, H. J.; Schrepp, W. *Acta. Polymer* **1998**, *49*, 272-293.
5. Bartsch, A.; Dempwolf, W.; Bothe, M.; Flakus, S.; Schmidt-Naake, G. *Macromol. Rapid. Commun.* **2003**, *24*, 614-619.
6. Nielen, M. W. F. *Mass Spec. Reviews* **1999**, *18*, 309-344.
7. Philipsen, H. J. A. *J. Chromatogr. A.* **2004**, *1037*, 329-350.
8. Jiang, X. L.; Schoenmakers, P. J.; Lou, X. W.; Lima, V.; van Dongen, J. L. J.; Brokken-Zijp, J. *J. Chromatogr. A.* **2004**, *1055*, 123-133.
9. Koenig, J. L. *Spectroscopy of Polymers,* 2nd ed.; Koenig, J. L., Elsevier Science Inc.: New York, 1999; pp 147-206.
10. Siesler, H. W. *J. Mol. Struct.* **1980**, *59*, 15-37.
11. Hummel, D.; Scholl, F. *Atlas of Polymer and Plastics Analysis: Vol. 2, Plastics, Fibres, Rubbers, Resins; Starting and Auxiliary Materials, Degradation Products. Part B/I. Text;* 2nd ed. Carl Hanser Verlag:

Munich, **1988**.

12. *NMR of Polymers*; Bovey, F. A.; Mirau, P. A., Academic Press: New York, 1996; pp 199-212.
13. Ji, S.; Hoye, T. R.; Macosko, C. W. *Macromolecules* **2005**, *38*, 4679-4686.
14. Rajan, M.; Cotiuga, I.; Ma, Y.; Picchioni, F.; Agarwal, U. S. *e-Polymers* **2003**, *046*, 1-7.
15. Johns, S. R.; Rizzardo, E.; Solomon, D. H.; Willing, R. I. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 29-32.
16. Moad, G. In *Annual Reports on NMR Spectroscopy* Academic Press: London, 1994; Vol. 29, pp 287-323.
17. Yin, Z.; Koulic, C.; Pagnoulle, C.; Jerome, R. *Macromol. Chem. Phys.* **2002**, *203*, 2021-2028.
18. Harrisson, S.; Wooley, K. L. *Polym. Prep.* **2004**, *45*, 545-546.
19. Goodlett, V. W. *Anal. Chem.* **1965**, *37*, 431-432.
20. Bose, A. K.; Srinivasan, P. R. *Tetrahedron* **1975**, *31*, 3025-3029.
21. Budešínský, M.; Samek, Z.; Tichý, M. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2784-2803.
22. Will, F. I.; Varsel, C. *Anal. Chim. Acta* **1969**, *44*, 233-234.
23. Mak, H. D.; Rogers, M. G. *Anal. Chem.* **1972**, *44*, 837-839.
24. Roos, G. H. P.; Watson, M. C. *S. Afr. Chem.* **1991**, *44*, 95.
25. Meirvenne, D. v.; Haucourt, N.; Goethals, E. J. *Polym.Bull.* **1990**, *23*, 185-190.
26. De Vos, R.; Goethals, E. J. *Polym. Bull.* **1986**, *15*, 547-549.
27. Ronda, J. C.; Serra, A.; Mantecón, A.; Cádiz, V. *Macromol. Chem. Phys.* **1994**, *195*, 3445-3457.
28. Kenwright, A. M.; Peace, S. K.; Richards, R. W.; Bunn, A. ; MacDonald, W. A. *Polymer* **1999**, *40*, 2035-2040.
29. Rajan, M.; Cotiuga, I.; Ma, Y.; Picchioni, F.; Agarwal, U. S. *e-Polymers* **2003**, *046*, 1-7.
30. Fox, B.; Moad, G.; Diepen, G. v.; Willing, I.; Cook, W. *Polymer* **1997**, *38*, 3035-3043.
31. Ma, Y.; Agarwal, U. S.; Vekemans, J. A. J. M.; Sikkema, D. J. *Polymer* **2003**, *44*, 4429-4434.

32. Spyros, A. *J. Appl. Polym. Sci.* **2002**, *83*, 1635-1642.
33. Spyros, A.; Argyropoulos, D. S.; Marchessault, R. H. *Macromolecules* **1997**, *30*, 327-329.
34. Donovan, R. A.; Moad, G. *Polymer* **2005**, *46*, 5005-5011.
35. Postma, A.; Moad, G.; Evans, R. A.; Davis, T. P.; O'Shea, M. *IUPAC - World Polymer Congress MACRO 2004, 40th International Symposium on Macromolecules* **2004**, P2.1-122.
36. Postma, A.; Moad, G.; O'Shea, M. S.; Davis, T. P. *React. Funct. Polym.* **2006**, *66*, 137-147
37. Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458-8468.
38. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379-410.
39. Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365-375.
40. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
41. Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337-377.
42. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689-3745.
43. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.
44. Li, G.; Moad, G. *27th Australasian Polymer Symposium* 2004; p P53.
45. Postma, A.; Evans, R. A.; Moad, G.; O'Shea, M. S.; Davis, T. P. *Macromolecules* **2005**, to be submitted.
46. Postma, A.; Davis, T. P.; Moad, G.; O'Shea, M. S. *Macromolecules* **2005**, *38*, 5371-5374.
47. Stefanova, R.; Rankoff, D.; Panayotova, S.; Spassov, S. L. *J. Am. Oil Chem. Soc.* **1988**, *65*, 1516-1518.
48. Motoki, S.; Saito, T.; Kagami, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 775-776.
49. Blagbrough, I. S.; Mackenzie, N. E.; Ortiz, C.; Scott, I. *Tet. Lett.* **1986**, *27*, 1251-1254.
50. Fry, A. *J. Am. Chem. Soc.* **1953**, *75*, 2686-2688.

51. Boiko, V. P.; Grishchenko, V. K. *Acta Polym.* **1985**, *36*, 459-472.
52. Zalipsky, S. *Bioconjugate Chem.* **1995**, *6*, 150-165.
53. Loccufier, J.; Van Bos, M.; Schacht, E. *Polym. Bull.* **1991**, *27*, 201-204.
54. Yang, L.; Heatley, F.; Blease, T. G.; Thompson, R. I. G. *Eur. Polym. J.* **1997**, *33*, 143-151.
55. Bain, B. M.; Phillipps, G. H.; Procopiou, P. A.; Steeples, I. P.; Upton, R. J. *J. Org. Chem.* **1998**, *63*, 7421-7424.
56. Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y. *Macromolecules* **2003**, *36*, 7446-7452.
57. Garamszegi, L.; Donzel, C.; Carrot, G.; Nguyen, T. Q.; Hilborn, J. *React. Funct. Polym.* **2003**, *55*, 179-183.

7 Polyolefin Graft Copolymers from Amino End-functionalised Polystyrene: Trials and Future Directions

7.1 Introduction

This chapter focuses on the formation of graft copolymers by interchain coupling of functional groups on polystyrene and polyolefins. Initial work was directed to the grafting of the functional monomers, maleic anhydride (MAh) and glycidyl methacrylate (GMA), onto metallocene catalysed ethylene 1-butene copolymers, linear low density polyethylene (LLDPE) and polypropylene (PP) by reactive extrusion, to form precursors for the synthesis of graft copolymers with end-functionalised polystyrenes. Primary amine polystyrene was synthesized via the RAFT technique and α-carboxy, ω-hydroxypolystyrene was synthesized by NMP as described in the previous chapters. Small scale coupling experiments were conducted in the melt and in solution with a view to assessing the system and to direct future trials. Additionally the formation of polyester-*block*-polystyrene copolymer was briefly investigated via the coupling of polyester oligomers with amine end-functional polystyrenes.

The formation of modified polyolefins (as block/graft copolymers) through chain functionalisation is particularly important and well known for the compatibilisation of polymer blends[1] and also for the adhesion between polymer interfaces.[2] Polyolefin graft copolymers are widely employed as compatibilisers for blends involving polyolefins and more polar polymers such as polyamides.[3] Polyethylene-*graft*-polystyrene (PE-*g*-PS) has also been studied as an effective compatibiliser for polyolefin/PS blends.[4]

Polyolefins themselves are widely used in a wide range of applications as they provide an excellent combination of mechanical and chemical properties as well

as processability. However, deficiencies such as a lack of functional reactive groups in the polymer structure have limited its end uses, in particular those in which adhesion and compatibility with other polymers is paramount. This disadvantage can be overcome by the formation of a modified polyolefin, by introducing suitable functional groups into the polyolefins.[4]

Interchain polymer reactions between mono-end-functional polymers and a modified polyolefin results in the formation of a new graft copolymer.[5] To date the major limitation to the exploitation of interchain polymer reactions of modified polyolefins has been the availability of suitable end-functional polymers. Commercially available end-functional polymers, largely used and applied in these areas, have included various condensation polymers, which, by their nature, have reactive end-groups. These have included nylons, polyesters, polycarbonates, polyethers as well as liquid crystalline polymers. For commercial samples of these polymers, end-group functionality is usually not specified and they often exist as variants that are mono/di-end capped with reactive and/or non reactive functionality. Studies of their interchain copolymer formation with modified polyolefin substrates have been reported but, as explained above, have mainly aimed at improving the properties of the polyolefin blends by in situ formation of a graft copolymer compatibiliser, rather than a graft copolymer as a product in its own right.[5,6] Whilst one does not discount the potential and value of these enormous studies, it is interesting to note that relatively little work has been carried out with other end-functional polymers or in a scope that extends beyond the context of compatibilisation.

The controlled synthesis of amino functional polystyrene as a reactive interchain coupling agent lends itself well for the production of high value added grafted polyolefins. One of the most commonly reported methods for the synthesis of end-functional polymers for use in this context is anionic polymerisation.[7,8] A patent issued to Himont[8] discloses the formation of graft copolymers by the reaction of end-functional polymers prepared by anionic polymerisation (including PS-NH_2, $\overline{M}_n$=60000 g mol^{-1}) with maleic anhydride-modified polyolefins (*e.g.* MAh-PP, MAh-PE). The process, done either in solution or by

extrusion of a mixture of the two components in a single screw extruder, was reported to give a high yield of copolymer.

Many of the important studies and aspects relating to polyolefin graft copolymers have already been discussed in Section 2.4, with a focus on the production of the graft with a 'grafting onto" approach, through interchain coupling onto the modified polyolefin backbone. Studies on the reactivities of terminal polymer functionalities were described and have focused this work on the amine/anhydride as well as the acid/epoxy systems.

The development of new and cheaper methods for producing controlled chain end-functional polymers (RAFT, ATRP) have prompted us to investigate the potential for using a α-aminomethylpolystyrene **5**, successfully synthesized by the RAFT technique, for graft copolymer formation by interchain reaction with a series of modified polyolefins. These modified polyolefins included a series of MAh-*g*-polyolefins and GMA-*g*-polyolefins produced in house via reactive extrusion. As an extension to the study, a sample of commercially available acid-terminal polyester was also examined.

The main focus of the investigation was to carry out interchain coupling trials with a view to directing future experiments.

7.2 Experimental

7.2.1 General

All chemicals and monomers were purchased from Aldrich unless stated otherwise, solvents 2-butanone (MEK) and xylene were of AR grade. Styrene (S) and glycidyl methacrylate (GMA) were purified by filtration through neutral alumina (70–230 mesh), to remove inhibitors immediately prior to use. Maleic anhydride (MAh) was obtained from Nippon Oils and Fats and used as received. Initiators *p*-methylbenzoyl peroxide (PMBP) and dibenzoyl peroxide (BPO) were obtained from Degussa; 2,5-bis(t-butylperoxy)-2,5-dimethylhexane (DHBP) was obtained from Akzo Nobel. Nitroxides, TEMPO and 4 hydroxy TEMPO (4 HO-

TEMPO) were obtained from Ciba Specialty Chemicals. ^{1}H NMR spectra were obtained with a Bruker Advance DRX500, Bruker Av400 or a Bruker AC200 spectrometer on samples dissolved in deuterochloroform, processed with XWin-NMR 3.5 or Mestre 2.3. Chemical shifts are reported in ppm from TMS. Gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump and Waters 717 Plus Autosampler equipped with Waters 2414 refractive index detector and 3×Mixed C and 1×mixed E PLgel column (each 7.5 mm×30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22±2 °C. GPC with UV detection was performed on a Waters 2695 Separations Module equipped with Waters 2414 refractive index detector and Waters 2996 photodiode array detector and 3×Mixed C and 1×mixed E PLgel column (each 7.5 mm×30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 30±2 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) ranging from 600 to 7.5 × 10^{6} g mol^{-1}. A third order polynomial was used to fit the $\log_{10}$M *vs* time calibration curve, which appeared to be linear across the molecular weight range 2×10^{2}–2×10^{6}.

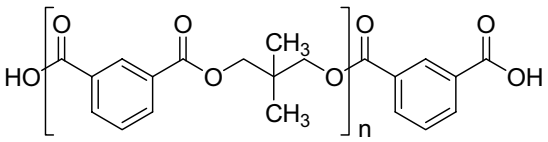
Differential scanning calorimetry (DSC) was carried out with a Mettler Toledo DSC 821 equipped with a TSO801RO sample robot under nitrogen. Samples were prepared in either 40 or 100 μL aluminium sample pans, crimp sealed and pierced.

High temperature solution experiments were conducted in a Mettler Toledo MultiMax™ 4×50 mL reactor with heat controlled temperature ramping to 180 °C fitted with argon purging, reflux condenser and a temperature sensor. The solutions were stirred with an overhead mechanical stirrer operating at 800-1000 rpm.

7.2.2 Polymers

Several polyolefins were used in this study, a conventional LLDPE (ethylene-*co*-1-hexene copolymer) designated Alkatuff AT820 manufactured by ICI Australia

(melt flow index (MFI) 20 g/10min, density 0.925 g/cm^3), conventional PP designated MOPLEN HP400N manufactured by Basel Polyolefins (MFI 11 g/10min, density 0.905 g/cm^3), three metallocene LLDPE (ethylene-*co*-1-butene copolymers) manufactured by Exxon Chemical; Exact 5008 (MFI 10 g/10 min, density 0.865 g/cm^3), Exact 4023 (MFI 30 g/10 min, density 0.882 g/cm^3) and Exact 4006 (MFI 10 g/10 min, density 0.880 g/cm^3). Ethylene-*co*-glycidyl methacrylate (E-*co*-GMA copolymer) designated Lotader® AX8840 manufactured by Atofina Chemicals (8 wt% GMA, MFI 5 g/10min) was used as a GMA internal standard. Information was obtained from material data sheets. MFI for LLDPE and metallocenes were measured at 190 °C; 2.16 kg, for PP at 230 °C; 2.16 kg according to ASTM D1238.



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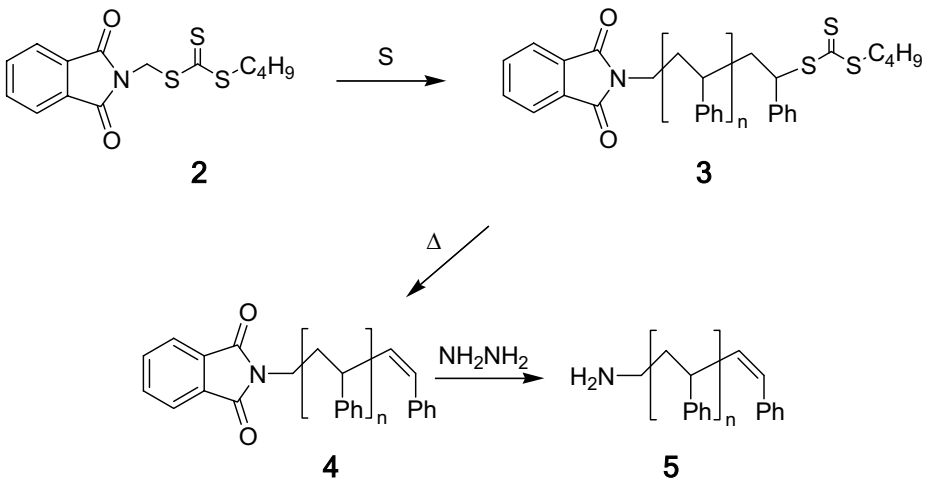
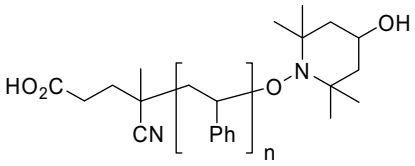
Polyester/oligoester neopentylglycol-isophthalic acid (NPG-IPA) (**1**) diacid end capped designated Crylcoat 2988, obtained from UCB ($\overline{M}_n^{NMR}$ =3800 g mol^{-1}, $\overline{M}_n$ =3300 g mol^{-1} (polystyrene equivalents), acid value 30 mg KOH g^{-1}, from data sheet). Acid end-group values were also obtained by NMR derivatisation techniques confirming diacid functionality.[9]

Primary amine end-functional polystyrene (**5**) was synthesized via RAFT polymerisation (Scheme 7.1) as described in Chapter 4, section 4.2.9.



Scheme 7.1. Synthesis of α-aminomethylpolystyrene by RAFT

The α-carboxy, ω-hydroxypolystyrene (**6**) was obtained by nitroxide mediated polymerisation as described in Chapter 6, section 6.2.5.



6

7.2.3 Reactive extrusion

Polyolefin grafting experiments to produce chain functional feedstocks (*i.e.* reactive modified polyolefins) were performed on a Japan Steel Works (JSW TEX 30) twin-screw extruder with a 30 mm screw diameter and an overall length to diameter (L/D) of 42 (comprising ten temperature controlled barrel sections of L/D3.5, three unheated sampling monitoring blocks of L/D 1.167 and a cooled feed block of L/D 3.5, Figure 7.1). The extruder screw was operated in co-rotation (intermeshing self wiping) modes with throughputs of between 5 and 10 kg/h. The screw design consisted of conveying, reversing and kneading elements, as shown in Figure 7.1. The screw speed was set at 155 rpm (40% of motor output). The residence time, determined as the peak intensity of a coloured marker, was measured at 5 minutes for a throughput rate of 5 kg/h and

2 minutes for 10 kg/h. The barrel temperature profile, used for the metallocene polyolefins, is shown in Figure 7.1. The melt temperatures and pressures were monitored at three points along the barrel (SP1-3) as well as in the die (not shown). Polyolefins were fed into the extruder via a JSW TTF20 gravimetric feeder. The monomer/initiator solutions were fed into the extruder through a liquid injector port at barrel section cylinder 4 (C4) using a volumetric liquid addition pump (Fuji Techno Industries model HYM-03-08), volatiles were vented from the vacuum port at C10 (0.06 MPa) see Figure 7.1, vacuum was applied using a vacuum pump.

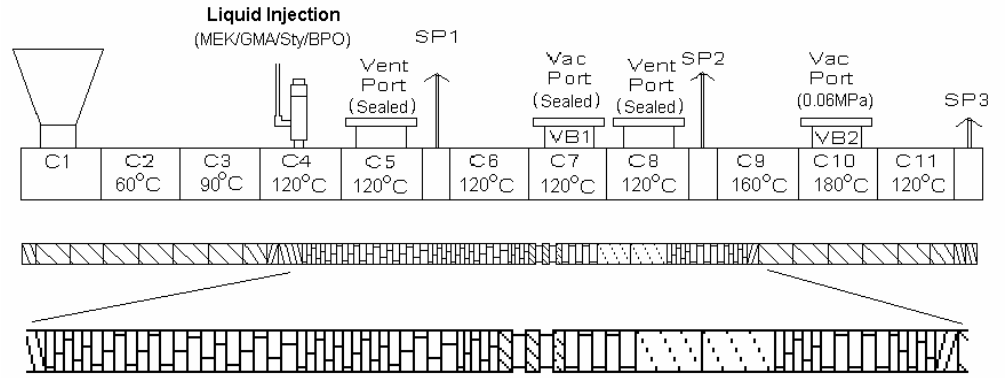


Figure 7.1. Screw and barrel profile of the JSW Tex 30 twin-screw extruder employed in melt grafting of polyolefins. Inset shows expansion of the grafting zone of the screw from C4-C9.

The extrudate was cooled in a water bath and dried over a stream of air prior to pelletisation. A selection of extrudate samples were taken and dissolved in hot xylene and precipitated into acetone (to remove any residual monomers or oligomers) prior to further analysis. Mass loss on precipitation (*i.e.* polymer fractionation) was monitored.

7.2.4 Fourier transform infrared (FTIR) analysis of GMA grafting levels

This procedure was based on an adapted method by Bray *et al.*[10] FTIR was measured on a BOMEM MB Series Instrument, 4 cm^{-1} resolution 16 scans. For FTIR analysis, a mixture comprising the base polymer (Exact 5008) and a

measured amount of the internal standard (AX8840) were co-dissolved in hot xylene and precipitated into acetone, filtered and dried in the vacuum oven for 16 hrs with minimal loss of polymer. Samples were melt pressed into *ca* 50 μm films and analysed by FTIR.

$$\%(\text{GMA}) = c + m\left(\frac{A_{C=O}}{A_{CH_2}}\right)$$

Where A_λ is the absorbance at λ cm^{-1} measured above a baseline drawn from the valleys either side of the methacrylate carbonyl (1734 cm^{-1}) absorption and the CH_2 polyolefin absorption band; metallocene and LLDPE (1379 cm^{-1}), PP (2721 cm^{-1}). The value for the intercept *c*, the gradient *m* and the correlation coefficient *r* are found in Table 7.1.

Table 7.1. Values for FTIR calibration of melt pressed films.

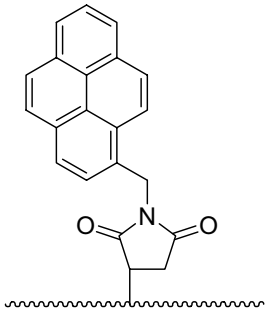
Polyolefin	m	c	r^2
5008	2.497	0.109	0.999
4023	1.951	0.053	0.999
4006	1.973	0.089	0.995
AT820	0.828	0.029	0.998
HP400N	0.644	0.103	0.993

GMA grafting levels were determined on samples dissolved in hot xylene and precipitated into acetone, filtered and dried in the vacuum oven for 16 hrs with minimal loss of polymer. FTIR was performed on *ca* 50 μm melt pressed film samples, applying the appropriate calibration relationship.

MAh grafting levels could not be pursued using this method due to the unavailability of a suitable polyolefin-*g*-MAh internal standard necessary for this technique. 2-Dodecen-1-yl succinic anhydride as an internal standard was also trialled, however, it was found to separate out under melt pressed conditions.

7.2.5 UV-Vis analysis of MAh grafting levels

UV-Vis absorption measurements were based on a pyrene labelling procedure by Zhang and Duhamel.[11] Absorption spectra were measured on a Shimadzu UV-3101PC scanning spectrophotometer. The pyrene (Py) extinction coefficient of a pyrene model compound, 1-pyrenemethylamine (PMA), was estimated from the absorption value at 344 nm over a range of [Py] in THF, found to be ε^{334} = 32466 cm^{-1} M^{-1}. The Py content, λ, of the polymer could be calculated from $\lambda = \frac{[Py]V}{m}$, where m is the carefully weighed out amount of Py labelled polymer in a known volume, *V*.



Scheme 7.2. 1-pyrenemethylamine (PMA) labelled maleated polyolefin.

Pyrene labelling was carried out in a Mettler Toledo MultiMax™ parallel reactor by following the previously described procedure.[11] Maleated Exact 5008 (0.11 g, assumed ~5wt% MAh) was introduced in the 50 mL reactor vessel to which 15 mL anhydrous dodecane was added under argon before it was heated to 130 °C for 6 h with stirring, allowing all grafted succinic acid groups to be reverted to their cyclised form. Next, an excess of a PMA solution, 10 ml in hexane (7.91×10^{-3} M), was added. The hexane was removed and the reaction temperature increased to 180 °C and maintained for 16 hrs under argon with vigorous stirring. The reaction was then quenched by precipitation into 100 mL acetone. The polymer was further precipitated from 5-10 mL hot hexane into 100 mL acetone to ensure removal of unreacted PMA. The polymer, as shown in

Scheme 7.2, was filtered and dried in a vacuum oven for 16 hrs prior to UV-Vis analysis.

Py labelled polymer (5 mg) was dissolved in 100 mL THF and measured on Shimadzu UV-3101PC scanning spectrophotometer.

7.2.6 Solution coupling

Solution coupling was performed in a Mettler Toledo MultiMax™. The maleated Exact 5008 sample (0.10 g, 1.59 wt% MAh) was introduced in the 50 mL reactor vessel to which 15 mL of anhydrous dodecane was added under argon before it was heated at 130 °C for 6 h with stirring, to ensure all grafted succinic acid groups are reverted to their cyclized form. Next, α-aminomethylpolystyrene (**5**) (0.08 g, $\overline{M}_n$ =4900 g mol^{-1}, 0.9 molar equivalence per MAh functional group) dissolved in 1.5 ml THF, was added. The THF was then removed and the reaction temperature increased to 180 °C and maintained for 16 hrs under argon with vigorous stirring. The solvent was removed, the contents re-dissolved in THF and precipitated into 100 mL of methanol. The polymer was filtered and dried in a vacuum oven for 16 hrs prior to analysis.

7.2.7 Melt coupling (non-mixing)

The maleated Exact 5008 sample (0.055 g, 1.2 wt%) and α-aminomethylpolystyrene (**5**) (0.03 g, $\overline{M}_n$ =4900 g mol^{-1}, ~0.9 molar equivalents per MAh functional group) were co-dissolved in 2 ml anhydrous chloroform and rotary evaporated down to an intimately mixed polymer blend. 10 mg of the polymer blend was transferred to a 100 μL aluminium DSC sample pan, crimp sealed and pierced. The sample was heated isothermally at 270 °C for 3 hrs. The resulting polymer was analysed by ^{1}H NMR and GPC with UV detection.

A similar procedure was used for GMA functionalised Exact 5008:

The GMA functionalised Exact 5008 sample (0.050 g, 0.28 wt%) and α-carboxy, ω-hydroxypolystyrene (**6**) (0.012 g, $\overline{M}_n$ =2824 g mol^{-1}) were co-dissolved in 2 ml anhydrous chloroform and rotary evaporated down to an intimately mixed polymer blend. 10 mg of the polymer blend was transferred to a 100 μL aluminium DSC sample pan, crimp sealed and pierced. The sample was heated isothermally at 180 °C for 3 hrs. The resulting polymer was analysed by ^{1}H NMR and GPC with UV detection.

7.3 Results and discussion

7.3.1 Modified polyolefins

The widespread method of introducing functionality into polyolefin substrates by reactive extrusion, involving free-radical induced grafting, was used to prepare a series of modified polyolefins. Many of the issues related to the synthesis of such polyolefin graft copolymers have already been discussed in Chapter 2. Free radical grafting of functional monomers onto the backbone of polyolefins can be considered the simplest and by far the most frequently studied method for preparing modified polyolefin graft copolymers, however, there are a large number of inter-dependant factors that need to be optimized in order to maximize grafting yields, to minimize side reactions and therefore to control the nature of the modified polymer.

The quest to define the conditions necessary for a robust process that provides high grafting efficiencies and minimal degradation or cross linking is rendered challenging by difficulties often encountered in trying to replicate and evaluate process conditions. Problems exist in comparing melt-phase processes carried out in different reactors as the exact process conditions can vary enormously even though quoted operating parameters appear notionally the same. Apparently contradictory results may in fact simply reflect subtle differences in mixing efficiency or parameters such as temperature or pressure. As such, production of a modified polyolefin substrate can be a lengthy and involved study in itself.

Our interest in grafting reactions which yield reactive functionality to yield modified polyolefins was in generating precursor materials which may subsequently be elaborated into block or graft copolymers by interchain coupling with controlled amino-functional polystyrene. Studies into further optimizing the REX modification processes are restricted to future experiments. The conditions used in this study were based on previous experiments carried out by Bray *et al.*[10] and can largely be seen as a continuation of their work. Our attention was in the production of maleated polyolefins and to a lesser extent, the production of GMA-modified polyolefins, which were largely aimed for future work on this project.

Extensive tables containing the general details, conditions and various results of widespread reaction extrusion experiments carried out in order to synthesize modified polyolefins are contained in Appendix 1. These supplementary set of details for the extruded samples are presented to serve as a basis for future and ongoing experiments and associated coupling trials, and as mentioned previously, their elaboration are essentially beyond the scope of this chapter.

7.3.2 Quantitation and characterisation experiments

The characterisation of grafted functionality on polyolefins is rendered difficult due to several aspects. The grafting levels of the functionalities tend to be small (typically 0.2–2 wt %) corresponding to one to ten grafts per typical polymer chain molecular weight ($\overline{M}_n$=40000–70000 g mol^{-1}), making analysis by NMR troublesome. The low solubilities of most polyolefins, especially conventional PE and PP in any solvent at room temperature and only a limited range of solvents at elevated temperatures, requires that special conditions need to be used in order to analyse these polymers with GPC. Usually this is performed with 1,2,4-trichlorobenzene at 130–140 °C as the mobile phase of a GPC.

However, certain metallocene polyolefins show enhanced solubility, particularly metallocenes with high branching levels and low densities (higher comonomer content). Of the three metallocenes used in this study, Exact 5008 (14.2%

branching) is soluble in THF and chloroform at room temperature, Exact 4023 (9.6% branching) and 4006 (9.5% branching) are soluble at 40 °C in THF and chloroform. Butene branching levels were obtained by ^{1}H and ^{13}C NMR analysis of these polymers via NMR techniques as previously documented in the literature.[12,13] Along with the enhanced solubilities of metallocenes, their polymer architecture is more homogeneous than that of the commercially available polyolefins, with polydispersities usually around ~2 as compared to 4–6 for LLDPE and PP. This permits the use of a range of characterisation techniques into the synthesis of graft copolymers and allows the production of well-defined graft copolymers to be formed. A complication and consideration, however, in choosing to use metallocenes is that low melt viscosities (a consequence of narrow polydispersity) makes the metallocenes more difficult to process.

Exact 5008, polyolefin due to it's homogenous nature, lower polydispersities and enhanced solubility, comprises a useful model system for analysing the interchain coupling reactions and therefore it's MAh-grafted analogues were pursued for our preliminary coupling trials, with a view of introducing some of the more complex issues involved in interchain coupling (such as interfacial aspects). They also allowed the exploitation of UV-Vis absorption measurements based on a pyrene labelling procedure by Zhang and Duhame,l[11] to effectively quantitate the level of maleic anhydride on the polyolefin. Furthermore, due to the broad processing conditions that necessarily come into play with reactive extrusion and which eventually require a lot of attention in themselves, we believed that this was a valuable starting point before undertaking larger scale extrusion trials

7.3.3 UV calibration

RI and UV GPC traces of the pyrene labelled polyolefin samples in Figure 7.2 look essentially the same, allowing us to assume that the full range of polymer chains, from low to high molecular weight, carry MAh functionalities. One exception is entry 7 (Figure 7.2), which shows a small but significant shift to

higher molecular weight in the UV trace. It must be noted that molecular weight represented by the UV intensity trace is proportional to $\overline{M}_n$ (*vs.* $\overline{M}_n{}^2$ for RI detection), thus a small shift to high molecular weight can be considered significant. This would indicate that the high molecular weight chains would have a significantly larger proportion of the grafted MAh for this particular sample. This warrants attention for results obtained in future trials using these particular samples.

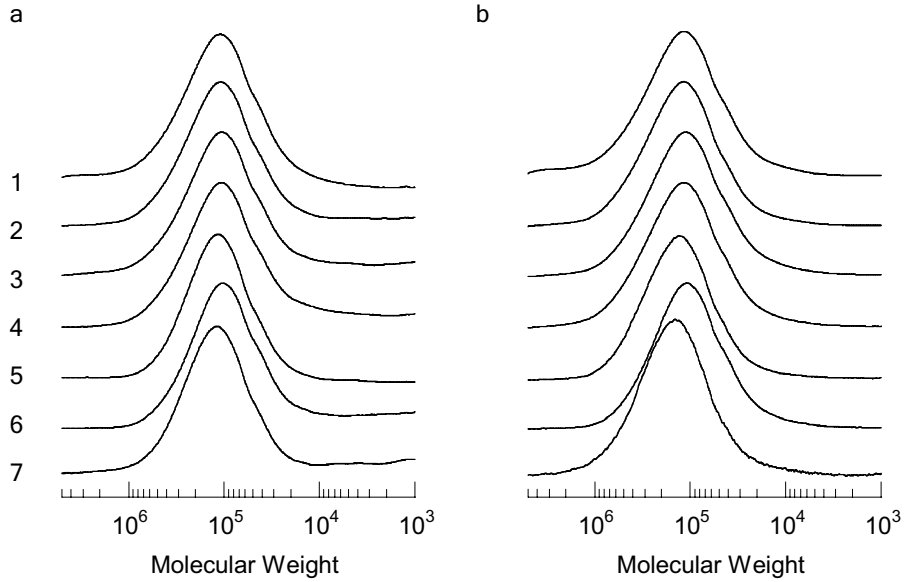


Figure 7.2. Normalised GPC traces of pyrene labelled Exact 5008-*graft*-MAh: (a) RI trace, (b) corresponding UV trace at 344 nm: (1) 2.18 wt%, (2) 1.68 wt%, (3) 1.59 wt%, (4) 1.18 wt%, (5) 0.88 wt%, (6) 0.74 wt%, (7) 0.63 wt%.

A small amount of oligomer and unbound PMA, remaining after the two precipitations, were also observed in the UV GPC trace (not shown). Integration of these peaks to the polymer peak showed them to contribute between 0.5-2.5% to the final MAh wt% value tabulated in Table 7.2. Exceptions are entries 5 (6 %) and 7 (9%), found in Table 7.2 and Figure 7.2.

Polyolefin-*g*-MAh samples show no absorption at 344 nm.

Table 7.2. MAh and GMA monomer grafting onto Exact 5008 (ethylene 1-butene) copolymer under reactive extrusion conditions.

Entry	Grafted Monomer	$\overline{M}_n$ (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	Graft level (wt%)[a]	Average graft/chain
1	MAh	68300	2.63	2.18	15.5
2	MAh	71300	2.64	1.68	12.4
3	MAh	66600	2.80	1.59	11.0
4	MAh	72500	2.55	1.18	8.8
5	MAh	70800	2.17	0.88	6.4
6	MAh	62800	2.27	0.74	4.8
7	MAh	75400	2.16	0.63	4.9
8	GMA	65500	1.83	0.28	1.3

[a] Weight percent MAh grafting levels determined UV analysis, GMA grafting levels determined by FTIR.

Table 7.2 represents the results obtained for the level of grafting for the modified polyolefins. These samples were chosen for subsequent coupling trials with amino-functionalised polystyrene (**5**) and an acid/hydroxyl-functionalised polystyrene (**6**). For further results of all other modified polyolefins as well as the reactive extrusion conditions used for all their production, refer to Appendix 1, Tables A1-A4

It is noteworthy to mention that a whole range of average number of MAh grafts per polyolefin chain were able to be synthesized for Exact 5008 and, moreover, without a concurrent change to molecular weight, although a broadening of polydispersity was observed for the higher graft samples. This may indicate some cross-linking from the grafting process (due to higher initiator levels

required to achieve higher MAh grafting), also supported by the lower solubility observed for the higher grafted samples in chloroform and THF. There may also be an inherent effect of polar grafted maleic anhydride groups on the GPC column.

7.3.4 Polyolefin coupling trials

There is no doubt that in attempting the interchain coupling between polymer-bound functional groups of different and largely immiscible polymers there are challenging issues that come into play. For example, issues of diffusion and reaction in an interface between the two immiscible polymers. Studies into this have attracted attention and many have focused on detailed kinetic estimations.[2,7,14] Certainly, in such studies, the use of narrow molecular weight distribution end-functional polymers, like **5**, could be useful, especially when considering the increased ease of preparation and also when model studies need to be scaled up and tested on a practical level. As mentioned earlier, most studies have used anionic polymerisation techniques in order to afford the end-functionalised reactants.

For the present study two systems were investigated: the solution mixing coupling and non-mixing melt coupling (refer to sections 7.2.6 and 7.2.7 respectively for experimental details; molar ratio of reactant species was kept constant). Product analysis was carried out using GPC equipped with a UV detector. The reactive system can be thought of as comprising three polymers: Polystyrene (**5** or **6**), polyolefin-*g*-polystyrene and modified polyolefin (in the most part maleated 5008). Of the three, the first two contain styrenic moieties and can be detected at 254 nm, the polyolefin being transparent at this wavelength won't be visible in the GPC trace. The conversion of the reaction can therefore be monitored since growth of the polymer which is detected and seen as a new higher molecular weight peak (even though not always well separated) will not be due to the starting polyolefin. This analytical method was used to monitor the success of the coupling trials and the results are represented in Figure 7.5–Figure 7.4.

Polymer reactions in the melt and in the absence of solvent, whilst being advantageous in terms of economic and environmental impact, raise several complications caused by the high viscosity of the polymer melts, heterogeneity of the reacting media, the slow diffusion of reactants, low polarity as well as more. This inherently renders difficult a proper control over selectivity over rate as well as yield.[7] Certainly the implicit nature of the reactant polymers, for example, the molecular weight of reactants; the level of functionality and the arrangement of functionality along the grafted polyolefin backbone, will greatly influence the outcome of the coupling. For heterogeneous polymer-polymer systems the mutual diffusion rates can be slow and when the two polymers are limited by immiscibility the reaction can be envisaged as being slow and challenging. When two immiscible polymers react, the reaction occurs mostly at the interfaces. It can be shown that in these cases interfacial mixing and diffusion often govern the overall reaction rates.

The rates of reactions between polymer bound functional groups can also be slowed by what is termed the excluded volume effect of the polymer backbone adjacent to the reactive functionality. In order to understand the characteristics and kinetics of interfacial coupling without any external flow, reactions at flat static interfaces have been investigated. It has been suggested that external flow in the mixer during polymer blending process accelerated the interfacial coupling rate from that of the static flat interface. It was found that in contrast to the case of static interface, the coupling in a heterogeneous polymer blend could be increased dramatically, by as much as 1000 times higher.[14]

Previous studies by Hu and Lambla[7] have suggested that the formation of polyolefin-*g*-PS at the interface , whilst being considered to be a very effective means to improve and stabilize the blend (*i.e.*, compatibilise), also tends to reduce the overall rate of reaction since this occupation at the interface reduces contact between reacting moieties, thus decreasing the overall reactivities (interfacial screen effect). The presence of graft copolymer at the interfaces can be effective at reducing interfacial tension and increasing the miscibility of the reaction mixture however this may only be fully advantageous when mixing is involved.

For the present study, it was envisaged that for the non-mixing melt coupling trials, the overall conversion, which would undoubtedly be limited by a lack of mixing, may be enhanced by the high temperatures used (200 °C and 270 °C). These could potentially increase the compatibilisation of the heterogeneous mixture. Furthermore the samples were prepared in a manner as to optimize the initial mixing of the reactant polymers. The samples were intimately mixed in solution and then the solvent was removed prior to carrying out the non-mixed melt reaction. This however, has the mitigating possibility of formation of phase structures on solvent removal (casting) which could preclude good interfacial coupling. Referring to the coupling results represented in Figure 7.3, for the samples studied, the highest conversion was achieved after 3 hours at the higher temperature. The proportion of unreacted polystyrene was relatively small compared to the formation of the high molecular weight graft copolymer. This is what we had expected in terms of the effect of temperature and the higher concentration of reactive functionalities (compared to solution mixing). However, the results were more promising than what was expected in terms of potential interfacial screening effects.

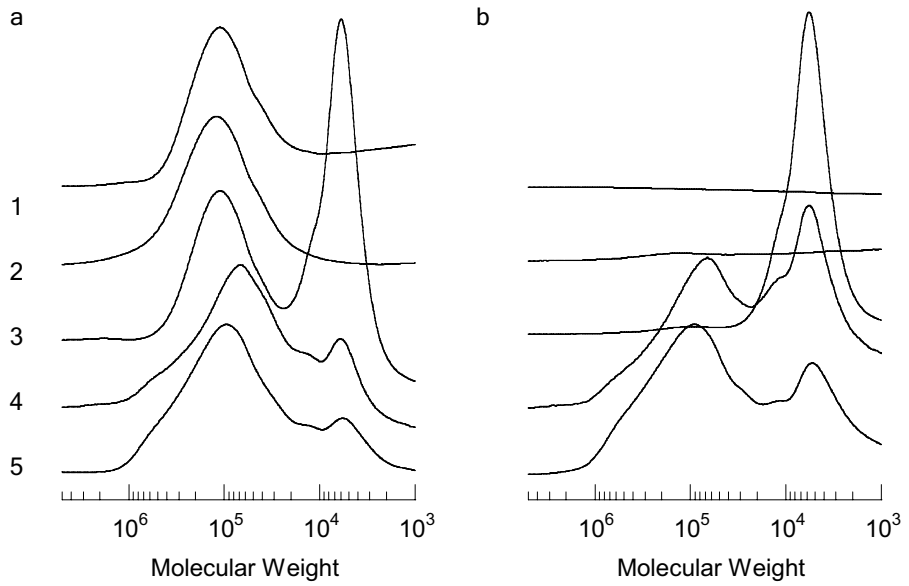


Figure 7.3. Normalised GPC traces of melt coupling: (a) RI trace, (b) corresponding UV trace at 254 nm. (1) Exact 5008, (2) 1.18 wt% MAh, (3) initial mixture of 5008-*graft*-MAh and polystyrene (**5**, $\overline{M}_n$ =4900 g mol^{-1}), (4) after 3h at 200 °C, (5) after 3h at 270 °C. (Note that polystyrene absorbs at 254 nm and that polyolefins are transparent in this region, thus only polystyrene and polyolefins-*graft*-polystyrene chains are observed)

In the case of the non-mixing melt coupling of the GMA functionalised polyolefin (Figure 7.4) with polystyrene **6** it is obvious that no reaction has taken place. (The small signal in the before and after UV trace was due to the grafted GMA). This indicates that for this reactive system (epoxy ring opening with the acid) more forcing conditions may be required (*i.e.* higher temperatures, mixing, catalyst). It is also assumed that the 4-hydroxy TEMPO end-group has cleaved off under the high temperature conditions of the reaction.[15] As mentioned previously, this system will largely be the scope of future experiments in this area.

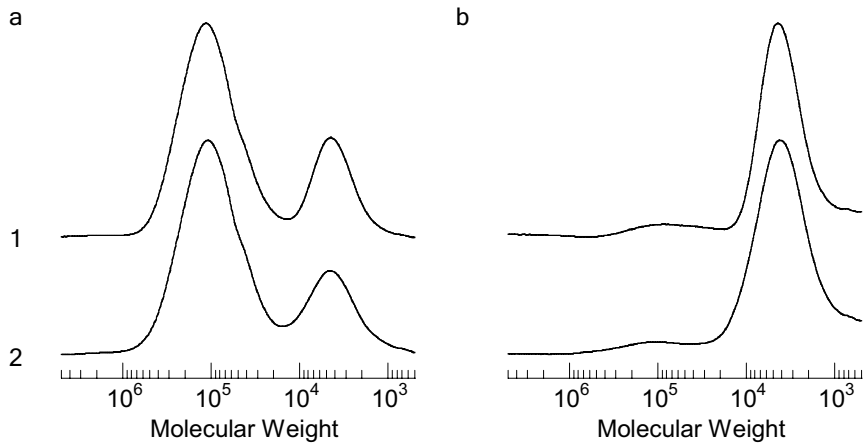


Figure 7.4. Normalised GPC traces of melt coupling: (a) RI trace, (b) corresponding UV trace at 254 nm. (1) initial mixture of 5008-*graft*-GMA (0.28 wt % GMA) and polystyrene (**6**, $\overline{M}_n$ =2824 g mol^{-1}), (2) after 3h at 180 °C.

Mechanical mixing is expected to generate and renew the interfacial area and to reduce the size of the dispersed phase, thus increasing the interfacial contact between the two reactive polymer phases. All these factors favour the overall reaction rate and are envisaged as helping to increase the contact between the reactive groups and also to remove and minimise the interfacial screen effect present at the interface.

Furthermore it has been reported that the presence of solvents can also enhance diffusion parameters. The choice of solvents can be rendered difficult due to the requirement of high boiling point, stability to the reaction conditions and the compatibility with the polymers and the reactive functionalities. In addition to enhancing of miscibility, interfacial mixing and diffusion, the addition of an optimum solvent, may also increase the direct contact of the reactive moieties.

For the present study the solution coupling was carried out in a small scale reactor which allowed for intense mixing and imparted fine control over the temperature (including control of high temperature ramping). The solvent used was dodecane, a non-polar, high boiling point solvent. For all of the trials conducted (1-7) it is evident in both the RI and the UV traces (Figure 7.5) that there is still a significant amount of unreacted polystyrene. Both the RI and UV

trace show a proportionately large polystyrene peak. All the UV traces do, however, show the formation of a higher molecular weight peak corresponding to the graft copolymer and the case is most pronounced for samples 1-3 (Figure 7.5) which had the highest amount of MAh grafted. The conversions of interchain coupling could be improved in future experiments by optimizing several factors: less dilution of reactive groups by using less solvent, more appropriate solvent selection. Furthermore, it would be interesting to conduct the experiments using a mixing reactor that could allow for higher temperatures, with intimate mixing and with less than 10% solvent.[7]

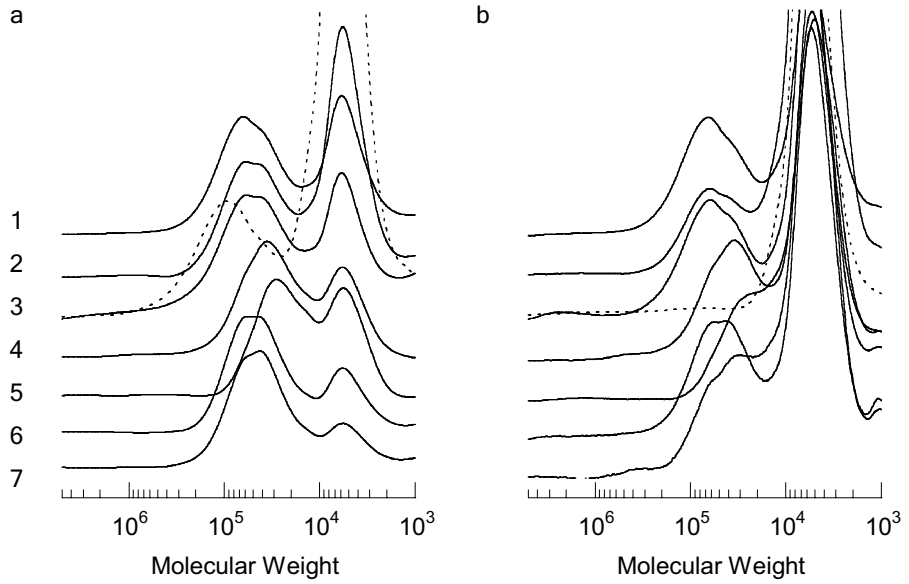


Figure 7.5. Normalised GPC traces of solution coupling: (a) RI trace, (b) corresponding UV trace at 254 nm. Polystyrene **5** ($\overline{M}_n$=4900 g mol^{-1}) with Exact 5008 (1) 2.18 wt%, (2) 1.68 wt%, (3) 1.59 wt%, (4) 1.18 wt%, (5) 0.88 wt%, (6) 0.74 wt%, (7) 0.63 wt%, (----) initial unreacted mixture for trace (3).

7.3.5 Polyester (NPG-IPA)-*block*-styrene

Polyester (NPG-IPA, **1**) labelling with 1-pyrenemethylamine was performed in solution under the same conditions as described in section 7.2.5. An equimolar amount of the amine end-group, on polystyrene **5**, to acid end-group on **1** was

used. The reaction proceed successfully, with an increase in molecular weight observed in the RI GPC trace (Figure 7.6a) and pyrene labelling evident in the UV trace at 344 nm (Figure 7.6b).

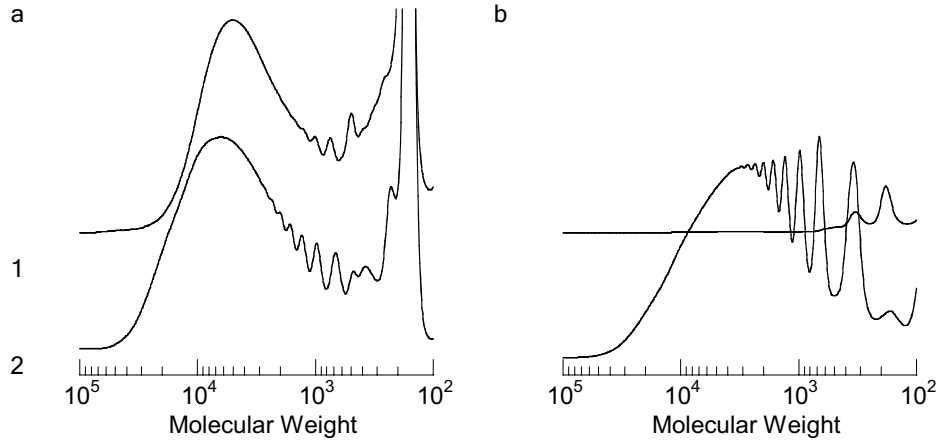
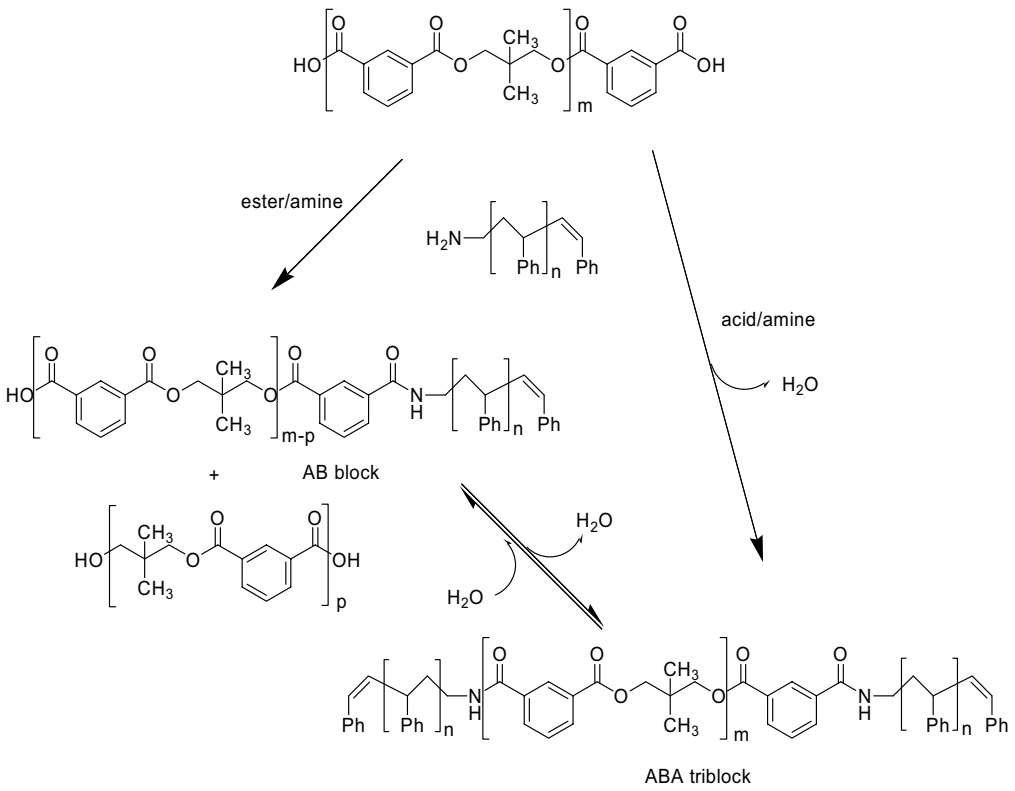


Figure 7.6. Normalised GPC traces of pyrene labelled polyester **1**: (a) RI trace, (b) corresponding UV trace at 344 nm. (1) **1** prior to labelling, (2) pyrene labelled **1**.

In the case of interchain coupling of a diacid capped polyester Crylcoat 2988 (**1**) with α-aminomethylpolystyrene (**5**, $\overline{M}_n$=4900 g mol^{-1}), the reaction can be envisaged as occurring according to Scheme 7.3. One of the possibilities is the formation of an AB block, through the reaction of the amine with the internal ester functionality, approximately doubling the molecular weight. This depends on the size of the cleaved oligomer. The reaction of the amine with the ester should be relatively fast. The other possibility is the formation of an ABA triblock through the reaction of the terminal acids with the amine, this reaction would initially form the ammonium salt and at elevated temperatures (250-270 °C) condense to form the amide linkage, tripling the molecular weight. Transesterification reactions occur with polyesters and could allow for the interchange of AB and ABA block copolymer structures. Although it has been found that neopentylglycol units reduce the amount of transesterification through steric hindrance of the methyl groups adjacent to the ester linkages.[16]



Scheme 7.3. Proposed structures formed in the melt reaction of oligoester **1** and polystyrene **5**.

Some overlap of absorption maxima of polystyrene and the polyester occurs (Figure 7.7) and makes the full resolution of the initial polymer components difficult. However the block copolymer formed in the melt reaction of polyester **1** with α-aminomethylpolystyrene **5** is still able to be distinguished to some degree in both the UV and RI traces. The reaction is assumed to be largely complete after 40 minutes at 270 °C. Furthermore, it is evident that there is essentially a doubling of molecular weight which would indicate the formation of an AB block copolymer.

These results are interesting from the point of view that there is no apparent published work in the area of polystyrene-*graft*-polyester copolymer synthesis via reactive melt blending. This has prompted us to further investigate this area, especially in terms of discovering the potential of new properties and new materials.

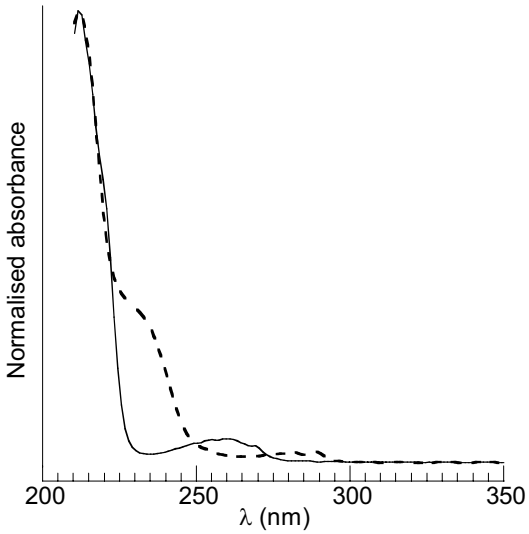


Figure 7.7. Normalised UV spectra of polystyrene **5** (—) and polyester **1** (----). Polystyrene absorption at 254 nm and of the isophthalic acid component in **1** at 289 nm were used for UV GPC analysis in Figure 7.8.

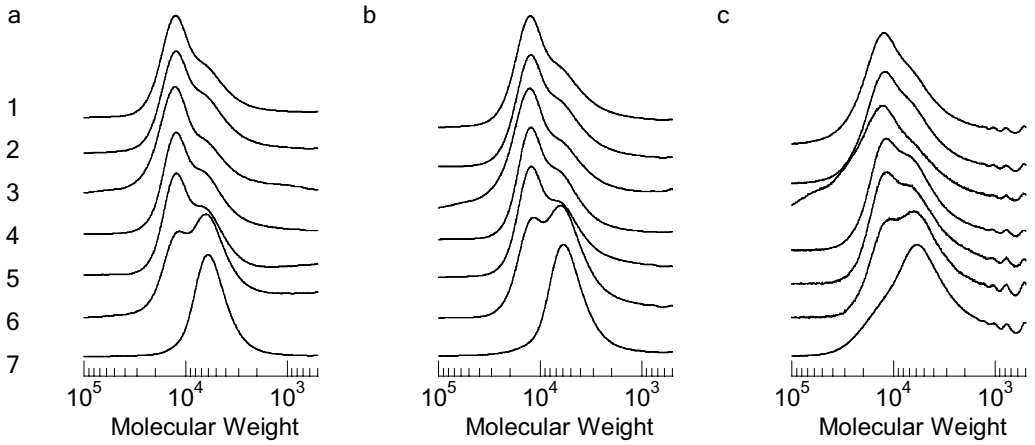


Figure 7.8. Normalised GPC traces of solution coupling: (a) RI trace, (b) corresponding UV trace at 254 nm, (c) and 289 nm. Polystyrene **5** ($\overline{M}_n$ =4900 g mol^{-1}) with Polyester heated isothermally at 270 °C for: (1) 160 min, (2) 80 min, (3) 40 min, (4) 20 min, (5) 10 min, (6) 2 min, (7) initial unreacted mixture.

7.4 Conclusions

Further melt blending work with the maleated and GMA functionalised polyolefins will be undertaken in the future as part of ongoing work at these laboratories. These will further investigate the potential of grafting amino end-functional polystyrene produced by RAFT, of a range of molecular weights with a range of modified polyolefins. This study has shown that the conditions used for interchain coupling can significantly affect the success of the reaction. For the metallocene polyolefin based coupling trials conducted, the highest conversion was achieved in the non mixed melt coupling, however, mixing will more than likely enable faster and more efficient coupling. Certainly, eventual large scale reactive extrusion trials will be conducted, this will undoubtedly introduce further reaction condition complexities which may warrant investigations in themselves. Analytical tools used will be largely be dictated by the nature and choice of the polyolefins used.

In order to fully realize the possibilities of these newly formed polyolefin (and polyester) segmented copolymers, further investigations into their formation are imminent. The scope of potential applications can therefore be further extended and fully realized.

7.5 References

1. Datta, S.; Lohse, D. J. *Polymeric Compatibilizers : Uses and Benefits in Polymer Blends;* Hanser: New York, 1996.
2. Orr, C. A.; Cernohous, J. J.; Guegan, P.; Hirao, A.; Jeon, H. K.; Macosko, C. W. *Polymer* **2001**, *42*, 8171-8178.
3. Yanjarappa, M. J.; Sivaram, S. *Prog. Polym. Sci.* **2002**, *27*, 1347-1398.
4. Chung, M. T. C. *Functionalization of Polyolefins ;* 1st ed. Academic Press: London, 2002.
5. Xanthos, M. *Reactive Extrusion: Principles and Practice*; Hanser Publishers: Munich, 1992.
6. Moad, G. *Prog. Polym. Sci.* **1999**, *24*, 81-142.
7. Hu, G.-H.; Lambla, M. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 97-

107.

8. Perego, G.; Albizzati, E. EP485982, May 20, 1992.
9. Donovan, R. A.; Moad, G. *Polymer* **2005**, *46*, 5005-5011.
10. Bray, T.; Damiris, S.; Grace, A.; Moad, G.; O'Shea, M.; Rizzardo, E.; Van Diepen, G. *Macromol. Symp.* **1998**, *129*, 109-118.
11. Zhang, M.; Duhamel, J.; van Duin, M.; Meessen, P. *Macromolecules* **2004**, *37*, 1877-1890.
12. Hansen, E. W.; Blom, R.; Bade, O. M. *Polymer* **1997**, *38*, 4295-4304.
13. Petrakis, L.; Seshadri, K. S. *Appl. Spectrosc.* **1979**, *33*, 138-145.
14. Jeon, H. K.; Macosko, C. W.; Moon, B.; Hoye, T. R.; Yin, Z. *Macromolecules* **2004**, *37*, 2563-2571.
15. Howell, B. A.; Li, I. Q.; Priddy, D. B.; Smith, P. B.; Ellaboudy, A. *Thermochim. Acta* **1999**, *340-341*, 279-283.
16. Moad, G.; Groth, A.; O'Shea, M. S.; Rosalie, J.; Tozer, R. D.; Peeters, G. *Macromol. Symp.* **2003**, *202*, 37-45.

8 General Conclusions

The synthesis of amine end-functional polystyrene was investigated using the controlled free radical techniques of ATRP and RAFT. The method adopted had to be efficient and easy to scale up with a view to using the polymers synthesized for interchain coupling reactions with reactive modified polyolefins, for the production block and graft copolymers with well-defined segmented chain lengths.

In Chapter 3 ATRP was applied to the synthesis of α primary amine functional polystyrene. Approaches based on ω-functionalisation, via substitution of the terminal bromo-group, gave products with poor end-group purity. This was found to be due to elimination of the terminal bromine to form an unsaturated chain end as a side reaction on substitution with potassium phthalimide. Attempts to make low molecular weight product at high conversion by using higher initiator concentration and longer reaction times also gave a product contaminated with unsaturated chain ends. The most viable route to the synthesis of primary amine functional polystyrene involved the α-functionalisation approach that used *N*-(bromomethyl)phthalimide as a functional initiator, albeit, only limited control over the polymerisation was obtained. Phthalimido-functional bromoisobutyrate initiators were also investigated as ATRP initiators. They imparted an improved control over the polymerisation, however, they were not useful for production of an amine functional polymer because of the susceptibility of the ester linkage to hydrolysis during amine deprotection with, consequent loss of the functionality

In Chapter 4 several *S'*-phthalimidomethyl trithiocarbonate RAFT agents were investigated to provide an effective and convenient synthesis of amine end-functionalised polystyrene using the α-functionalisation approach. The RAFT agents can be synthesized in high yield from commercially available precursors, were found to provide very good control over the polymerisation, yielding

polymers with narrow polydispersities and molecular weights. The polymers were analysed to establish the activity of the novel RAFT agents. The RAFT agents were also used to provide α-phthalimido poly(*n*-butyl acrylate) (PBA) and poly(*N*-isopropylacrylamide) (PNIPAAm) of controlled molecular weight (1k-100k g mol^{-1}) and low polydispersity and this was advanced by briefly investigating *N*-vinyl pyrrolidinone (NVP) polymerisation. A phthalimidomethyl xanthate RAFT agent was used to provide end-functional poly(vinyl acetate) (PVA). The RAFT approach proved successful, scaleable, with hydrazinolysis affording primary α-aminomethylpolystyrene of low polydispersity and with controlled molecular weights.

The thiocarbonylthio group of RAFT polymers reacts rapidly with primary and secondary unprotected amine functionalities. This incompatibility necessitated the removal of the thiocarbonylthio functionality prior to the amine deprotection step. Several thiocarbonylthio removal techniques (*i.e.* aminolysis, radical reduction, thermolysis) were therefore investigated in Chapter 5. Thermolysis was found to be an efficient and straightforward technique that required no chemical treatment, this being on the premise that the polymer and any other functionalities present are stable to the thermolysis conditions. The method was developed and applied to polystyrene and poly(*n*-butyl acrylate). The relatively inert unsaturated thermolysis product for polystyrene was formed by a concerted elimination mechanism. For poly(*n*-butyl acrylate) the main thermolysis product has a macromonomer chain end which was found to arise by consecutive C-S bond homolysis, intra- or intermolecular radical transfer and β-scission. The development of such methods clarified and expanded an understanding of the RAFT mechanism and the activities of the phthalimido RAFT agents investigated in the previous chapter. Furthermore, the thermolysis technique was successfully scaled up which was important in view of the anticipated applications.

In chapter 6 it was shown that the convenient and reliable *in situ* TAI derivatisation method can be used for the determination of a wide range of protic (hydroxy, carboxy, amino) end-groups in synthetic polymers. It was shown that the method can be successfully applied to the characterisation of

polymer end-groups formed in conventional and living radical polymerisation (RAFT, ATRP, NMP) and was extended to characterise polymers and block copolymers based on poly(ethylene oxide). The method can also be applied to end-group analysis of polyesters, further broadening its scope and was shown to be a valuable tool for the characterisation of end-functional polymers synthesized for use in the production of segmented grafted copolymers. The technique was also used to determine the level of functionality imparted by the RAFT polymerisation process. For polymers with molecular weight <40k the end-group purity was found to be high (>90%) which was an optimum result for the amino end-functional polystyrene employed for the graft copolymer formation, meaning that compromises to end-functionality would not be a prevailing issue. The level of functionality was found to be significantly less for higher molecular weights and it was explicated that the low functionality in that case is most likely a consequence of radical-radical termination in RAFT polymerisation under the reaction conditions when low concentrations of RAFT agent are used. Notably, the derivatisation experiments with TAI also confirmed that the efficiency of conversion of the phthalimido group to the amino group is quantitative and within experimental error. Ongoing work into the technique will continue to investigate the so-far limited scope for analysis of thiol-functional polymers and hopefully will explain the incomplete derivatisation observed.

The formation of graft copolymers by interchain coupling of functional groups was finally investigated in Chapter 7. Initial work was directed at the grafting of the functional monomers, maleic anhydride (MAh) and glycidyl methacrylate (GMA), onto polyolefins by reactive extrusion. This afforded precursors for the synthesis of polyolefin graft copolymers and allowed an investigation into the interchain coupling reaction largely with α-aminomethylpolystyrene (synthesized using the RAFT technique) and also with α-carboxy, ω-hydroxypolystyrene synthesized using NMP. Small scale coupling experiments were conducted in the melt and in solution with a view to assessing the potential of the system, by investigating the coupling issues involved and also in order to direct future trials. The formation of polyester-polystyrene block copolymer was also briefly investigated via the coupling of polyester oligomers with amine end-functional polystyrene. The trials showed that the conditions used for interchain coupling

can significantly affect the success of the reaction. The highest conversion was achieved in the non mixed melt coupling, however, taking into consideration interfacial issues it is proposed that mixing will more than likely enable faster and more efficient coupling. The results obtained have prompted further melt blending work with the maleated and GMA functionalised polyolefins to be undertaken with the aim of investigating the full potential of grafting amino end-functional polystyrene produced by RAFT, of a range of molecular weights with a comprehensive range of modified polyolefins.

The work described in this thesis is a detailed study into the efficient synthesis of amino-functional polystyrene, to provide a (reactive) precursor polymer which can be used to prepare polyolefin (and polyester) grafted copolymers with controlled and well defined segmented lengths. This was advanced by applying controlled radical polymerisation techniques and was achieved using RAFT. Its exploration uncovered novel RAFT agents and a thorough analysis revealed their behavior and activity. Importantly, it was shown that the complete procedure to produce α primary amine functional polystyrene with an inert ω-group could be carried out efficiently, the products analyzed readily and it could also be scaled up, which are all important aspects in terms of potential industrial applications.

Interchain coupling trials allowed the formation and investigation of grafted polyolefins and polyesters with controlled segment lengths, polymers which are expected to show interesting properties. The results presented along with the future perspectives proposed have significance in broad areas such as compatibilisation of commodity plastics and also in the continued expansion of the area of living radical polymerisation.

ROT YOUNG

A terrible infant, called Peter,
sprinkled his bed with a gheter.
His father got woost,
took hold of a cnoost
and gave him a pack on his meter.
- John O'mill

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[1] To my dad, not because HE was a rot young.

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Can science achieve a unified theory of complex systems?

Like carbon dioxide you messing with the chemicals, warfare different stars in the atmospheres like Haley's comet computers that will make you vomit. Change the earth south saliva run in your mouth gastric juice more beyond since mother goose created shapes the first man was hairy apes…

Biology 101 - Dr. Octagon

Appendices

Appendix 1. Supplementary data for the reactive extrusion grafting of functional monomers onto polyolefin (Chapter 7)

Table A1.1 Experimental data for grafting of maleic anhydride (MAh) onto polyolefins (PO) under reactive extrusion conditions at 190 °C. Stock solution feeding of styrene (S) in Butanone (MEK), MAh fed in feedthroat as powder mixed with PO. Total amount of PO fed is 5 kg h^{-1}.

Polyolefin	Stock solution			Feed Rate			S feed (wt%)	MAh feed (wt%)	MAh UV (wt%)	Graft Efficiency (%)	MFI (g $10min^{-1}$)
	MEK (g)	S (g)	DHBP (g)	MAh (g h^{-1})	S (g h^{-1})	DHBP (g h^{-1})					
5008	1300	0	13	220	0	11.3	0.00	4.40	2.19	50	0.01
5008	1000	300	13	220	262	11.3	5.24	4.40	1.68	38	0.65
5008	1000	300	13	110	130	5.64	2.60	2.20	0.63	29	4.85
5008	1000	300	13	60	72	3.12	1.44	1.20	0.88	73	4.21
AT820	1300	0	13	220	0	11.3	0.00	4.40	-	-	0.03
AT820	1300	0	13	110	0	5.64	0.00	2.20	-	-	0.48
AT820	1000	300	13	220	262	11.3	5.24	4.40	-	-	4.71
AT820	1000	300	13	110	131	5.67	2.62	2.20	-	-	7.22
AT820	1000	300	13	60	74	3.21	1.48	1.20	-	-	9.03

Table A1.2 Experimental data for grafting of maleic anhydride (MAh) onto polyolefins (PO) under reactive extrusion conditions at 190 °C. Stock solution feeding of MAh in Butanone (MEK). PO fed at 10 kg h^{-1}.

Polyolefin	Stock solution			Feed Rate		MAh feed	MAh UV	Graft Efficiency	MFI
	MEK (g)	MAh (g)	DHBP (g)	MAh (g h^{-1})	DHBP (g h^{-1})	(wt%)	(wt%)	(%)	(g $10min^{-1}$)
5008	750	500	26	271	14.1	2.71	1.59	59	0.10
5008	750	500	26	180	9.39	1.80	1.18	659	0.34
5008	750	500	26	90	4.69	0.90	0.74	829	2.90
4023	750	500	26	271	14.1	2.71	-	-	0.97
4023	750	500	26	180	9.39	1.80	-	-	4.15
4023	750	500	26	90	4.69	0.90	-	-	14.7
4006	750	500	26	271	14.1	2.71	-	-	0.02
4006	750	500	26	180	9.39	1.80	-	-	0.11
4006	750	500	26	90	4.69	0.90	-	-	1.45
AT820	750	500	26	180	9.39	1.80	-	-	0.68
AT820	750	500	26	90	4.69	0.90	-	-	2.88

Table A1.3 Experimental data for styrene (S) assisted grafting of glycidyl methacrylate (GMA) onto polyolefins (PO) under reactive extrusion conditions at 190 °C. PO fed at 5 kg h^{-1}.

Polyolefin	Stock solution				Feed Rate			S feed	GMA feed	GMA FTIR	Graft Efficiency	MFI
	MEK (g)	GMA (g)	S (g)	DHBP (g)	GMA (g h^{-1})	S (g h^{-1})	DHBP (g h^{-1})	(wt%)	(wt%)	(wt%)	(%)	(g $10min^{-1}$)
5008	750	250	172	13	225	155	11.7	3.10	4.51	0.51	11	4.87
5008	750	250	172	13	109	75	5.66	1.50	2.18	0.28	13	7.78
5008	750	250	172	13	57	39	2.96	0.78	1.14	0.20	18	8.69
5008	750	500	344	34.7[a]	243	167	16.8	3.34	4.85	0.97	20	3.31
5008	750	500	344	34.7[a]	121	83	8.42	1.67	2.43	0.45	18	6.08
5008	750	500	344	34.7[a]	61	42	4.21	0.83	1.21	0.24	20	7.69
4023	750	500	344	34.7[a]	221	152	15.3[a]	3.04	4.42	1.22	28	12.0
4023	750	500	344	34.7[a]	120	82	8.31[a]	1.65	2.39	0.49	21	19.7
4023	584	154	84.5	8.5[a]	72	40	3.99[a]	0.79	1.44	0.23	16	23.7
4023	750	500	344	26	222	153	11.6	3.06	4.44	0.44	10	5.76
4023	750	250	172	13	220	152	11.5	3.03	4.41	0.53	12	18.7
4023	584	123	84.5	8.5	111	76	7.65	1.52	2.21	0.20	9.2	24.7
4023	584	123	84.5	8.5	62	43	4.30	0.86	1.24	0.14	11	26.7

Polyolefin	Stock solution				Feed Rate			S feed	GMA feed	GMA FTIR	Graft Efficiency	MFI
	MEK (g)	GMA (g)	S (g)	DHBP (g)	GMA (g h^{-1})	S (g h^{-1})	DHBP (g h^{-1})	(wt%)	(wt%)	(wt%)	(%)	(g $10min^{-1}$)
4006	750	250	172	13	222	152	11.5	3.05	4.43	0.50	11	4.578
4006	750	250	172	13	111	76	5.76	1.52	2.22	0.28	13	6.63
4006	750	250	172	13	57	39	2.96	0.78	1.14	0.17	15	7.67
AT820	750	250	172	20	214	147	17.1	2.94	4.28	0.54	13	8.38
AT820	750	250	172	20	107	74	8.56	1.47	2.14	0.26	12	11.37
AT820	750	250	172	20	60	41	4.78	0.82	1.20	0.10	8.2	14.24

[a] Dibenzylperoxide (BPO) was used as an initiator for lower temperature (120 °C) grafting.

Table A1.4 Experimental data for styrene (S) and TEMPO assisted grafting of glycidyl methacrylate (GMA) onto polyolefins (PO) under reactive extrusion conditions at 190 °C. PO fed at 5 kg h^{-1}.

Polyolefin	Stock solution					Feed Rate				S feed	GMA feed	GMA FTIR	Graft Efficiency	MFI
	MEK (g)	GMA (g)	S (g)	DHBP (g)	TEMPO (g)	GMA (g h^{-1})	S (g h^{-1})	DHBP (g h^{-1})	TEMPO (g h^{-1})	(wt%)	(wt%)	(wt%)	(%)	(g $10min^{-1}$)
5008	375	125	86	13	2.6	202	139	21.0	4.20	2.78	4.04	0.58	14	0.07
AT820	721	262	164	26.7	4.8[a]	213	133	21.8	3.91	2.67	4.27	0.39	9.1	19.8
AT820	721	262	164	26.7	4.8[a]	112	70.0	11.4	2.05	1.40	2.24	0.18	7.8	12.9
AT820	721	262	164	26.7	4.8[a]	53.3	33.3	5.44	0.98	0.67	1.07	0.08	8.0	23.7
AT820	376	136	87	16	2.5[a]	264	169	31.1	4.86	3.38	5.29	0.52	9.9	5.76
AT820	376	136	87	16	2.5[a]	159	101	18.7	2.91	2.03	3.17	0.31	9.8	26.7
AT820	375	136	86.4	14	3.8	265	169	27.3	7.41	3.37	5.31	0.47	8.9	6.63
AT820	375	136	86.4	14	3.8	212	135	21.9	5.93	2.70	4.24	0.39	9.2	7.67
AT820	375	135	86.4	14	3.8	161	103	16.7	4.53	2.06	3.22	0.29	9.2	4.58
AT820	376	136	88	14	3.8	106	68	11.0	2.95	1.37	2.11	0.16	7.6	24.7
AT820	376	136	88	14	3.8	52.8	34	5.44	1.48	0.68	1.06	0.12	11	18.7
HP400N	375	135	86	5[c]	3.8	214	137	7.94	6.03	2.74	4.30	0.21	5.0	11.4
HP400N	375	135	86	5[c]	3.8	201	128	7.44	5.65	2.56	4.02	0.21	5.4	8.38

Polyolefin	Stock solution					Feed Rate				S feed (wt%)	GMA feed (wt%)	GMA FTIR (wt%)	Graft Efficiency (%)	MFI (g 10min^{-1})
	MEK (g)	GMA (g)	S (g)	DHBP (g)	TEMPO (g)	GMA (g h^{-1})	S (g h^{-1})	DHBP (g h^{-1})	TEMPO (g h^{-1})					
HP400N	375	135	86	5[c]	3.8	107	68	3.97	3.02	1.37	2.15	0.19	8.6	14.2
HP400N	375	135	86	5[c]	3.82	107	68	3.97	3.03	1.37	2.15	0.18	8.3	8.69
HP400N	375	135	86	5[c]	3.82	53.6	34	1.98	1.52	0.68	1.07	0.14	13	7.78
HP400N	375	135	86	5[c]	3.8	53.6	34	1.98	1.51	0.68	1.07	0.16	15	4.87
HP400N	375	135	86	5[c]	3.8	208	132	7.69	5.84	2.66	4.15	0.20	4.8	-
HP400N	375	135	86	5[c]	3.8	107	68.3	3.97	3.02	1.37	2.14	0.15	7.1	-
HP400N	375	135	86	5[c]	3.8	53.6	34.1	1.98	1.51	0.68	1.07	0.13	13	-
HP400N	375	135	86	5[c]	3.8	53.6	34.1	1.98	1.51	0.68	1.07	0.13	12	-
HP400N	240	85.4	54.4	0[c]	2.4	214	137	0	6.02	2.74	4.29	0.17	4.0	-
HP400N	240	85.4	54.4	0[c]	2.4	53.6	34.1	0	1.51	0.68	1.07	0.12	12	-
HP400N	189.4	67.5	43	2.5[c]	0	214	137	7.94	0	2.74	4.29	0.46	11	-
HP400N	230.5	67.5	0	2.5[c]	1.9	214	0	7.94	6.03	0	4.29	0.19	4.5	-

[a] 4-hydroxyTEMPO. [b] Xylene was used as the delivery solvent in the stock solution. [c] An additional 0.0196 g of initiator DMBP was added to the existing DHBP.