NMR studies on the mechanism of iodine mediated polymerisation

by

Trevor Wright

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Supervisor: Prof. Harald Pasch

Faculty of Science

Department of Chemistry and Polymer Science

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DECLARATION

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ABSTRACT

In reverse iodine transfer polymerisation (RITP), chain transfer agents (CTAs) are generated *in situ* from the reaction between 2,2'-azobis(isobutyronitrile) (AIBN) and molecular iodine. This stage of RITP is the inhibition period, which ends when all iodine has been consumed. The evolution of CTAs was studied for the polymerisation reactions of n-butyl acrylate and styrene respectively. RITP of n-butyl acrylate was performed at 70 °C. *In situ* ^{1}H nuclear magnetic resonance (NMR) experiments were carried out to study the evolution of CTAs during the inhibition period of n-butyl acrylate polymerisation and the structures *A-I* and *A-*M_n*-I* (where *A* represents the moiety originating from AIBN, *M* represents the monomer unit and *n* is the mean number degree of polymerisation) were observed. A polymer with the general structure *A-*M_m*-I* is formed. The molecular weight of poly(n-butyl acrylate) (PnBA) was evaluated with size exclusion chromatography (SEC) and NMR. Structural analysis of PnBA was done using NMR spectroscopy and matrix-assisted laser desorption/ionisation time-of-flight (MALDI-ToF) mass spectrometry. Similar conditions to those used for n-butyl acrylate polymerisation were used for RITP of styrene. The evolution of CTAs during the inhibition period of styrene polymerisation was studied using *in situ* ^{1}H NMR. The inhibition period of styrene polymerised by RITP was much shorter than expected. This is due the consumption of iodine in the reaction between styrene and iodine which reversibly forms 1,2-diiodo-ethyl benzene. The CTAs *A-I* and *A-*M_n*-I* are formed, as well as 1-phenylethyl iodide (1-PEI). The molecular weight of polystyrene (PS) was determined using SEC and NMR and the functionality was evaluated using ^{1}H NMR. The structure of PS was confirmed with ^{1}H NMR and MALDI-ToF mass spectrometry. By increasing the temperature of the reaction, the inhibition period can be shortened. Both polymerisation systems retain control over molecular weight with an increase in temperature, however, n-butyl acrylate is limited due to the possible formation of mid-chain radicals. The formation of an *A*–M_m–*A* population (direct combination of the initiator and styrene) in RITP of styrene results in more initiator being consumed than for n-butyl acrylate, despite limited conversion of styrene to polymer.

OPSOMMING

In omgekeerde-jodium-oordrag polimerisasie, is die kettingoordragagente gegenereer *in situ* van die reaksie tussen 2,2'-azobis(isobutironitriel) (AIBN) en molekulêre jodium. Hierdie fase van RITP is die inhibisie tydperk wat eindig wanneer alle jodium verbruik is. Die evolusie van kettingoordragagente is vir die polimerisasiereaksies van butielakrilaat en stireen onderskeidelik bestudeer. Omgekeerde-jodium-oordrag polimerisasie van butielakrilaat was uitgevoer by 70 °C. *In situ* ^{1}H kernmagnetieseresonans (KMR) eksperimente is uitgevoer om die evolusie van die kettingoordragagente te bestudeer tydens die inhibisie van butielakrilaat polymerisasie en die strukture *A-I* en *A-*M_n*-I* (waar *A* die gedeelte voorstel wat afkomstig is van AIBN, *M* die monomeer-eenheid en *n* die gemiddelde aantal polymerisasiegraad verteenwoordig) is ge-identifiseer. 'n Polimeer met die algemene struktuur *A-*M_m*-I* is gevorm. Die molekulêre gewig van poli(butielakrilaat) (PnBA) was geëvalueer deur grootte-uitsluitings chromatografie en KMR spektroskopie. Strukturele ontleding van PnBA is gedoen deur die KMR spektroskopie en matriks ge-assisteerde laser desorpsie/ionisasie tyd-van-vlug massaspektroskopie. Soortgelyke kondisies as dié wat gebruik word vir butielakrilaat polymerisasie, is gebruik vir omgekeerde-jodium-oordrag polimerisasie van stireen. Die evolusie van die ketting oordrag agente gedurende die inhibisie periode van stireen polymerisasie is deur *in situ* ^{1}H KMR bestudeer en die inhibisie periode is baie korter as verwag. Dit is as gevolg van die opname van jodium in die reaksie tussen stireen en jodium wat omkeerbare stireen-di-jodied tot gevolg hê. Die ketting oordrag agente *A-I* en *A-*M_n*-I* is gevorm, sowel as 1-feniel-etiel jodied. Die molekulêre massa van polistireen (PS) is bepaal met behulp van grootte-uitsluitings chromatografie en KMR spektroskopie en die funksioneering is geëvalueer met behulp van ^{1}H KMR. Die struktuur van PS is bevestig deur ^{1}H KMR en matriks ge-assisteerde laser desorpsie/ionisasie tyd-van-vlug massaspektroskopie. Deur die verhoging van die temperatuur van die reaksie, kan die inhibisie periode verkort word. Beide polimerisasie sisteme behou beheer oor die molekulêre massa met 'n toename in temperatuur, alhoewel butielakrilaat beperk word as gevolg van die moontlike vorming van middel kettingradikale. Die vorming van die *A-*M_m*-A* spesie (direkte kombinering van AIBN en stireen) in omgekeerde-jodium-oordrag polimerisasie van stireen veroorsaak dat meer AIBN verbruik word as butielakrilaat, ten spyte van die beperkte omskakeling van stireen tot polimeer.

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GLOSSARY OF TERMS

AIBN	: 2,2'-azobis(isobutyronitrile)
ATRP	: atom transfer radical polymerisation
BPO	: benzoyl peroxide
C_6D_6	: deuterated benzene
$CDCl_3$	: deuterated chloroform
CMRP	: cobalt mediated radical polymerisation
CROP	: cationic ring-opening polymerisation
CRP	: controlled/living radical polymerisation
CTA	: chain transfer agent
DHB	: 2,5-dihydroxy-benzoic acid
Dithranol	: 1,8,9-trihydroxy-anthracene
DMF	: dimethyl formamide
DMSO	: dimethyl sulphoxide
DT	: degenerative chain transfer
ESI	: electrospray ionisation
FAB-MS	: fast atom bombardment mass spectrometry
FRP	: free radical polymerisation
GCMS	: gas chromatography–mass spectrometry
GPC	: gel permeation chromatography
HABA	: 2-(4-hydroxy-phenylazo) benzoic acid
HPLC	: high-performance liquid chromatography

IAA	: 3-β-indoleacrylic acid
IR	: infra-red
ITP	: iodine transfer polymerisation
LDPE	: low density polyethylene
MALDI-ToF	: matrix-assisted laser desorption/ionisation time-of-flight
MCR	: mid-chain radical
MS	: mass spectrometry
NMP	: nitroxide-mediated polymerisation
NMR	: nuclear magnetic resonance
PDI	: polydispersity index
PEG	: polyethylene glycol
1-PEI	: 1-phenylethyl iodide
PnBA	: poly (n-butyl acrylate)
PRE	: persistent radical effect
PRT	: primary radical termination
PS	: polystyrene
PVC	: polyvinyl chloride
RAFT	: reversible addition fragmentation chain transfer
RI	: refractive index
RITP	: reverse iodine transfer polymerisation
SEC	: size exclusion chromatography
SFRP	: stable free radical polymerisation
TEMPO	: 2,2,6,6-tetramethylpiperidinyloxy

THAP	: 2,4,6-trihydroxy acetophenone hydrate
THF	: tetrahydofuran
UHP	: ultra high purity
UV	: ultraviolet

LIST OF SYMBOLS

f	: initiator efficiency
$F^{iodine,\ theory}$	: theoretical iodine functionality
F^{iodine}	: iodine functionality
F_n	: number average functionality
k_d	: initiator decomposition rate constant
k_{ex}	: chain transfer rate constant
k_p	: propagation rate constant
M_n	: number average molecular weight
$t_{1/2}$	: half life
$t_{inh,\ exp}$	: experimental inhibition time
$t_{inh,\ theory}$	: theoretical inhibition time
δ	: chemical shift
Δ	: heat
$\int$	: integral

1 INTRODUCTION

1.1 Subject of the study

This project concerns NMR studies on the mechanism of reverse iodine transfer polymerisation (RITP), specifically following the polymerisation of the homopolymers polystyrene (PS) and poly(n-butyl acrylate) (PnBA). The chemical heterogeneity of chain transfer agents and polymers formed by RITP is investigated to establish a better understanding of the mechanism. The livingness of the homopolymers chain ends is also investigated.

1.2 Background to the project

Conventional free radical polymerisation (FRP) is the most widely used process in industry to produce a large assortment of polymers with high molecular weight and various properties. FRP is an attractive polymerisation process due to the wide range of conditions it can be performed under.[1-3] However, there are some disadvantages to using FRP, such as poor control over molecular weight, polydispersity, end group functionality, chain architecture and composition.[3]

To overcome these limitations, controlled/living radical polymerisation (CRP) techniques were developed. The control over polymerisation is achieved either by a reversible deactivation/activation process or a reversible degenerative chain transfer. Systems that employ a reversible deactivation/activation mechanism include nitroxide-mediated polymerisation (NMP),[4] atom transfer radical polymerisation (ATRP),[5] stable free radical polymerisation (SFRP)[1] and cobalt mediated radical polymerisation (CMRP).[1] The systems that follow a degenerative transfer mechanism include reversible addition-fragmentation chain transfer (RAFT)[6] and iodine transfer polymerisation (ITP and RITP).[7-10] Reportedly, the three most effective methods of controlling radical polymerisation are NMP, ATRP and RAFT.[3]

The focus of this project is on reverse iodine mediated polymerisation (RITP). For RAFT polymerisation, chain transfer agents that control the polymerisation are synthesised separately. Polymers prepared by RAFT polymerisation contain thiocarbonate end groups that give the polymer colour and odour. Therefore, commercial applications require the end group to be removed after polymerisation.[11] ATRP involves the use of a transition metal catalyst which must also be removed

after polymerisation. NMP does not require any additives, but the nitroxides must be removed by radical chemistry.

RITP is a relatively simple technique compared to RAFT and ATRP. All that is required for this polymerisation technique is an initiator (AIBN), molecular iodine and monomer (e.g. styrene).The chemical structure of the polymer formed is *A*-M_m-*I* (α-end derived from initiator and iodide leaving group at the ω-end). The iodine at the ω-end is what makes this system living. RITP has previously been studied, with emphasis on investigating the mechanism and confirming the resulting polymer.[8-10] Therefore, the main focus of this work is to investigate the control over the molecular weight, the livingness of the polymers synthesised, and the evolution of chain transfer agents (CTAs) to establish the potential for this technique industrially.

1.3 Objectives of the thesis

The objectives of this project were to:

i synthesise PS and PnBA by reverse iodine transfer polymerisation (RITP)

- investigate the chemical structure of the chain transfer agents generated during the inhibition period
- follow the conversion of these chain transfer agents to polymers
- investigate the chemical structure of the various polymer chains present
- determine the molecular weight control and livingness of the polymerisation system

ii compare the mechanisms for PS and PnBA

- compare the evolution of chain transfer agents
- compare the change in concentration of initiator
- follow and compare the conversion of the homopolymers

1.4 Plan of development

A brief introduction to the project and objectives for the work are given in Chapter 1.

An overview of the background to this work is presented in Chapter 2. This includes a brief history of radical polymerisation and the various polymerisation techniques that are available. A short introduction to copolymerisation using CRP is described and the methods for polymer characterisation are also mentioned.

The polymerisation of n-butyl acrylate by RITP is investigated in Chapter 3. The chemical structures of chain transfer agents and polymers formed are studied and the livingness of the polymers reported. The polymers are characterised using size exclusion chromatography (SEC), NMR and matrix-assisted laser/desorption ionisation time-of-flight mass spectrometry (MALDI-ToF).

In Chapter 4, the polymerisation of styrene by RITP is investigated to elucidate the chemical structures of chain transfer agents and polymers formed by this technique. The period wherein chain transfer agents are generated *in situ* (inhibition period) is studied by kinetic ^{1}H nuclear magnetic resonance spectroscopy (NMR) and the livingness of the resulting polymers is described. The polymers are characterised using SEC, NMR and MALDI-ToF mass spectrometry.

In Chapter 5, comparisons are made between the mechanisms for RITP of styrene and n-butyl acrylate. The formation of chain transfer agents, the decrease in initiator concentration and the generation of polymers for the two systems are compared.

Lastly, Chapter 6 gives a summary of the results found in this work and a few suggestions for future work.

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2 LITERATURE REVIEW

2.1 Brief history of radical polymerisation

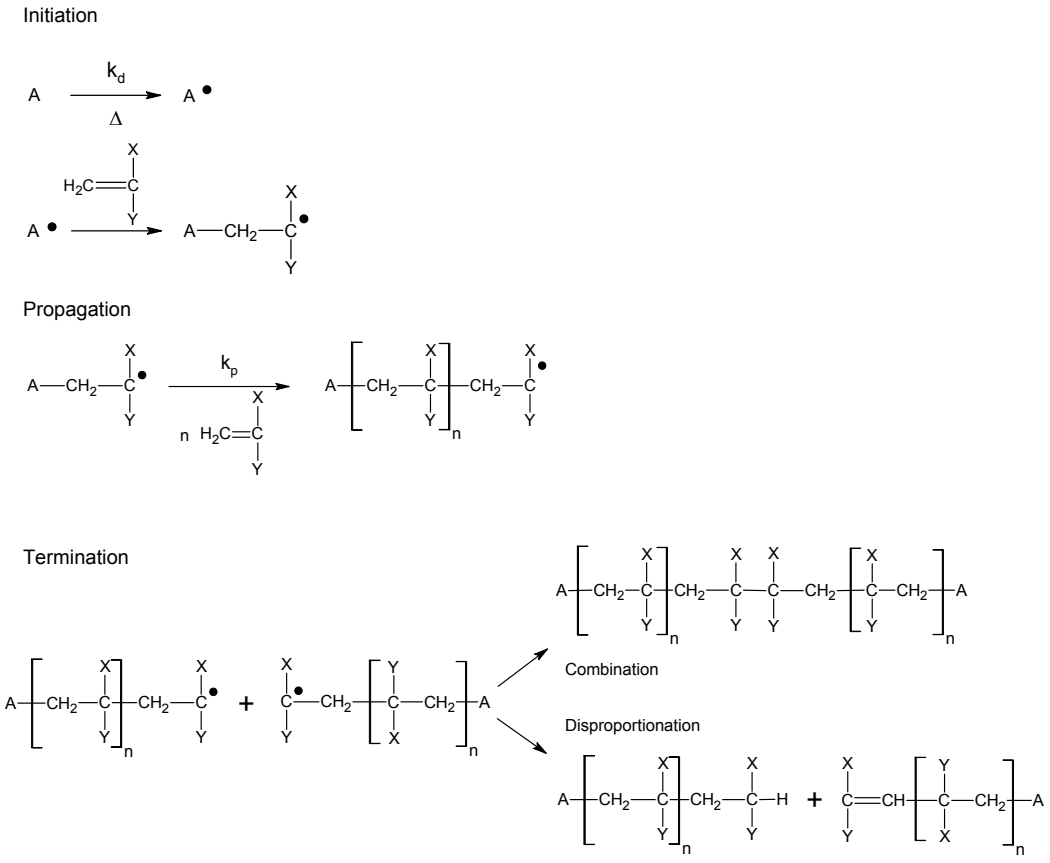
Living anionic vinyl polymerisation was developed by Michael Szwarc,[1] who based his research on the exclusion of transfer and termination reactions from chain growth polymerisation. With regards to polymerisation, “living” refers to the ability of a polymer chain to grow without termination. In time, the procedure became widely used in industry to produce well-defined block copolymers with thermoplastic properties.[2] For many years anionic polymerisation was the only known form of living polymerisation. In the mid 1970’s, however, cationic ring-opening polymerisation (CROP) of tetrahydofuran (THF) illustrated the existence of two types of active species. After expanding living CROP to other heterocyclic monomers, the procedure was used to synthesise well-defined polymers and copolymers.[2,3]

Living cationic vinyl polymerisation was once regarded as implausible due to a dominant transfer process. However, procedures that facilitate fast exchange between growing carbocations and a dormant species (meaning that the reactivity of these species is much lower that that of free radicals) allowed for progress in living carbocationic vinyl polymerisation research. Advances in new controlled/living systems were possible due to the fast, adjustable equilibria between active and dormant species.[2,4]

Industrially, free radical polymerisation (FRP) is attractive due to the wide range of conditions it can be performed under. For instance, RP can be performed in bulk monomer, in solution and in dispersed media such as suspension and various forms of emulsion. These reactions can be conducted through a broad range of temperatures. This range spans from a temperature of -100 °C to temperatures in excess of 200 °C.[1,2,5] However, there are some disadvantages to using FRP, such as poor control over molecular weight, polydispersity, end group functionality, chain architecture and composition.[5]

There are three fundamental steps in FRP, namely initiation, propagation and termination, as illustrated in Scheme 2.1. The initiator (*A*) is thermally decomposed, with a decomposition rate coefficient k_d, to form an initiating radical (*A*•). The radicals formed in this way are added onto the less substituted end of the double bond of the monomer and propagation proceeds with a propagation rate coefficient of k_p.

The growing chains can be terminated, either by combination between two growing chains or by disproportionation, whereby two different products are formed. Termination may also occur due to the transfer of initiating radicals to the solvent or impurities.[6] The active species in FRP are sp^2 hybridised organic radicals with poor stereoselectivity. Nevertheless, the regioselectivity and chemoselectivity of polymers formed by FRP is good.



Scheme 2.1: Mechanism of conventional free radical polymerisation.

When the reaction conditions are in a steady state, the rate of initiation (which is quite slow) is equivalent to the rate of termination. The rate of termination must be much lower than that of propagation in order for long chains to grow. The lifetime of growing polymer chains is ≈ 1 s and therefore any manipulation of chain architecture is impossible. This is due to the fact that a polymer that is terminated at the chain ends can not propagate any further and the polymer chains are termed as being "dead".

Industrially, FRP is used to produce about 50% of all commercial polymers such as low density polyethylene (LDPE), polyvinyl chloride (PVC), polystyrene (PS) to name just a few. However, no polymers with controlled architecture or pure block copolymers can be prepared using conventional radical polymerisation.[2]

To overcome these limitations, controlled/living radical polymerisation (CRP) techniques were developed.

2.2 Controlled/living radical polymerisation (CRP)

A living polymerisation system is one where initiation is quick and there is no irreversible chain transfer and termination.[7] A key aspect of CRP is that a reagent is reversibly terminated by the propagating radicals, resulting in a dormant species. The concentration of the active species can therefore be controlled, which allows for control over composition, chain architecture as well as molecular weight.[6]

The functionality of end groups is another key aspect in CRP. The functionality gives an indication of how many dead chains are present and hence, the livingness of the system. The functionality of polymers usually decreases with increasing monomer conversion.[8,9] There are several indications that a system is living, as described by Quirk and Lee:[10]

- polymerisation will continue until full monomer consumption and may persist with the addition of more monomer (block copolymers are possible)
- the molecular weight increases linearly with conversion
- the concentration of the active species remains constant
- the molecular weight distribution is narrow
- the end groups are retained

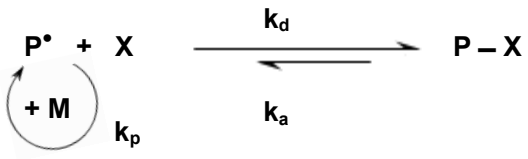
The amount of dead chains in CRP is usually less than 10%, due to the quick initiation and lack of termination.[2] A dynamic equilibrium exists between the propagating radicals and the dormant species, whereby these radicals are involved in either a reversible deactivation/activation process, or a reversible degenerative chain transfer.

The synthesis of block copolymers with various desired properties is possible using CRP techniques.[8,11-13] Block copolymers can be easily synthesised using CRP

techniques because very few chains are terminated. It is the living nature of these polymers that makes block copolymerisation possible.[14]

2.2.1 Reversible deactivation/activation process

For this mechanism, the propagating radical reacts with a stable radical to give a dormant chain. These systems are controlled by the persistent radical effect (PRE) (Scheme 2.2).[15,16]

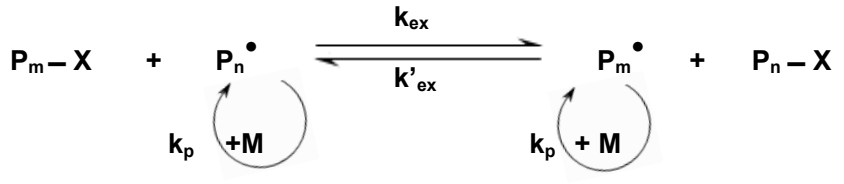


Scheme 2.2: General mechanism of a reversible deactivation/activation process.[2]

During the deactivation process (with a deactivation rate coefficient of k_d) the propagating radicals (P_n•) are trapped by a persistent radical (*X*), usually a stable radical such as a nitroxide[12,17] or an organometallic compound such as porphyrin.[2] The dormant species (*P*–*X*) is activated (with activation rate coefficient k_a) and radicals can propagate (with propagation rate coefficient k_p). The persistent radicals (*X*) reversibly cross-couple with the growing polymer chains and therefore every radical-radical termination results in an irreversible increase in the concentration of *X*. As the concentration of *X* increases, the likelihood of termination decreases and growing polymer chains react primarily with *X*.

2.2.2 Reversible degenerative chain transfer

In a degenerative chain transfer (DT) mechanism (Scheme 2.5), the concentration of the transfer agent is usually much higher than that of the initiator. This results in the transfer agent taking the role of the dormant species (P–X).



Scheme 2.3: General mechanism of reversible degenerative chain transfer.[2]

DT is an exchange reaction, where the propagating radical (P_n•) attacks the dormant species (P_m–X) to form the active species (P_m•). A small quantity of radicals consumes monomer, causing the growing chain to terminate. Alternatively, the radicals can degeneratively exchange with the dormant species. Good control over molecular weight, polydispersity and chain architecture are achieved through fast exchange between the active and dormant species. [2,16,18] Systems that proceed by a DT mechanism include reversible addition-fragmentation chain transfer (RAFT)[13] and iodine transfer polymerisation (ITP).[11] A more recently developed iodine mediated polymerisation technique, reverse iodine transfer polymerisation (RITP)[19], also follows a DT mechanism.

Systems that employ a reversible deactivation/activation mechanism include nitroxide-mediated polymerisation (NMP),[12] atom transfer radical polymerisation (ATRP),[20] stable free radical polymerisation (SFRP)[2] and cobalt mediated radical polymerisation (CMRP).[2]

A comparison is made between FRP and CRP, as shown in Table 2.1.

Table 2.1: Comparison of the polymerisation mechanisms of FRP and CRP.

Step in polymerisation	**FRP**	**CRP**
Initiation	slow	fast
Polymerisation	fast	slow (faster with lower MW)
Lifetime of growing chains	~ 1s	> 1h
Establishment of steady state radical concentration	similar rates of initiation and termination	(PRE) balance between rates of activation and deactivation
Termination	between long chains and new chains	(PRE) rate drastically decreases with time (DT) throughout the reaction
Dead chains	> 99%	< 10%

2.2.3 Persistent radical effect controlled CRP techniques

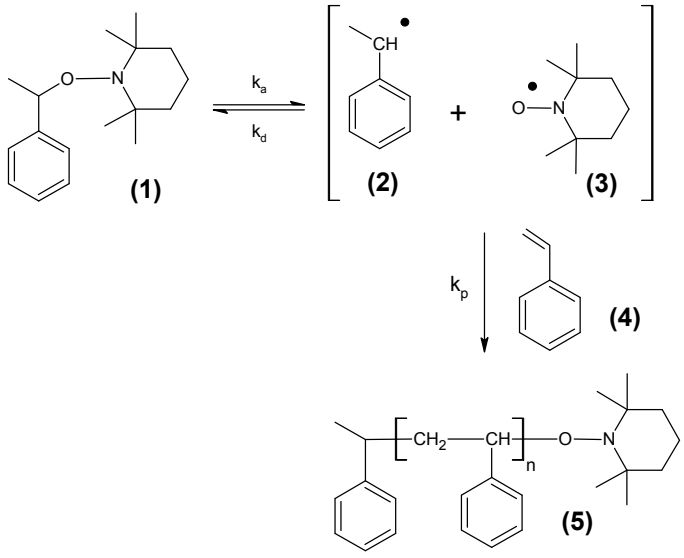
2.2.3.1 Nitroxide mediated polymerisation

Derivatives of nitroxides were commonly used as radical scavengers for polymer stabilisation before research into nitroxide-mediated polymerisation (NMP) began. Nitroxides were used for their ability to trap carbon-centred radicals. [14]

In the 1980's, reactions of initiator-derived radicals with monomers were investigated, where nitroxides such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (**3**) were used as a radical trap.[21] These studies showed that under certain conditions the nitroxides could reversibly trap propagating radicals. Interest into living free radical polymerisation continued to grow following the work of Georges *et al*[17], who synthesised high molecular weight, low polydispersity polystyrene.

The general mechanism of NMP is illustrated in Scheme 2.4. The thermolytically unstable alkoxyamine derivative (**1**) is cleaved at the C-O bond upon heating (k_a and k_d) to give rise to an initiating radical (**2**) and a persistent nitroxide radical (**3**). [22]

The initiating radicals are added (k_p) to the monomer (**4**) and are deactivated to the dormant species (**5**) by the addition of the nitroxide radicals to the polymer chain. NMP is a widely used method for synthesising polymers from acrylates (excluding methacrylates), acrylamides and styrenes.[12,23,24]



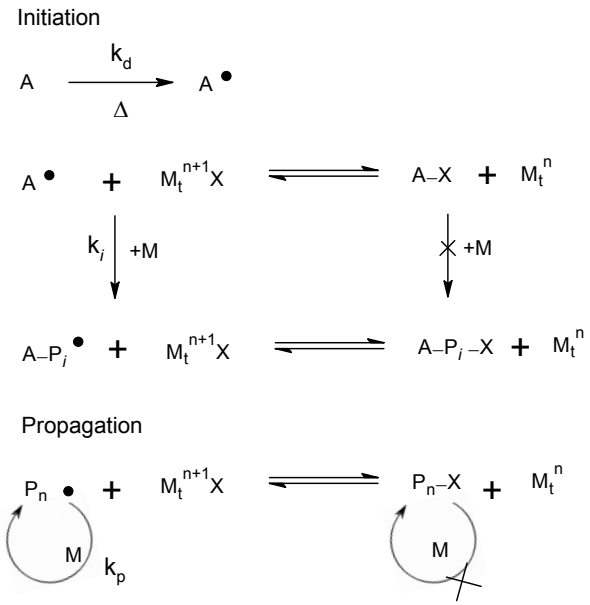
Scheme 2.4: General mechanism of NMP (unimolecular).

2.2.3.2 Atom transfer polymerisation

As the name implies, the key reaction in ATRP is the atom transfer step. The general mechanism of ATRP is shown in Scheme 2.5. The initiator (*A*) is thermally decomposed to form an initiating radical (*A*•). The oxidised transition metal complex ($M_t^{n+1} - X$) donates a halogen atom (*X*) to the initiating radical (*A*•) or the propagating radical ($A–P_i$•).

This reaction forms a reduced transition metal species (M_t^n) and the dormant species *A*–*X* and P_i –*X*. The rate at which the polymer chain grows when radicals are added to the monomer is governed by the propagation rate coefficient (k_p). The reduced transition metal species (M_t^n) reacts with *A*–*X* to help start a new redox cycle.[25-27] Termination is also possible in ATRP; however this occurs in very small proportions (< 5%).

The use of an appropriate catalyst (transition metal complex) and initiator (alkyl halides) allows for control over the chain architecture and end group functionality.[28] Several monomers can be polymerised using ATRP, such as styrenes[26,29-32], acrylates[25,27,33], methacrylates[32,34-38], acrylonitriles[39], (meth)acrylamides, and (meth)acrylic acids.



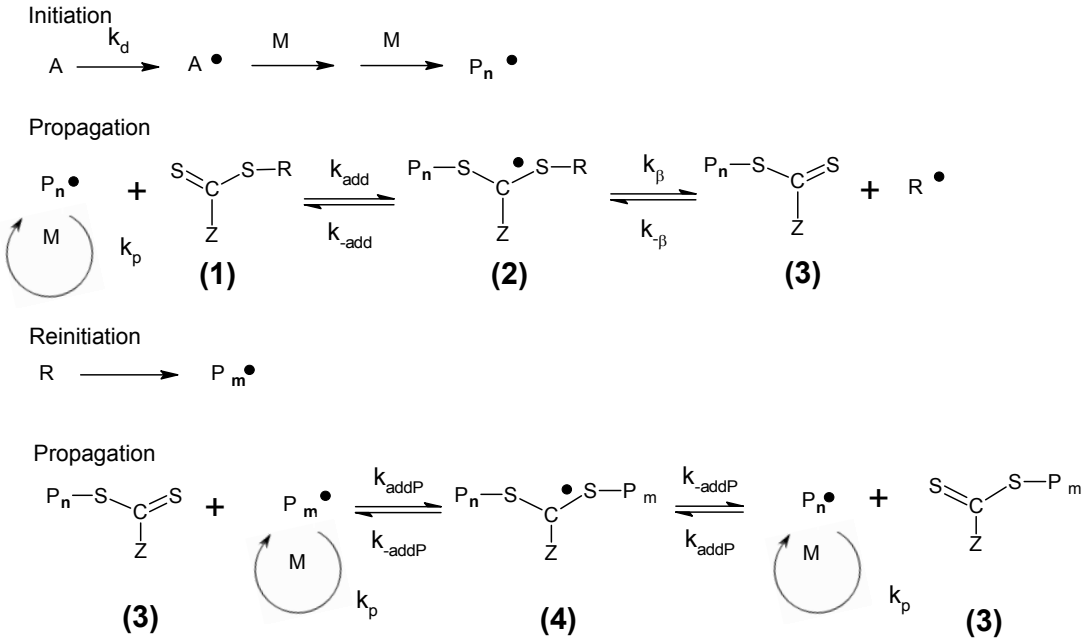
Scheme 2.5: General reaction mechanism for transition metal catalysed ATRP.

2.2.4 Degenerative transfer controlled CRP techniques

2.2.4.1 Reversible addition-fragmentation chain transfer polymerisation

The initiation and termination steps in RAFT polymerisation follow conventional radical polymerisation. The general mechanism of RAFT mediated polymerisation can be seen in Scheme 2.6.[13,40]

After the propagating radical (P_n•) is formed, it is added to a thiocarbonylthio compound (**1**). Thereafter, the intermediate radical (**2**) is fragmented to form a thiocarbonylthio polymer (**3**) and a radical (*R*•). The radical (*R*•) reacts with monomer to form a new propagating radical (P_m•). There is equilibrium between the active species (P_n• and P_m•) and the dormant species (**3**) and hence polymers can be synthesised with control over molecular weight and end group functionality.



Scheme 2.6: General mechanism of RAFT mediated polymerisation.

2.2.4.2 Iodine transfer polymerisation

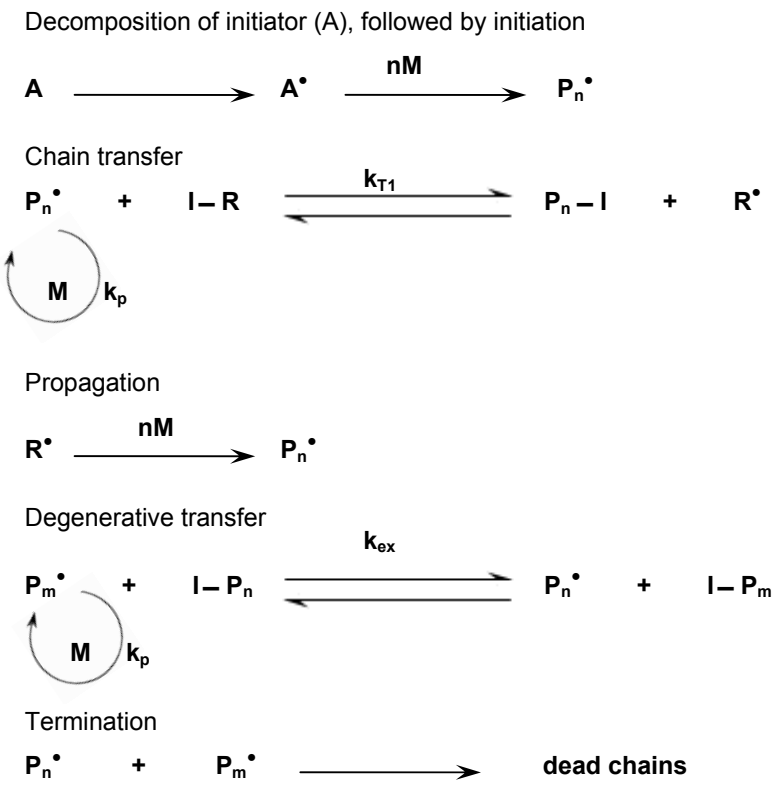
In the late 1970's, Tatemoto performed ITP using iodofluorocompounds as initiating agents.[11] Iodocompounds are molecules containing a labile C–I bond, where iodine is a good leaving atom. The reactivity of iodocompounds makes them quite efficient chain transfer agents (CTAs) for radical polymerisation.

Often, in the presence of UV light, a thermal source or in redox catalysis, iodinated compounds are unstable and can decompose readily. Therefore, iodocompounds are used as CTAs, because they are able to initiate polymerisation and the transfer of the iodine atom onto the growing polymer chain. [11,19,41-43] Typically, CTAs are synthesised to mimic a propagating chain end so as to ensure that there is almost no change in free energy during the transfer reaction.

There are two main requirements for an iodinated chain transfer agent, namely:

- it must contain a labile C–I bond
- the radical that forms from iodine abstraction must be stabilised by inductive or resonance effects

The concentration of the CTA and the chain transfer rate constant (k_{ex}) are key parameters in DT polymerisation techniques. The concentration of the CTA controls the molecular weight of the polymer and the value of k_{ex} influences the polydispersity index (PDI) values (high k_{ex} values give rise to low PDI values).[11] The mechanism of ITP can be seen in Scheme 2.7 below.



Scheme 2.7: General mechanism of ITP.

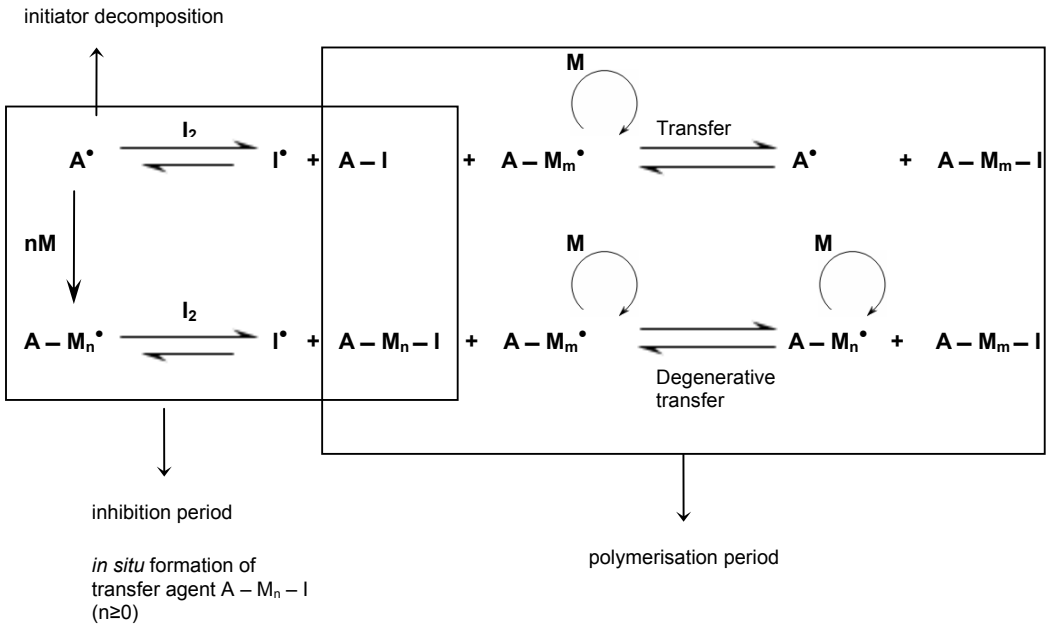
The first step involves the thermal decomposition of the initiator (*A*) to form an initiating radical (*A*•). Typical initiators include 2,2'-azobis(isobutyronitrile) (AIBN) or benzoyl peroxide (BPO).The next step is initiation, whereby *A*• adds onto the monomer (*M*) and forms a propagating radical (P_n•).

Next, iodine from the transfer agent (*R*–*I*) is exchanged to P_n•, forming the polymer alkyl iodide (P_n–*I*) and an initiating radical (*R*•). It is favourable for *R* to be structurally similar to the propagating radical so as to allow for a thermodynamically neutral transfer. The DT step is thermodynamically neutral because P_n and P_m both have the same structure. Thereafter, either *R*• or P_n• are added onto the monomer and propagation proceeds. Finally, polymerisation is terminated resulting in some dead chains. [11]

ITP is a useful technique for the polymerisation of most vinylic monomers. However, there are some drawbacks associated with this type of polymerisation. For instance, alkyl iodides are susceptible to change while being stored. Also, the control of the polydispersity of methyl methacrylates is poor using this method, due to the slow degenerative transfer. This can only be improved by using alkyl iodides with a better leaving group, which are more unstable.[42,44]

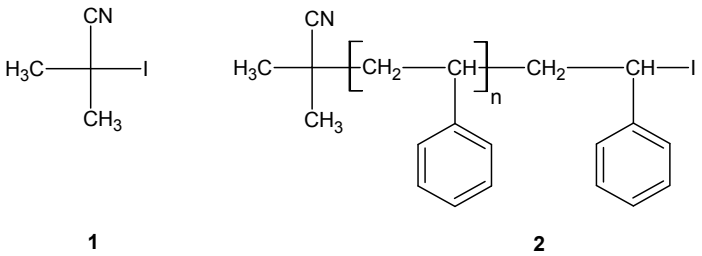
2.2.4.3 Reverse iodine transfer polymerisation

To overcome some of the shortcomings of ITP, a variation of iodine mediated polymerisation was developed. RITP differs from ITP in that molecular iodine is reacted with initiator radicals to form alkyl iodide CTAs *in situ* as opposed to adding the CTA to a reaction mixture.[19,41,45] The basic mechanism of RITP is shown in Scheme 2.8.



Scheme 2.8: Basic mechanism of RITP.

Mechanistically, RITP is divided into two stages; (1) inhibition period and (2) polymerisation period. Iodine is a strong inhibitor and therefore the inhibition period is ended only once all iodine has been consumed. Throughout the inhibition period, free radicals (*A*•) generated by the decomposing initiator (AIBN) react directly with iodine to form iodinated CTAs. The CTAs generated are *A–I* and *A–M*$_n$*–I* (*n* ≥ 0), where *A* is a radical from the initiator, *M* is a monomer unit, *n* is the average number degree of polymerisation and *I* is the iodine atom. The chemical structure of these CTAs is shown in Figure 2.1.

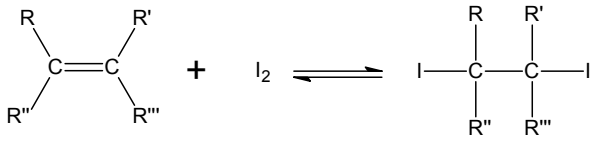


1 **2**

Figure 2.1: The chemical structures of the (1) A-I adduct and (2) A-M$_n$-I adduct (styrene repeat units in this case) formed during RITP.

During the inhibition period, iodine can also react with the double bonds of a monomer molecule to form a 1,2-disubstituted olefin.

The formation of these compounds is reversible (Scheme 2.9) and they tend to be very unstable in UV light.[19,46,47]



Scheme 2.9: Reversible formation of 1,2-disubstituted olefin in the presence of iodine.

The monomer conversion during the inhibition period is insignificant. Thereafter, however, the monomer is converted during the polymerisation period, a process that is governed by a DT mechanism. RITP of several monomers is possible, including acrylates, methacrylates and styrene.[19,41,45]

In addition to this, a broad range of solvents can be used in RITP of acrylates, whilst maintaining good control over the molecular weight of the polymer. The inhibition period in RITP is undesirable industrially.

For experiments conducted using *n*-butyl acrylate, the inhibition time can be drastically reduced by increasing the temperature, while having little impact on the control over the molecular weight of the polymer.[19] The end group functionality of methyl methacrylate polymerised by RITP is high, concurring with the model of limited termination for CRP.[41] Due to the livingness of the end groups, block copolymerisation is possible. Block copolymers such as poly(methyl acrylate)-*b*-polystyrene,[19] and poly(styrene)-*b*-poly(butyl acrylate)[48] have been reported in literature.

2.3 Characterisation of polymers synthesised by CRP

Polymers synthesised by CRP can be studied using a variety of spectroscopic and chromatographic methods. A few of these methods include:

- electrospray ionisation mass spectrometry (ESI)
- high-performance liquid chromatography (HPLC)
- infra-red spectroscopy (IR)
- ultraviolet-visible spectroscopy (UV)
- matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-ToF)
- nuclear magnetic resonance spectroscopy (NMR)
- size exclusion chromatography (SEC)

End group analysis of polymers can be done using these techniques, however, prior knowledge of the end groups is required and only low molecular weight polymers can be analysed.[21]

2.3.1 Size exclusion chromatography

The molecular structure of a polymer is defined by its size, chemical structure and molecular architecture. Polymers are polydisperse molecules and can therefore be characterised by the number average molecular weight (M_n).

SEC, also known as gel permeation chromatography (GPC), is the most widely used method for separating polymers from one another according to molecular size. It is a relative method that is founded on the physical behaviour of the polymer and its interaction with a solvent. Therefore, it is necessary to calibrate the SEC instrument, prior to measurements, with samples of known molecular weight.

Calibrations can be done using narrow or broad polymer standards. The polymer samples are separated according to their hydrodynamic volume which, in the case of homopolymers, is related to the molecular weight. The accuracy of the molecular weight average and polydispersity is influenced by the number of calibration standards, as well as the molecular weight range that the standards cover. Analysis of copolymers is, however, more difficult and therefore multiple detectors are used. This is because the hydrodynamic volume is influenced by molecular weight and chemical composition.[18,49]

The average functionality of polymers can be expressed quantitatively as the number average functionality (F_n), where F_n is the ratio between the total number of functional groups and the total number of molecules in a reaction system.[49]

As with all chromatographic techniques, there is a stationary phase and a mobile phase. A sample is dissolved in a solvent (mobile phase) which passes through a porous column (stationary phase) and the separation is measured by detectors, such as UV and refractive index (RI) detectors. Typically, the stationary phase is porous silica or a highly cross-linked organic gel. Some commonly used solvents include THF, chloroform and toluene.[50]

2.3.2 Infra red and ultraviolet-visible spectroscopy

IR and UV-visible spectroscopy can be used for end group analysis of polymers synthesised by CRP. The kinetics of initiation of polymerisation can also be examined using these techniques. However, IR and UV-visible spectroscopy should only be used in cases where the chromophores are in a clear region of the spectrum, and the absorptions must be sensitive to the chromophores so that end groups can be differentiated from the initiator and its by-products. Garcia-Rubio *et al* showed for polymerisation of styrene and methyl methacrylate initiated by BPO that the aliphatic and aromatic benzoate groups can be examined using UV spectroscopy.[21] UV spectroscopy is also useful to detect thiocarbonylthio chromophores of RAFT polymers, as the end group absorbs strongly in UV in the range 300–310 nm.[51]

2.3.3 Nuclear magnetic resonance spectroscopy

NMR is a powerful analytical technique used to study polymers. Several nuclei (^{1}H, ^{13}C, ^{29}Si, ^{19}F, ^{31}P and ^{15}N) can be observed in solution NMR for the elucidation of polymeric materials. Of these nuclei, the most predominantly used are ^{1}H and ^{13}C, due to their sensitivity. When preparing NMR samples, the sample to be investigated must be dissolved in a deuterated solvent in order to observe a locked signal (i.e. the magnetic field is locked to ensure field stability).

Some commonly used deuterated solvents include acetone-d_6, benzene-d_6, chloroform-d, dimethyl sulfoxide-d_6 and toluene-d_8.[52] The degree of structure elucidation relies on the resolution of the NMR spectrum. Several factors influence the resolution, such as concentration, solvent, temperature, nuclei, linewidth and the field strength of the spectrometer.[21,53,54] The main drawback to using NMR to characterise polymers is that of resonance assignments.

A variety of techniques are available to aid this, such as chemical shift predictors and two-dimensional NMR. Nevertheless, NMR is a useful means for characterisation of chain architecture and end groups.

In polymers, there are relatively few end groups relative to the polymer chain. Consequently, the resonance signals of the polymer backbone can often overlap those of the end groups. However, the signal intensity of the end groups is relative to the targeted molecular weight, and will alter accordingly. That is, the relative signal intensity of the end groups increases with decreasing molecular weight. Another method of end group analysis is to label the end group with NMR active nuclei.[54] Once the end groups have been assigned, there are a few parameters that can be evaluated. The assigned end groups can be used to calculate conversion,[19,41,55] molecular weight,[55,56] and functionality.[9,41] *In situ* ^{1}H NMR can be used to study the kinetics of a polymerisation system.[13,20,57-60]

2.3.4 Mass spectrometry

Mass spectrometry can be used to analyse polymers prepared by various CRP techniques. Polymers can be examined by mass spectrometry to identify the mass of repeat units, verify the structure of end groups and determine molecular weight and polydispersity. Characterisation of polymers by mass spectroscopic techniques such as fast atom bombardment mass spectrometry (FAB-MS) and gas chromatography–mass spectrometry (GCMS) were conventional methods for the analysis of polymers with relatively low molecular weight.

More recently, soft ionisation techniques, MALDI-ToF and ESI, have become popular for analysing polymers with high molecular weights. Each mass spectrometry technique has its advantages and its disadvantages.[61-63] The choice between MALDI-ToF and ESI depends on the molecular weight range of the polymers to be analysed. ESI mass analysers usually have a m/z range of 1–2000,[64] whereas MALDI-ToF can be used to analyse polymers with extremely high molecular weights.

Proteins of around 300 000 Da and synthetic polymers up to 1 500 000 Da have been analysed by MALDI-ToF.[62,65,66] Conversely, ESI is better suited to analyse monodisperse biopolymers. This is due to the fact that the mass distribution in ESI spectra are obscured by multiply charged ion distributions (salt cluster ions).[21,61-63,67]

Sample preparation is required prior to any analysis. For MALDI-ToF analysis, the polymer and matrix are dissolved in an appropriate solvent (e.g. THF) and often a

metal ion is added. There are many different matrices that can be used. Some of the most commonly used matrices include dithranol (1,8,9-trihydroxy-anthracene), DHB (2,5-dihydroxy-benzoic acid), IAA (3-β-indoleacrylic acid), HABA (2-(4-hydroxy-phenylazo) benzoic acid) and THAP (2,4,6-trihydroxy acetophenone hydrate). Most polymers with heteroatoms are able to cationise with the addition of sodium or potassium salts, whilst polymers without heteroatoms can cationise when silver or copper salts are added.

The spectra produced by a MALDI-ToF spectrometer are reasonably clear because only singly charged molecules are observed. During MALDI-ToF analysis, there is almost no fragmentation.[65-67] However, polymers prepared by RITP do exhibit some fragmentation of dormant chains due to the labile nature of the end groups.[61] This fragmentation is particularly prominent for polystyrene, as shown by Nonaka.[68] For accurate analysis of end groups using MALDI-ToF spectrometry, polymers should be less than 5000 $g.mol^{-1}$. The sensitivity of this technique is dependant on the stability of the polymer and its ability to cationise.[61-63,65]

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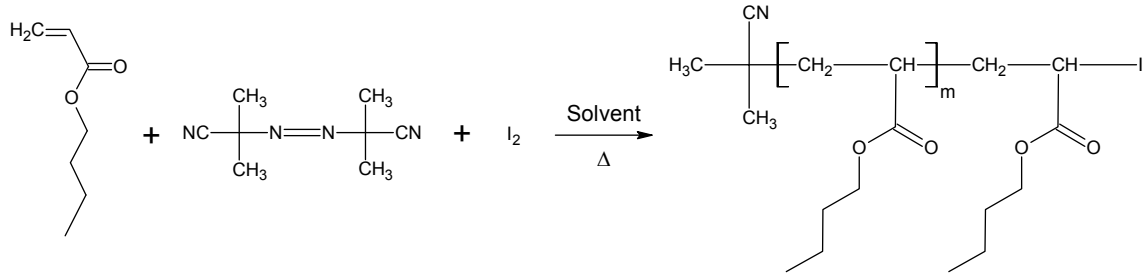
3 SYNTHESIS OF POLY(N-BUTYL ACRYLATE)

3.1 Introduction

The main objectives of this work were to synthesise poly(n-butyl acrylate) (PnBA) by RITP and to investigate the chemical structures of chain transfer agents formed during the inhibition period as well as the polymers formed. In addition to this, the molecular weight control of this RITP system was also investigated. A simplified mechanism of n-butyl acrylate polymerisation by RITP is shown in Scheme 3.1.



Scheme 3.1: The synthesis of poly (n-butyl acrylate) by RITP.

In RITP of acrylates, the amount of dead chains increases after a high monomer conversion (>95%) is reached.[1] Therefore, to limit the amount of dead chains formed, our experiments were run for 22 hours. The temperature range was chosen to avoid the formation, as far as possible, of mid-chain radicals (MCRs). These radicals have been reported to form at temperatures above 80°C, but the likelihood of their formation has not been ruled out for lower temperatures. [2-5]

In this study, n-butyl acrylate was polymerised by RITP at 70°C using different [AIBN]/[I_2] ratios while targeting molecular weights in the range of 1500 – 8000 g.mol^{-1}. The molecular weight of the polymers was determined by SEC and the monomer conversion determined by ^{1}H NMR. Chemical structures of compounds formed during RITP were examined using ^{1}H NMR and substantiated by mass spectrometry.

3.2 Polymerisation of n-butyl acrylate

3.2.1 Materials

N-butyl acrylate (Sigma-Aldrich) was washed with an aqueous solution of sodium hydroxide and then washed with distilled de-ionised water. The monomer was dried with anhydrous magnesium sulphate over night and distilled under vacuum and stored in a refrigerator at – 5 °C. 2,2'-Azobis(isobutyronitrile) (AIBN, Riedel de Haën) was recrystallised from methanol, dried under vacuum and stored in a refrigerator at – 5 °C. Toluene (Sigma-Aldrich 99%), deuterated benzene (C_6D_6, Sigma-Aldrich 99%) and iodine (I_2, ACROS Organics) were used as received.

3.2.2 Synthesis of poly(n-butyl acrylate) by reverse iodine transfer polymerisation

In a typical homopolymerisation reaction, n-butyl acrylate (1.35 g, 1.05 x 10^{-2} mol), toluene (1.73g, 1.88 x 10^{-2} mol), AIBN (67.2 mg, 4.09 x 10^{-4} mol), iodine (61.3 mg, 2.42 x 10^{-4} mol) and a magnetic stirrer were added into a Schlenk flask and mixed by magnetic stirring. The mixture was then degassed by three successive freeze-pump-thaw cycles and then back filled with argon. The flask was then immersed in an oil bath that was preheated to 70°C. The polymerisation was carried out with magnetic stirring in the dark. After 22 hours, the polymerisation was halted by removing the flask from the oil bath and placing the flask in a container of ice. The polymer was then precipitated from methanol, filtered and dried in a vacuum oven over night.

Homopolymerisation of n-butyl acrylate was also followed by *in situ* ^{1}H NMR at 70 °C in benzene-d_6. The ^{1}H NMR spectra were obtained on a Varian Unity INOVA 400 MHz spectrometer, with a pulse width of 3 μs (40°) and a 4 second acquisition time. The sample NMR tube was inserted into the NMR spectrometer and a reference spectrum was acquired at 25°C. The temperature of the NMR spectrometer was then equilibrated at 70°C for 30 minutes before the NMR tube was reinserted into the spectrometer. The first spectrum was acquired 8 – 15 minutes after the sample was reinserted. Thereafter, spectra were obtained by taking 15 scans every 15 minutes for 41 hours.

All NMR spectra were processed using ACD Labs 10.0 ^{1}H NMR processor®. The spectra were phased automatically, whereas baseline correction and integration were done manually. From the processed spectra it was possible to construct concentration profiles relative to an insert of a DMF reference.

In a typical *in situ* ^{1}H NMR polymerisation reaction, n-butyl acrylate (2.00 g, 19.2 x 10^{-3} mol), AIBN (99.5 mg, 6.06 x 10^{-4} mol), iodine (90.5 mg, 3.57 x 10^{-4} mol) were weighed carefully and mixed thoroughly in a glass vial. The mixture (0.25 mL) was introduced into a J Young NMR Tube, followed by the addition of 0.25 mL of toluene-d_8. An internal reference of 20 µL DMF was inserted into the J Young NMR tube. The sample in the NMR tube was degassed by three successive freeze-pump-thaw cycles and then filled with UHP argon gas.

3.3 Analyses of polymer samples

3.3.1 SEC analysis

SEC was carried out using a SEC instrument equipped with a Waters 717plus Autosampler, Waters 600E system controller and a Waters 610 fluid unit. For detection, a Waters 2414 differential refractometer was used. Two PLgel 5 µm Mixed-C columns and a PLgel 5 µm guard column were used. Polymer samples of 2 mg were dissolved in 2 mL of THF and 100 µL of the sample volume was injected into the column, with the oven temperature kept at 30 ºC. The eluent that was used was THF (HPLC grade, BHT stabilised) at a flow rate of 1mL/min. Calibrations were done using narrow polystyrene standards with a molecular range of 800–2 x 10^{6} g.mol^{-1}. Data obtained from SEC is reported as polystyrene equivalents.

3.3.2 NMR analysis

^{1}H NMR spectra were obtained on a Varian Unity INOVA 400 MHz spectrometer. Chloroform ($CDCl_3$) was the solvent used for crude PnBA samples, whereas benzene-d_6 was used for on-line kinetic ^{1}H NMR.

3.3.3 MALDI-ToF analysis

MALDI-ToF analysis was performed using an AximaToF2 spectrometer (Shimadzu Biotech) equipped with a nitrogen laser (337 nm). The instrument was operated at an accelerating potential of 20 kV. All analyses were carried out in the linear positive mode, with calibrations carried out using a 1450 Da polyethylene glycol (PEG) standard. Samples were dissolved in dioxane with a concentration of 2 $mg.mL^{-1}$. The sample solutions were mixed with a 40 $mg.mL^{-1}$ solution of the matrix (dithranol/dioxane) in THF. The salt used to enhance ion formation was lithium chloride (LiCl), with a concentration of 2 $mg.mL^{-1}$. The analyte-to-matrix ratio was 1:2. 1 µL of the mixture was deposed on a stainless steel target, air-dried, and introduced into the spectrometer.

3.4 Results and discussion

Several RITP experiments were performed using n-butyl acrylate in toluene at 70 °C. Different molecular weights (1500 – 8000 $g.mol^{-1}$) were targeted by varying the [AIBN]/[I_2] ratios. The molecular weight and polydispersity of samples was determined by means of SEC. ^{1}H NMR analysis was performed on crude samples in $CDCl_3$ to determine the monomer conversion.

In RITP, molecular iodine is used to generate iodinated chain transfer agents $A–M_n–I$ (n≥0) *in situ*, where *A* represents the AIBN moiety (-C(CN)(CH_3)$_2$), *M* represents the monomer unit, *n* stands for the mean number degree of polymerisation and *I* stands for the iodine atom. Thereafter, the system is governed by a DT mechanism, which affects molecular weight and the molecular weight dispersity.[6-8] The inhibition time for n-butyl acrylate synthesised by RITP can be shortened by increasing the temperature, whilst still maintaining reasonable control over the molecular weight of the polymer.[9] However, this may result in the formation of MCRs which could hamper the elucidation of structures for this particular RITP system as well as complicate the polymerisation mechanism.[2-4]

The structures of AIBN, *A–I* and *A–A* respectively were examined by ^{1}H NMR prior to running a polymerisation reaction. The *A-I* adduct is formed from a combination of initiator radicals (*A*•) with iodine, while the *A-A* adduct is formed by the combination of two free initiator radicals.

For the ^{1}H NMR experiment, a solution of AIBN and iodine in deuterated benzene (C_6D_6) was heated to 70 °C. The peak assignments are shown in Figure 3.1; AIBN (δ=1.15 ppm), *A–I* (δ=1.54 ppm) and *A–A* (δ=1.03 ppm). These assignments are comparable with those observed in literature for a solution of AIBN and iodine in deuterated benzene (C_6D_6) at 70 °C.[9] The chemical shifts referring to the CH_3 group of *A*. The peaks shift slightly, AIBN (δ=1.31 ppm), *A–I* (δ=1.77 ppm) and *A–A* (δ=1.33 ppm), when n-butyl acrylate is added to the reaction mixture.

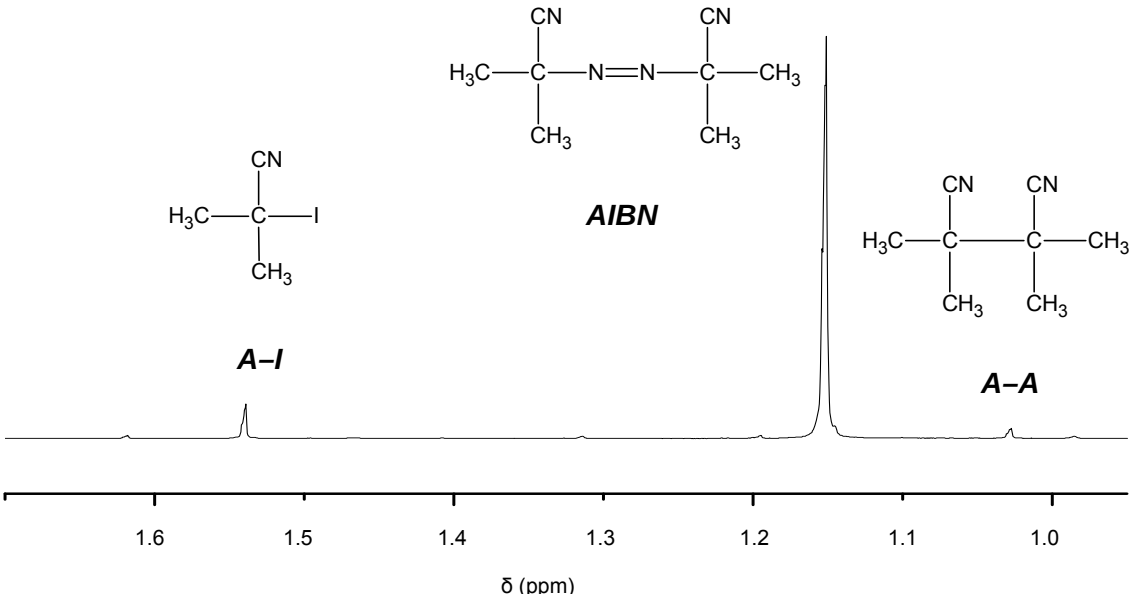


Figure 3.1: ^{1}H NMR spectrum of a solution of AIBN and iodine in C_6D_6 at 70°C, showing the proton signals for the *A-I* adduct, *A-A* adduct and AIBN respectively.

3.4.1 Molecular weight determination of poly(n-butyl acrylate)

This section involves the calculations and techniques used to determine the molecular weight. ^{1}H NMR and SEC were used to evaluate the molecular weight of PnBA synthesised by RITP. From ^{1}H NMR the conversion is determined using equation 3.1

$$Conversion = \left(1 - \frac{I_1}{I_2}\right) \times 100 \qquad (3.1)$$

where I_1 is the integral of the vinyl protons (($\int CH_2$=CH)/3) of n-butyl acrylate at 5.8 ppm, 6.1 ppm and 6.4 ppm. I_2 is the integral of the methyl protons (($\int CH_3$)/3) of butyl acrylate units at 0.9 ppm (Figure 3.2).

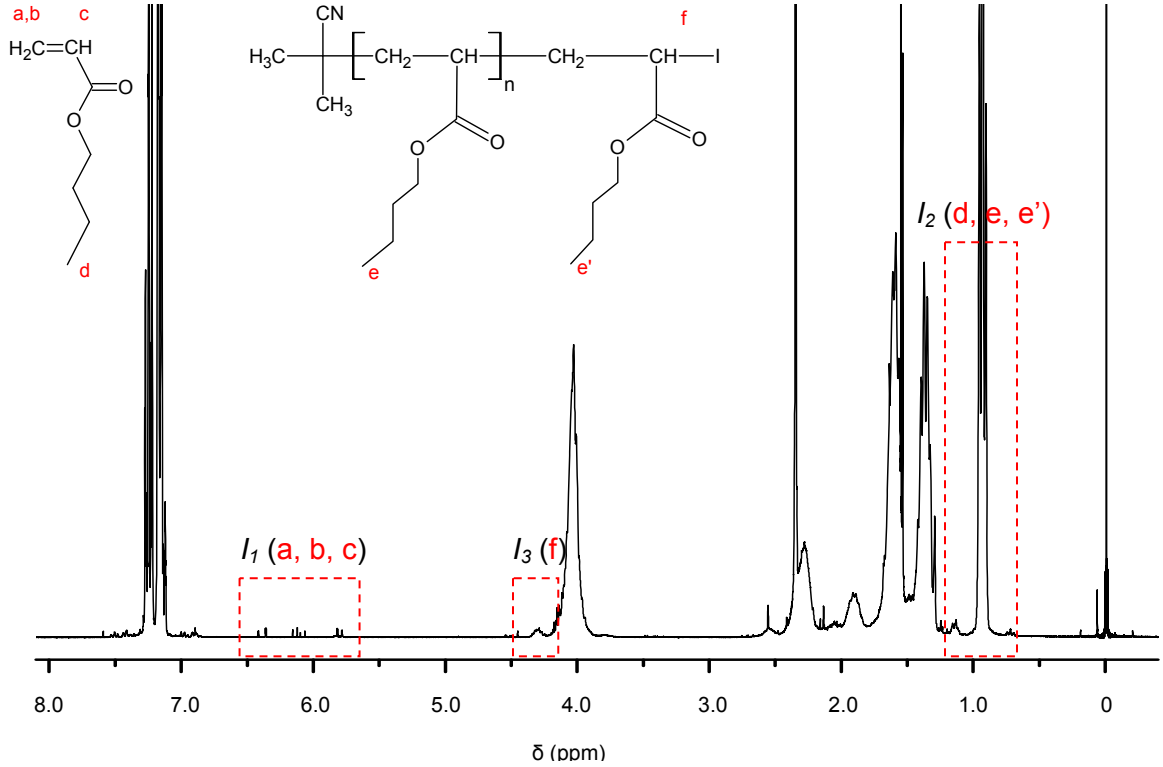


Figure 3.2: ^{1}H NMR spectrum in $CDCl_3$ of n-butyl acrylate polymerised by RITP for 22 hours at 70°C in toluene, showing the regions for the integrals I_1, I_2 and I_3 respectively.

After calculating the conversion, the theoretical molecular weight ($M_{n,\,theory}$) was determined using equation 3.2

$$M_{n,theory} = \frac{m_{butyl\ acrylate} \times conversion}{2 \times n_{iodine}} + M_{chain\ ends} \qquad (3.2)$$

where $m_{butyl\ acrylate}$ is the mass of n-butyl acrylate, n_{iodine} is the number of moles of molecular iodine and $M_{chain\ ends}$ is the combined molecular weight of the cyanoisopropyl and iodine chain ends (195 g.mol^{-1}).[9,10]

Assuming that all the polymer chain ends are living (*A*-M_m-*I*), the molecular weight was determined from ^{1}H NMR ($M_{n,\,NMR}$) using equation 3.3

$$M_{n,NMR} = \frac{(I_2 \times M_{butyl\ acrylate})}{I_3} + M_{chain\ ends} \qquad (3.3)$$

where I_2 is the integral of the methyl protons (($\int CH_3$)/3) of butyl acrylate units at 0.9 ppm, I_3 is the integral of the methine proton (($\int CH$) of PnBA at 4.3 ppm, $M_{butyl\ acrylate}$ is the molecular weight of n-butyl acrylate (128 g.mol^{-1}) and $M_{chain\ ends}$ is the molecular weight of the chain ends (195 g.mol^{-1}).[11] The cyanoisopropyl end group could not be considered, as the peaks are overlapped by polymers signals.

The results obtained from polymerisation of n-butyl acrylate by RITP are shown in Table 3.1.

Table 3.1: Results of n-butyl acrylate polymerisation by means of RITP for 22 hours at 70°C.[a]

Run	[AIBN]/[I_2]	$M_{n,\,target}$ (g.mol^{-1})	$t_{inh,\,theory}$ (h)[b]	$t_{inh,\,exp}$ (h)	Conv (%)[c]	$M_{n,\,theory}$ (g.mol^{-1})[d]	$M_{n,\,SEC}$ (g.mol^{-1})[e]	$M_{n,\,NMR}$ (g.mol^{-1})[f]	PDI
1	1.7	1500	14	18	97	1450	1400	1550	2.00
2	1.7	3000	14	16	98	2950	3450	3700	2.04
3	1.7	8000	14	15	96	7650	8650	8950	2.10
4	1.9	3000	10.5	15	98	2950	3400	3850	2.05
5	1.9	8000	10.5	14	98	7850	8300	9300	2.13

[a] Polymerisation of n-butyl acrylate ([n-butyl acrylate] = 3.01 M) in toluene ([toluene] = 5.39 M) at 70°C with AIBN and molecular iodine.

[b] Calculated by $t_{inhibition,\,theory} = (-\ln((1-[iodine]_0)/f[initiator]_0))/k_d$ where $k_d = 3.71 \times 10\text{-}5\ s^{-1}$ and $f = 0.7$.

[c] Determined by ^{1}H NMR in $CDCl_3$ by conversion = $(1-(I_1/I_2)) \times 100$ where I_1 is the integral of the vinyl protons (($\int CH_2{=}CH$)/3) of n-butyl acrylate at 5.8 ppm, 6.1 ppm and 6.4 ppm. I_2 is the integral of the methyl protons (($\int CH_3$)/3) of butyl acrylate units at 0.9 ppm.

[d] calculated by $M_{n,\,theory} = ((m_{butyl\ acrylate} \times conversion)/(2 \times n_{iodine})) + M_{chain\ ends}$.

[e] Calibrated using polystyrene standard.

[f] Calculated by $M_{n,NMR} = (I_2 \times M_{butyl\ acrylate})/I_3 + M_{chain\ ends}$, where I_2 is the integral of the methyl protons (($\int CH_3$)/3) of butyl acrylate units at 0.9 ppm and I_3 is the integral of the methine proton (($\int CH$) of PnBA at 4.3 ppm.

From these results there is no real evidence to suggest that conversion of the monomer is significantly affected by the [AIBN]/I_2 ratio.

3.4.2 Molecular weight distribution of poly(n-butyl acrylate)

The size exclusion chromatograms of runs 1–3 (Table 3.1) are shown in Figure 3.3. Broad, unimodal distributions are observed with a shift towards higher molecular weights with increasing targeted molecular weights. There is also some low molecular weight tailing. The PDI values of the PnBA samples are in an acceptable range (1.5 – 2.1) for n-butyl acrylate polymerised in by degenerative transfer the presence of AIBN.[9,12]

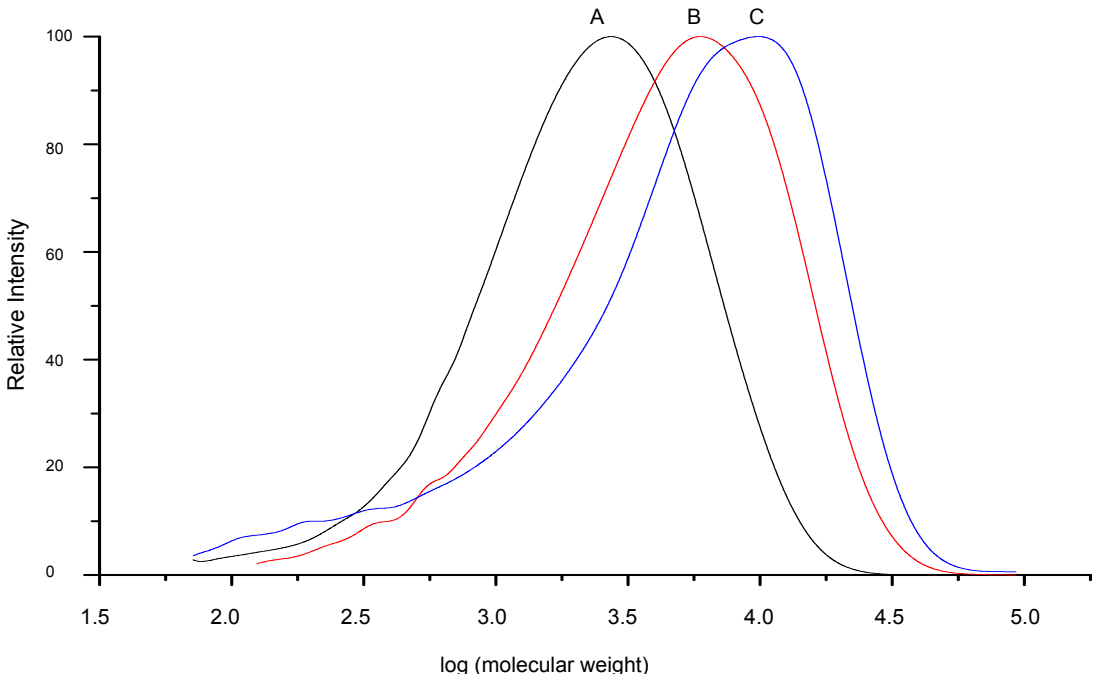


Figure 3.3: Size exclusion chromatograms of polymers prepared by RITP ([n-butyl acrylate] = 3.01 M, [toluene] = 5.39 M) for 22 hours at 70°C: (A): $M_{n,\,theory}$ = 1500 g.mol^{-1}, [AIBN] = 0.17 M and [I_2] = 9.83 x 10^{-2} M, conversion = 97%, $M_{n,\,SEC}$ = 1400 g.mol^{-1}, PDI = 2.00; (B): $M_{n,\,theory}$ = 3000 g.mol^{-1}, [AIBN] = 0.12 M and [I_2] = 6.90 x 10^{-2} M, conversion = 98%, $M_{n,\,SEC}$ = 3450 g.mol^{-1}, PDI = 2.04; (C): $M_{n,\,theory}$ = 8000g.mol^{-1}, [AIBN] = 4.18 x 10^{-2} M and [I_2] = 2.49 x 10^{-2} M, conversion = 96%, $M_{n,\,SEC}$ = 8650 g.mol^{-1}, PDI = 2.10).

3.4.3 The inhibition period and chain transfer agents generated

The mechanism of RITP of n-butyl acrylate was studied further by running kinetic ^{1}H NMR experiments. Several aspects such as monomer conversion and evolution of chain transfer agents were investigated. The theoretical inhibition time is affected by the temperature of the reaction as well as the ratio of initiator to iodine.[9,10,13] The $t_{inh,\ theory}$ was calculated using equation 3.4

$$t_{inhibition,\ \ theory} = \left(-ln \frac{1-[iodine]_0}{f[initiator]_0} \right) \Big/ k_d \qquad (3.4)$$

where $[I_2]_0$ is the initial concentration of molecular iodine in the reaction medium, f is the initiator efficiency with a value of 0.7,[10,14] $[initiator]_0$ is the initial concentration of initiator (AIBN) in the reaction medium and k_d is the rate of dissociation constant. The inhibition times are shown in Table 3.1 and the evolution of the A-I adduct in Figure 3.4.

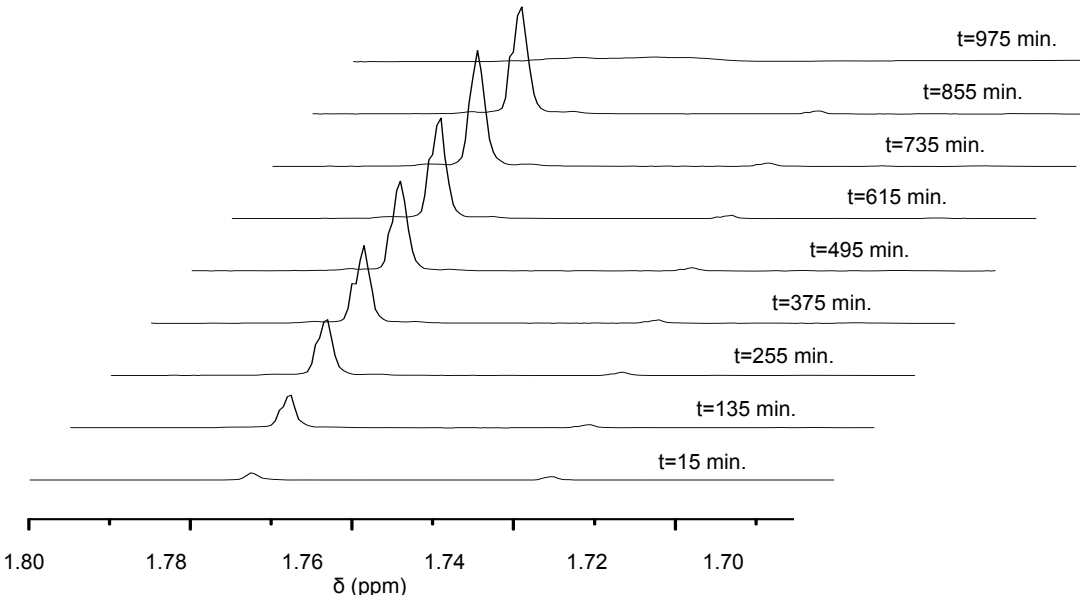


Figure 3.4: Enlarged portion (1.70 – 1.80 ppm) of the ^{1}H NMR spectrum of A-I synthesised during RITP of n-butyl acrylate in toluene-d_8 at 70°C for 22 hours ([n-butyl acrylate] = 3.57 M, [toluene-d_8] = 4.42 M, [AIBN] = 0.14 and $[I_2] = 8.15 \times 10^{-2}$ M). The increase in concentration of the A–I adduct during the inhibition period ($t_{inh,\ exp}$ ~ 360 minutes) is followed by the decrease in concentration at the end of the inhibition period.

The results indicate that the experimental $t_{inh,\ exp}$ is in good agreement with the theoretical times. This suggests that there are very few, if any, side reactions taking place that could result in other CTAs different to the expected being formed.

The inhibition period decreases with increasing molecular weight, as was the case with other acrylates[9,10] and styrene[13] polymerised by RITP. During the inhibition period, molecular iodine is reacted with initiator radicals (AIBN) to form chain transfer agents (*A–I* adduct) *in situ*. It can be seen from Figure 3.3 that the concentration of the *A–I* adduct increases over time and is consumed towards the end of the inhibition period ($t_{inh,\ exp}$ ~ 900 minutes). The clearly visible drop in the *A–I* adduct concentration, together with the synchronised increase in monomer conversion, is indicative of the end of the inhibition period. The conversion *versus* time profile for the monomer and evolution of the *A–I* adduct concentration are shown in Figure 3.5.

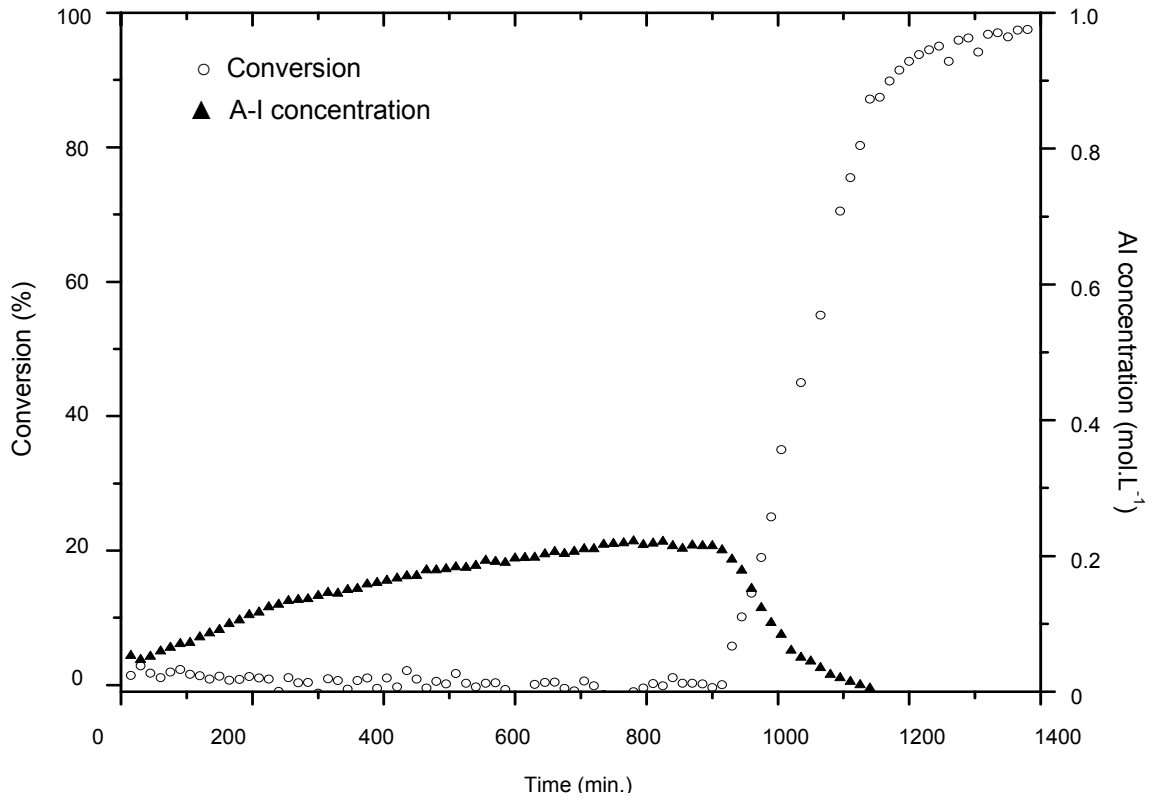


Figure 3.5: Evolution of n-butyl acrylate conversion and the concentration of the A–I adduct ($t_{inh,\ exp}$ ~ 360 minutes) for the synthesis of PnBA by RITP at 70°C for 22 hours ([n-butyl acrylate] = 3.57 M, [toluene-d_8] = 4.42 M, [AIBN] = 0.14 and [I_2] = 8.15 x 10^{-2} M).

The polymerisation period for n-butyl acrylate synthesised by RITP is quite fast (conversion of 6% to 95% in approximately 360 minutes). Similar behaviour is observed for RITP of methyl acrylate[9] as well as CRP using alkyl iodides.[12]

The evolution of the initiator concentration is shown in Figure 3.6. The decrease in concentration is expected as iodine is reacted with free initiator radicals during the inhibition period.

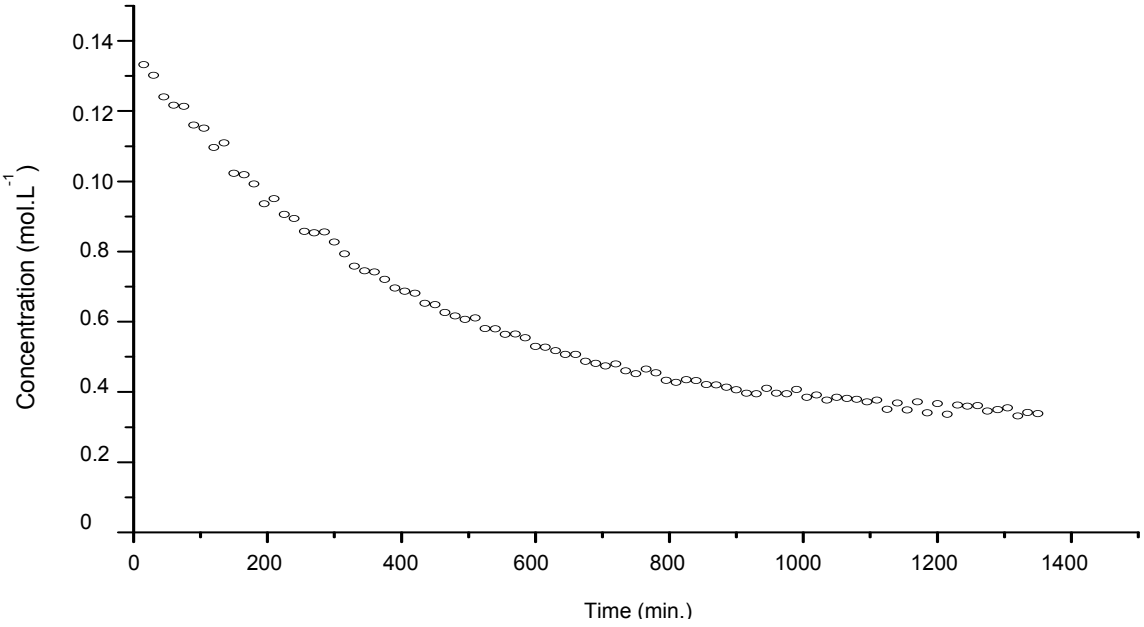


Figure 3.6: Evolution of AIBN concentration during the synthesis of PnBA by RITP at 70°C for 22 hours ([n-butyl acrylate] = 3.57 M, [toluene-d_8] = 4.42 M, [AIBN] = 0.14 and [I_2] = 8.15 x 10^{-2} M).

3.4.4 Mass spectrometry of poly(n-butyl acrylate)

The structures identified in the ^{1}H NMR spectra of PnBA samples prepared by RITP were substantiated using MALDI-ToF analysis in the linear mode. As was the case with the polystyrene samples, the terminating ends of the PnBA samples would be expected to be iodinated, but are instead fragmented by the salt due to the labile nature of the end group. Hence, this fragmentation leaves the structures unsaturated due to the abstraction of iodine.[13] The MALDI-ToF spectrum of PnBA synthesised by RITP is shown in Figure 3.7 and an enlarged portion of this spectrum is shown in Figure 3.8.

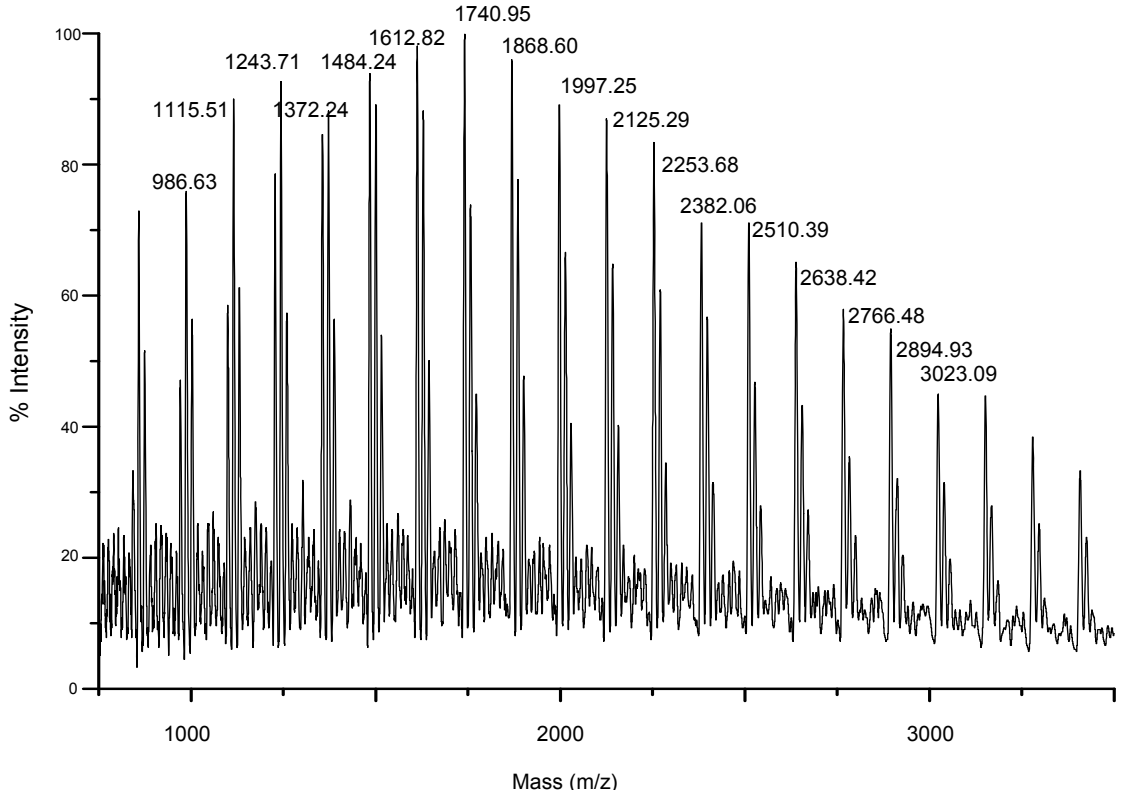


Figure 3.7: The MALDI-ToF spectrum (linear mode) of PnBA synthesised by RITP at 70°C for 22 hours ([n-butyl acrylate] = 3.01 M, [toluene] = 5.39 M, [AIBN] = 0.12 M and [I_2] = 6.90 x 10^{-2} M, conversion = 98%, $M_{n,\,SEC}$ = 3450 g.mol^{-1}, PDI = 2.04).

The structures, together with the predicted masses are listed in Table 3.2, where M_m represents the polymer backbone and the AIBN moiety end group is represented by the letter *A*.

Table 3.2: Peak assignments for MALDI-ToF analysis (linear mode) of n-butyl acrylate synthesised by RITP at 70°C in toluene for 22 hours.

Structure	m	Experimental mass (m/z)	Theoretical mass (m/z)
A–M_{m-1}–$C_7H_{12}O_2$, -HI (Li^+)	14	1997.25	1996.32
A–M_{m-1}–$C_7H_{12}O_2$, -HI (Na^+)	14	2013.68	2012.29
A–M_{m-1}–$C_7H_{12}O_2$, -HI (K^+)	14	2029.09	2028.26

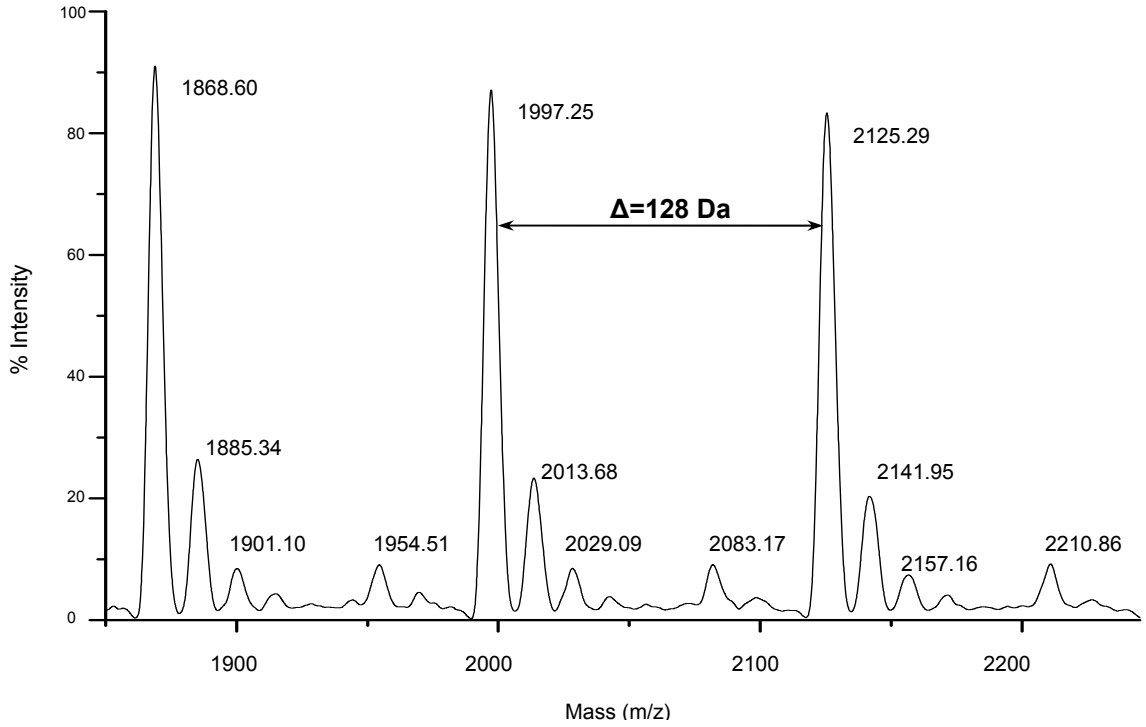


Figure 3.8: Enlarged portion of the MALDI-ToF spectrum (linear mode) of PnBA synthesised by RITP at 70°C for 22 hours ([n-butyl acrylate] = 3.01 M, [toluene] = 5.39 M, [AIBN] = 0.12 M and $[I_2]$ = 6.90 x 10^{-2} M, conversion = 98%, $M_{n,\,SEC}$ = 3450 g.mol^{-1}, PDI = 2.04).

In the spectrum we observe three populations. The mass increment between the major populations of PnBA samples is 128 Da, which corresponds to the monomer repeat unit for n-butyl acrylate. The major population has the structure $A–M_{m-1}–CH=C(C_5H_9O_2)H$ (Figure 3.9). The structure appears at m/z of 1997.25, 2013.68 and 2029.09, respectively.

Each of these populations is the unsaturated structure with a mass difference of 16 Da, according to the mass difference between Li and Na as well as Na and K. Although LiCl was the salt chosen for the analyses, sodium and potassium salts are ubiquitous and are the resulting species are often seen in MALDI-ToF spectra. The unsaturated structure has been reported in literature for RITP of methyl acrylate.[9]

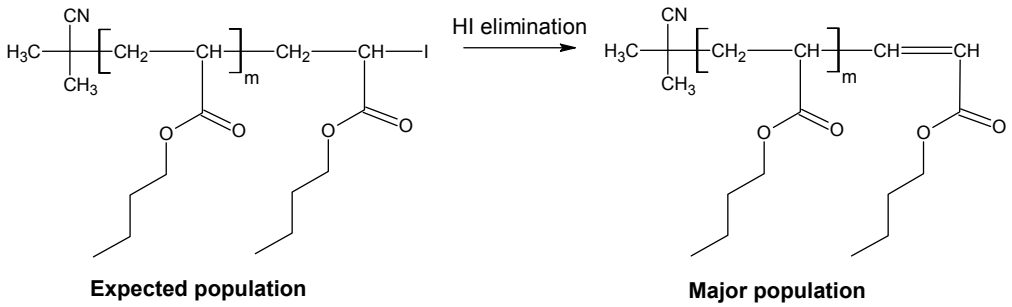


Figure 3.9: The structure identified from the MALDI-ToF analysis of PnBA synthesised by RITP for 22 hours at 70°C in toluene.

3.4.5 End group functionality of poly(n-butyl acrylate)

The functionality of polymers synthesised by RITP is a parameter of great interest. One would expect to see a high percentage of living chains for PnBA synthesised by RITP (> 90%), since this is the case for methyl acrylate[1] and methyl methacrylate.[10] Using the PREDICI simulation program, Tonnar *et al*.[1] showed in simulations for RITP of methyl acrylate that the percentage of dead chains is independent of the targeted molecular weight, but increases when increasing the ratio of initiator to iodine.

The functionality of polymers can be evaluated using NMR. However, these calculations can not be used in the case of PnBA, since the cyanoisopropyl (α end group) protons and methine proton (ω end group) signals are overlapped by polymer signals in the ^{1}H NMR spectrum.

3.5 Conclusions

Previously studied acrylates polymerised by RITP include methyl acrylate[9] and methyl methacrylate[10], with a brief study on n-butyl acrylate.[9] Our studies of n-butyl acrylate polymerised by RITP have been more detailed than previous reports. The polymer was prepared under similar conditions to those reported in literature and similar observations were made. The experimental inhibition times are in reasonable agreement with the calculated theoretical times and there are no significant side reactions taking place during the inhibition period, where the *A-I* and *A-*M_n*-I* transfer agents are generated. Polymers with the general structure *A-*M_m*-I* are formed during the polymerisation stage. MALDI-ToF analysis confirmed the structure, but an unsaturated structure was observed due to fragmentation of the labile iodinated end group. The functionality analysis of PnBA was not possible using NMR, as the end group signals are overlapped by polymer signals.

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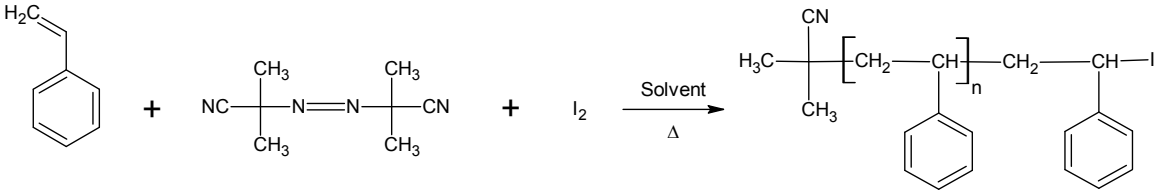
4 SYNTHESIS OF POLYSTYRENE

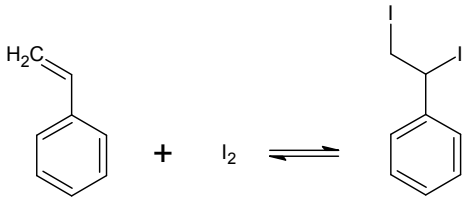
4.1 Introduction

The main objectives of this work were to prepare polystyrene by reverse iodine transfer polymerisation (RITP) in order to investigate the chemical structures of chain transfer agents formed during the inhibition period and the resultant polymer, as well as to establish the molecular weight control and livingness of the RITP system. The simplified mechanism for RITP of styrene is shown in Scheme 4.1.



Scheme 4.1: The synthesis of polystyrene by RITP.

Studies of styrene polymerisation by RITP have been reported by Tonnar *et al*.[1] and Shiman *et al*.[2] It was observed that the mechanism for RITP of styrene differs significantly from that of acrylates and methacrylates. The experimental inhibition times reported were much shorter than the theoretical times. Although it was speculated that the short inhibition period is attributed to the formation of 1,2-diiodo-ethyl benzene (Scheme 4.2), which depletes free iodine, no experimental proof has been reported in literature of this compound being formed during the inhibition period of RITP. This side reaction does not, however, interfere with the formation of iodinated chain transfer agents, as it is reversible and iodine is liberated from the 1,2-diiodo-ethyl benzene throughout the polymerisation.



Scheme 4.2: The reversible formation of 1,2-diiodo-ethyl benzene.

In this study, polystyrene was synthesised by RITP at 70°C, where various [AIBN]/[I_2] ratios were used and molecular weights from 1500 – 8000 g.mol^{-1} were targeted. Molecular weight was determined by using SEC and ^{1}H NMR was used to determine monomer conversion. The chemical structures of CTAs and polymers formed during RITP were studied using ^{1}H NMR and confirmed by means of mass spectrometry. The experimental iodine functionality of the polystyrene samples were investigated by ^{1}H NMR and compared to calculated theoretical values.

4.2 Polymerisation of styrene

4.2.1 Materials

Styrene (Sigma-Aldrich) was washed three times with an aqueous solution of sodium hydroxide followed by distilled de-ionised water. The monomer was then dried with anhydrous magnesium sulphate over night and distilled under reduced pressure and stored in a refrigerator at – 5 °C. 2,2'-Azobis(isobutyronitrile) (AIBN, Riedel de Haën) was recrystallised from methanol, dried under vacuum and stored at – 5 °C in a refrigerator. Toluene (Sigma-Aldrich 99%), deuterated toluene (C_7D_8, Sigma-Aldrich 99%) and iodine (I_2, ACROS Organics) were used as received.

4.2.2 Synthesis of polystyrene by reverse iodine transfer polymerisation

In a typical homopolymerisation reaction, styrene (1.00 g, 9.60 x 10^{-3} mol), toluene (1.25g, 1.36 x 10^{-2} mol), AIBN (49.7 mg, 3.03 x 10^{-4} mol), iodine (45.3 mg, 1.78 x 10^{-4} mol) and a magnetic stirrer were added into a Schlenk flask and mixed by magnetic stirring. The mixture was then degassed by three successive freeze-pump-thaw cycles and then back filled with argon. The flask was then immersed in an oil bath that was preheated to 70°C. The polymerisation was carried out with magnetic stirring in the dark. After 24 hours, the polymerisation was halted by removing the flask from the oil bath and placing the flask in a container of ice. The polymer was dried in a vacuum oven over night.

Styrene homopolymerisation was also followed by *in situ* ^{1}H NMR at 70 °C in toluene-d_8. The ^{1}H NMR spectra were obtained on a Varian Unity INOVA 400 MHz spectrometer, with a pulse width of 3 μs (40°) and a 4 second acquisition time.

The sample NMR tube was inserted into the NMR spectrometer and a reference spectrum was acquired at 25°C. The temperature of the NMR spectrometer was then equilibrated at 70°C for 30 minutes before the NMR tube was reinserted into the spectrometer. The first spectrum was acquired 8 – 15 minutes after the sample was reinserted. Thereafter, spectra were obtained by taking 15 scans every 15 minutes for 23 hours.

All NMR spectra were processed using ACD Labs 10.0 ^{1}H NMR processor®. The spectra were phased automatically, whereas baseline correction and integration were done manually. From the processed spectra it was possible to construct concentration profiles relative to an insert of a DMF reference.

In a typical *in situ* ^{1}H NMR polymerisation reaction, styrene (2.00 g, 19.2 x 10^{-3} mol), AIBN (99.5 mg, 6.06 x 10^{-4} mol), iodine (90.5 mg, 3.57 x 10^{-4} mol) were weighed carefully and mixed thoroughly in a glass vial. The mixture (0.25 mL) was introduced into a J Young NMR Tube, followed by the addition of 0.25 ml of toluene-d_8. An internal reference of 20 µL DMF was inserted into the J Young NMR tube. The sample in the NMR tube was degassed by three successive freeze-pump-thaw cycles and then filled with UHP argon gas.

4.3 Analyses of polymer samples

4.3.1 SEC analysis

SEC was carried out using a SEC instrument equipped with a Waters 717plus Autosampler, Waters 600E system controller and a Waters 610 fluid unit. For detection, a Waters 2414 differential refractometer was used. Two PLgel 5 µm Mixed-C columns and a PLgel 5 µm guard column were used. Polymer samples of 2 mg were dissolved in 2 mL of THF and the sample volume injected into the column was 100 µL, with the oven temperature kept at 30 ºC. The eluent that was used was THF (HPLC grade, BHT stabilised) at a flow rate of 1mL/min. Calibrations were done using narrow polystyrene standards with a molecular range of 800–2 x 10^{6} g.mol^{-1}. Data obtained from SEC is reported as polystyrene equivalents.

4.3.2 NMR analysis

^{1}H NMR spectra were obtained on a Varian Unity INOVA 400 MHz spectrometer. The solvent used for crude polystyrene samples was chloroform ($CDCl_3$), with toluene-d_8 being used for on-line kinetic ^{1}H NMR experiments.

4.3.3 MALDI-ToF analysis

MALDI-ToF analysis was performed using an AximaToF2 spectrometer (Shimadzu Biotech) equipped with a nitrogen laser (337 nm). The instrument was operated at an accelerating potential of 20 kV. All analyses were carried out in the linear positive mode, with calibrations carried out using a 1450 Da polyethylene glycol (PEG) standard. Samples were dissolved in dioxane with a concentration of 2 mg.mL^{-1}. The sample solutions were mixed with a 10 mg.mL^{-1} solution of the matrix (dithranol/dioxane) in THF. The salt used to enhance ion formation was copper chloride (CuCl), with a concentration of 2 mg.mL^{-1}. The analyte-to-matrix ratio was 1:2. 1 µL of the mixture was deposited on a stainless steel target, air-dried, and introduced into the spectrometer.

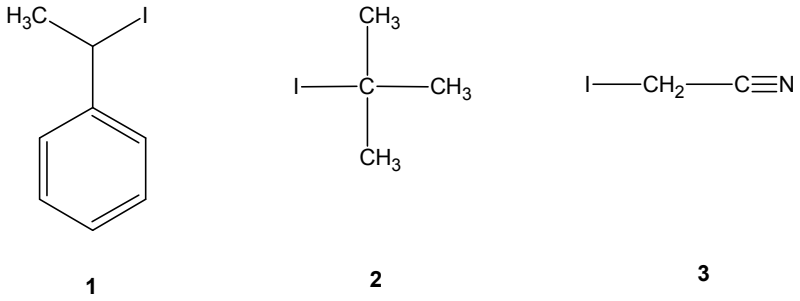
4.4 Results and discussion

Several RITP experiments with styrene were run in toluene at 70 °C. Different [AIBN]/[I_2] ratios (1.5, 1.7 and 2.0) were used for targeted molecular weights of 1500, 3000, 5500 and 8000 g.mol^{-1} respectively. The molecular weight and polydispersity of samples were determined by SEC. The monomer conversion of styrene was determined by ^{1}H NMR by analysing the crude polystyrene samples in deuterated chloroform ($CDCl_3$).

There is an inhibition period in RITP where iodinated chain transfer agents are generated *in situ*. The polymerisation period of RITP is governed by a degenerative transfer (DT) mechanism. The DT mechanism plays a key role, as it influences the molecular weight and the molecular weight dispersity. The important parameters are (1) the concentration of the transfer agent, which controls the molecular weight and (2) the chain transfer rate constant (k_{ex}) which affects the PDI (higher k_{ex} values give rise to lower PDI values).[3-5]

A study of several alkyl iodides (with a general structure of R–I) used in styrene polymerisation was reported by Gaynor *et al*.[4] The study showed that chain transfer agents such as (1) 1-phenylethyl iodide (1-PEI), (2) iodoform and (3) iodoacetonitrile resulted in the narrowest PDI values.

The radical formed by the loss of the iodine atom from such chain transfer agents is stabilised by the R group, either by inductive or resonance effects. The structures of these transfer agents are given in Figure 4.1.



1 2 3

Figure 4.1: Structures of chain transfer agents used in DT governed polymerisation of styrene that result in low PDI values (1) 1-phenylethyl iodide (2) iodoform and (3) iodoacetonitrile.

In Section 3.4, the ^{1}H NMR peaks for AIBN, *A–I* and *A–A* were investigated for a solution of AIBN and iodine in deuterated benzene (C_6D_6) at 70 °C. The peak assignments were AIBN (δ=1.15 ppm), *A–I* (δ=1.54 ppm) and *A–A* (δ=1.03 ppm). The peak assignments change slightly when styrene is added to the reaction mixture: AIBN (δ=1.25 ppm), *A–I* (δ=1.65 ppm) and *A–A* (δ=0.90 ppm).

4.4.1 Molecular weight determination of polystyrene

In this section, NMR and SEC were used to determine the molecular weight of PS prepared by RITP. After experiments were completed, crude samples were submitted for ^{1}H NMR and SEC. Using ^{1}H NMR, the monomer conversion was determined with equation 1.1

$$Conversion = \left(1 - \frac{I_1}{I_2}\right) \times 100 \qquad (4.1)$$

where I_1 is the integral of the vinylic protons H_a and H_b (($\int CH_2=C$)/2) of styrene at 5.1 ppm and 5.6 ppm, and I_2 is the integral of the aromatic protons (($\int C_6H_5$)/5) of styrene and the resulting polystyrene (Figure 4.2).[6]

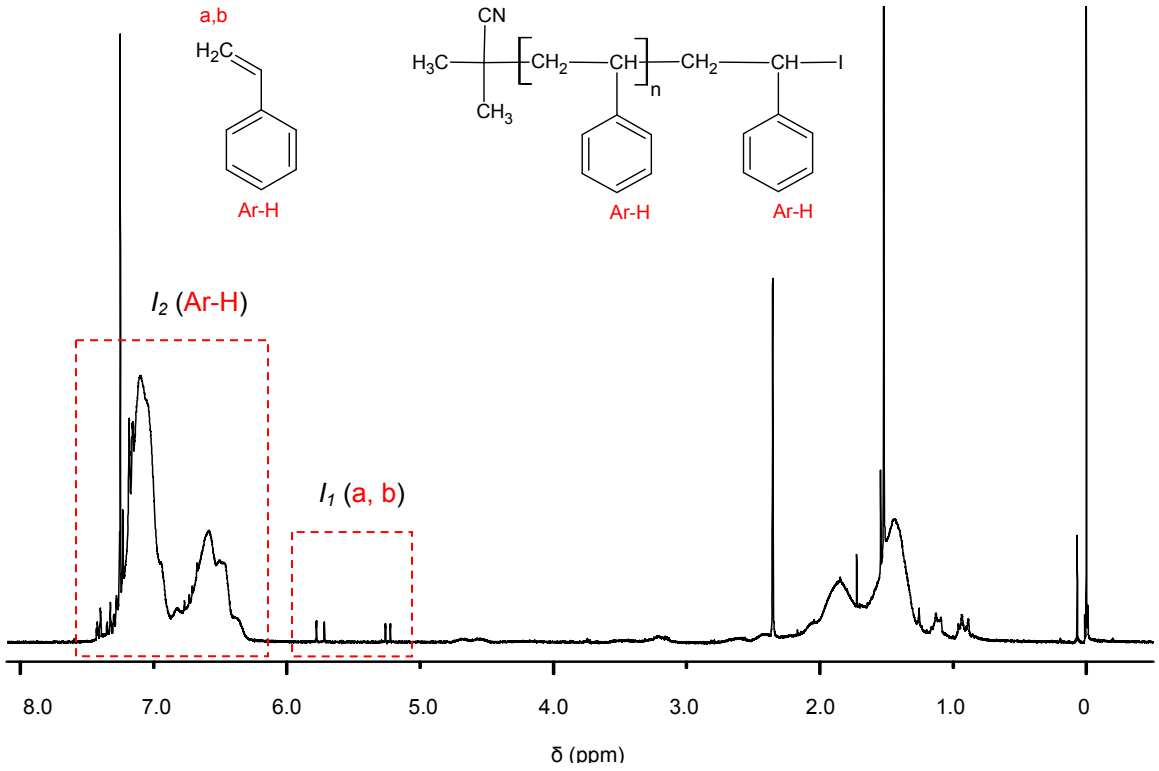


Figure 4.2: ^{1}H NMR spectrum in $CDCl_3$ of styrene polymerised by RITP for 24 hours at 70°C ([styrene] = 3.70 M, [toluene] = 5.44 M, [AIBN] = 0.12 M and [I_2] = 6.86 x 10^{-2} M, conversion = 70%, $M_{n,\,SEC}$ = 2400 g.mol^{-1}, $M_{n,\,NMR}$ = 2500 g.mol^{-1}), showing the regions for the integrals I_1 and I_2 respectively.

From the conversion the theoretical molecular weight ($M_{n,\,theory}$) was calculated using equation 4.2

$$M_{n,theory} = \frac{(m_{styrene} \times conversion)}{(2 \times n_{iodine})} + M_{chain\ \ ends} \qquad (4.2)$$

where $m_{styrene}$ is the mass of styrene, n_{iodine} is the number of moles of molecular iodine and $M_{chain\ ends}$ is the combined molecular weight of the cyanoisopropyl and iodine chain ends (195 g.mol^{-1}).[1,7,8]

In Chapter 3, the molecular weight of PnBA could be calculated from NMR ($M_{n, NMR}$) using equation 3.3. The use of such an equation to calculate molecular weight has been reported for styrene polymerised by iodine mediated polymerisation.[6,9] However, the equation requires the integral of the methine proton. Since there are several polymer species present in RITP of styrene (to be discussed later), the methine end group is not in all polymer species and the value of $M_{n, NMR}$ is therefore not a true reflection of the molecular weight. The cyanoisopropyl end group was also considered, however the same dilemma arises as exhibited for the methine end group. The results for styrene polymerised by RITP at 70°C for 24 hours are shown in Table 4.1.

Table 4.1: Results of styrene polymerisation by RITP for 24 hours at 70°C.[a]

Run	[AIBN]/[I_2]	$M_{n, target}$ ($g.mol^{-1}$)	$t_{inh, theory}$ (h)[b]	$t_{inh, exp}$ (h)	Conv (%)[c]	$M_{n, theory}$ ($g.mol^{-1}$)[d]	$M_{n, SEC}$ ($g.mol^{-1}$)[e]	PDI
1	1.5	8000	23	8	63	5100	4600	1.60
2	1.7	1500	14	8	62	900	700	1.53
3	1.7	3000	14	6	70	2150	2400	1.50
4	1.7	5500	14	5	68	3800	3600	1.58
5	1.7	8000	14	4	65	5250	4850	1.74
6	2.0	8000	9	4	72	5700	5300	1.76

[a] Polymerisation of styrene ([styrene] = 3.70 M) in toluene ([toluene] = 5.44 M) at 70 °C with AIBN and molecular iodine.

[b] Calculated by $t_{inhibition, theory} = (-\ln((1-[iodine]_0)/f[initiator]_0))/k_d$ where k_d = 3.71 x 10-5 s^{-1} and f = 0.7.

[c] Determined by ^{1}H NMR in $CDCl_3$ by conversion = $(1-(I_1/I_2)) \times 100$ where I_1 is the integral of the vinylic protons (($\int CH_2{=}C$)/2) of styrene at 5.1 ppm and 5.6 ppm, and I_2 is the integral of the aromatic protons (($\int C_6H_5$)/5) of styrene and polystyrene.

[d] Calculated by $M_{n, theory} = ((m_{styrene} \times conversion)/(2 \times n_{iodine})) + M_{chain\ ends}$.

[e] Calibrated using polystyrene standard.

The conversion is not particularly high and is usually in the region of 65%. This may be explained by the fact that the concentration of AIBN is low near the end of polymerisation and there are insufficient numbers of initiator radicals to consume the iodine that is liberated from 1,2-diiodo-ethyl benzene (to be discussed later).[1] The monomer conversion also increases with increasing initiator to iodine ratio.

4.4.2 Molecular weight distribution of polystyrene

The M_n values determined by ^{1}H NMR and SEC were in reasonable agreement (Table 4.1). Figure 4.4 shows the refractive index (RI) detector traces of runs 3–5 (Table 4.1). The distributions are unimodal with some low molecular weight tailing and a shift towards higher molecular weights as would be expected with increasing targeted molecular weights.

The PDI values (Table 4.1) of the polystyrene samples are in an acceptable range (1.5 – 1.7) for polymers synthesised by an iodine mediated system.[3,4] The chain transfer agent 1-PEI gives rise to low PDI values for degenerative transfer mediated polymerisation of styrene.[4] The relatively low PDI values obtained for the RITP of styrene may be attributed to the formation of 1-PEI during the inhibition period. In addition to this, the polymerisation of styrene is quite slow, which leads to low PDI values.[10]

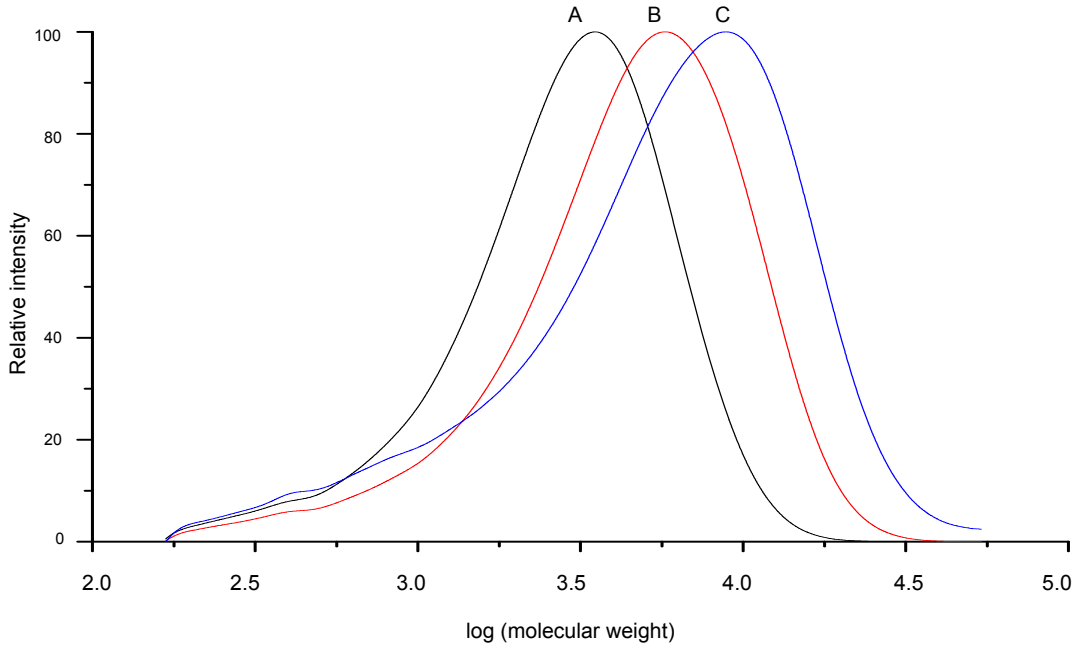


Figure 4.3: Size exclusion chromatograms (RI traces) of polymers prepared by RITP ([styrene] = 3.70 M, [toluene] = 5.44 M) for 24 hours at 70°C: (A): $M_{n,\,theory}$ = 3000 g.mol^{-1}, [AIBN] = 0.12 M and [I_2] = 6.86 x 10^{-2} M, conversion = 70%, $M_{n,\,SEC}$ = 2400 g.mol^{-1}, PDI = 1.50; (B): $M_{n,\,theory}$ = 5500 g.mol^{-1}, [AIBN] = 6.16 x 10^{-2} M and [I_2] = 3.63 x 10^{-2} M, conversion = 68%, $M_{n,\,SEC}$ = 3600 g.mol^{-1}, PDI = 1.58; (C): $M_{n,\,theory}$ = 8000g.mol^{-1}, [AIBN] = 4.19 x 10^{-2} M and [I_2] = 2.46 x 10^{-2} M, conversion = 65%, $M_{n,\,SEC}$ = 4850 g.mol^{-1}, PDI = 1.74).

4.4.3 The inhibition period and chain transfer agents generated

Kinetic ^{1}H NMR experiments were run to investigate the mechanism of RITP of styrene by examining the monomer conversion as well as the inhibition period and the evolution of chain transfer agents therein. The results in Table 4.1 show the experimental inhibition times ($t_{inh,\ exp}$) as well as the theoretical inhibition times ($t_{inh,\ theory}$) for the various experiments. The $t_{inh,\ theory}$ was calculated using equation 4.4

$$t_{inhibition,\ \ theory} = \left(-ln \frac{1 - [iodine]_0}{f[initiator]_0} \right) \Big/ k_d \qquad (4.4)$$

where $[iodine]_0$ is the initial concentration of molecular iodine in the reaction medium, f is the initiator efficiency with a value of 0.7,[7,11] $[initiator]_0$ is the initial concentration of initiator (AIBN) and k_d is the rate of dissociation constant.

During the inhibition period, the initiator decomposes to form radicals that react with molecular iodine to generate CTAs. The end of the inhibition period is marked visually by the change of colour of the mixture from brown to colourless. This change in colour is due to the complete consumption of iodine. According to the RITP mechanism (Section 2.2.4), CTAs are formed and consumed during the inhibition period, which is composed of two stages. In the first stage, iodine is consumed to form the *A*–*I* adduct, whilst in the second stage the *A*–*I* adduct is consumed to form oligomers.[7] The decrease in concentration is indicative of the *A*-*I* adduct forms oligomers, and polymerisation commences as soon as the *A*-*I* adduct is consumed. The evolution of the *A*–*I* adduct over time is shown in Figure 4.4.

The theoretical inhibition time for acrylates and methacrylates is dependant on the temperature and the ratio of initiator to molecular iodine, whilst being independent of the targeted molecular weight.[1,7,8] However, for styrene polymerised by RITP, $t_{inh,\ exp}$ is dependant on the targeted molecular weight.[1] From Table 4.1 it is evident that $t_{inh,\ exp}$ is much shorter than that of $t_{inh,\ theory}$. This will be discussed in more detail at a later stage. It can also be seen that $t_{inh,\ exp}$ decreases with increasing targeted molecular weight.

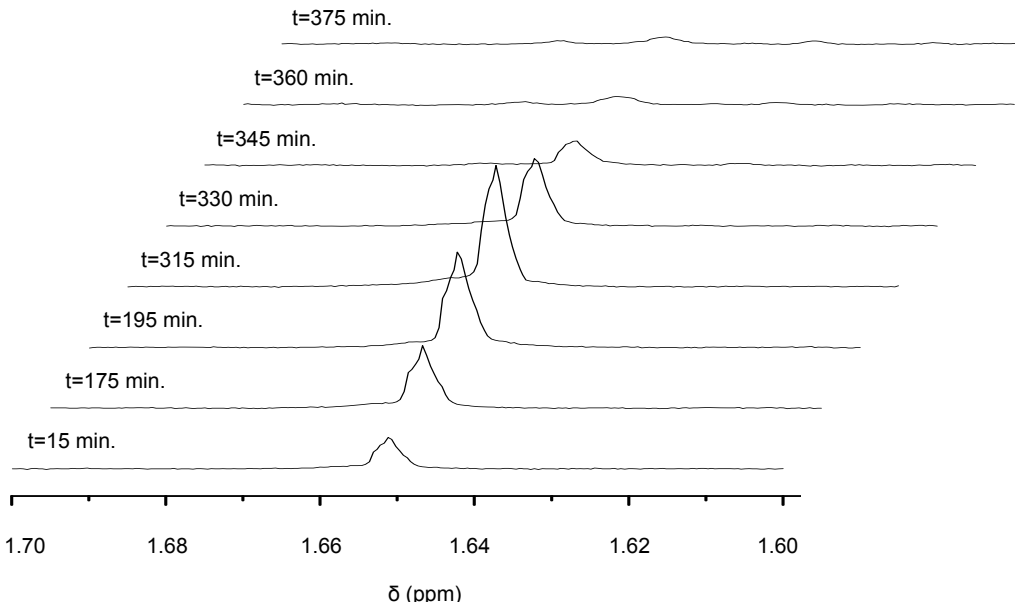


Figure 4.4: The enlarged region (1.60 – 1.70 ppm) of the ^{1}H NMR spectrum of A-I synthesised during RITP of styrene in toluene-d_8 for 23 hours at 70°C ([styrene] = 4.27 M, [toluene-d_8] = 4.82 M, [AIBN] = 0.13 M and [I_2] = 7.91 x 10^{-2} M), showing the formation and consumption of the A–I adduct during the inhibition period ($t_{inh, exp}$ ~ 360 minutes).

The inhibition period can be seen clearly by a conversion *versus* time profile, as shown in Figure 4.5. The plot shows that the *A–I* adduct concentration increases over time to a maximum and then decreases. Upon complete consumption of the *A–I* adduct, one can see the onset of polymerisation. Throughout the polymerisation period, the monomer is being converted, yet, towards the higher end of monomer conversion (>50%) there is a downward curvature (t ~ 700 minutes). This may indicate a reduction in the rate of polymerisation.

The half life ($t_{1/2}$) of AIBN at 70 °C is about 5 hours and the reason for this decrease in the rate of polymerisation may be due to the low concentration of AIBN at the end of polymerisation (Figure 4.6). This implies that there are insufficient initiator radicals to consume the iodine that is liberated from 1,2-diiodo-ethyl benzene, hence the limited monomer conversion.[1]

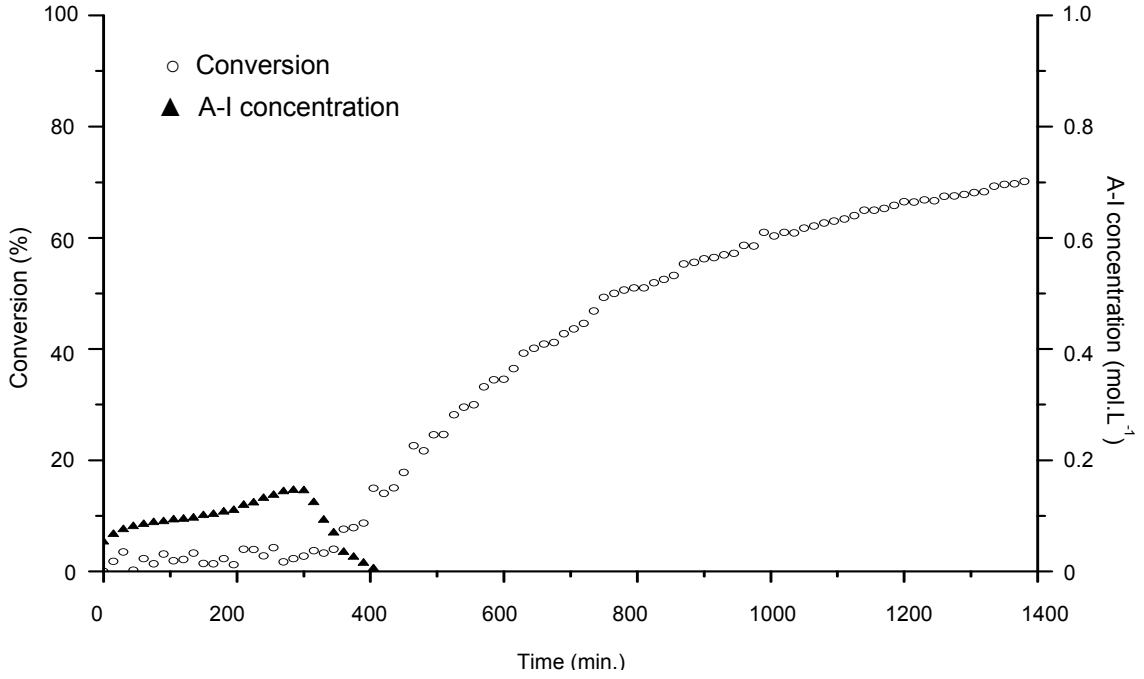


Figure 4.5: The evolution of styrene conversion and the A–I adduct ($t_{inh,\ exp}$ ~ 360 minutes) for the polymerisation of styrene by RITP for 23 hours at 70°C ([styrene] = 4.27 M, [toluene-d_8] = 4.82 M, [AIBN] = 0.13 M and [I_2] = 7.91 x 10^{-2} M).

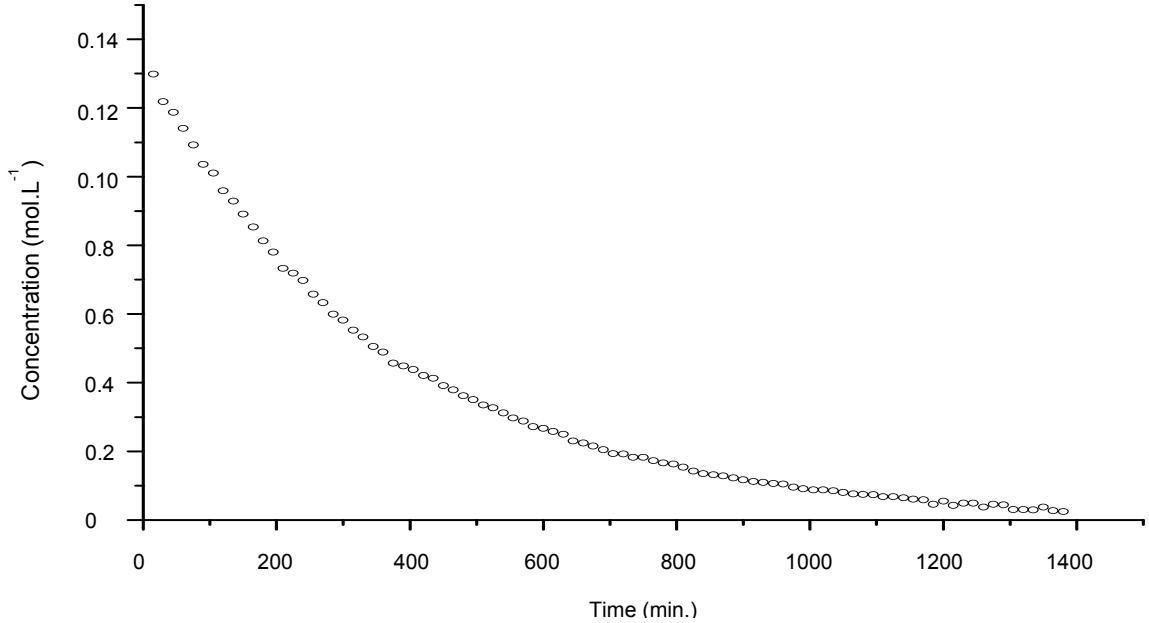
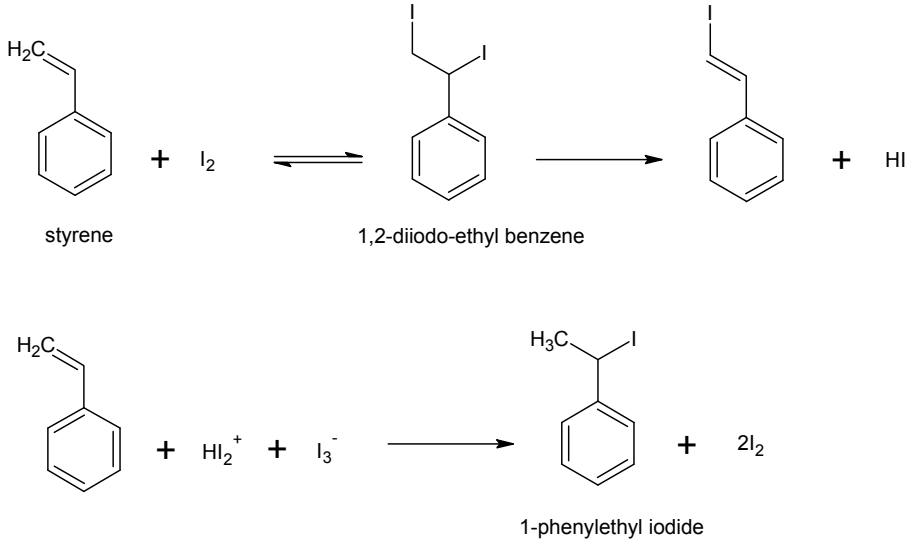


Figure 4.6: The evolution of AIBN concentration for the polymerisation of styrene by RITP for 23 hours at 70°C ([styrene] = 4.27 M, [toluene-d_8] = 4.82 M, [AIBN] = 0.13 M and [I_2] = 7.91 x 10^{-2} M).

The shorter experimental inhibition time compared to the theoretical can be explained by the complex chemistry between iodine and styrene.[12,13] The most notable reactions between iodine and styrene are: (1) cationic polymerisation of styrene by iodine, (2) reversible formation of 1,2-diiodo-ethyl benzene and (3) formation of a charge transfer complex. Tonnar *et al*.[1] suggested that the inhibition time for styrene polymerised by RITP is shortened due to the formation of 1,2-diiodo-ethyl benzene (Scheme 4.3).



Scheme 4.3: The general mechanism for the formation of 1,2-diiodo-ethyl benzene and the subsequent formation of 1-phenylethyl iodide.

When styrene and iodine are reacted with one another, a colourless compound is formed. This colourless compound is 1,2-diiodo-ethyl benzene. Subsequently, hydrogen iodide is generated and an equilibrium reaction with free iodine gives I_3^- and HI_2^+ respectively. The cation (HI_2^+) is added to the monomer to generate 1-PEI, a commonly used chain transfer agent in ITP.[13,14]

In order to identify 1,2-diiodo-ethyl benzene in RITP, the ^{1}H NMR spectrum of a mixture of styrene and iodine in $CDCl_3$ (Figure 4.7 A) was studied. The proton signals for 1,2-diiodo-ethyl benzene in this mixture were observed around 3.85 – 3.97 ppm.

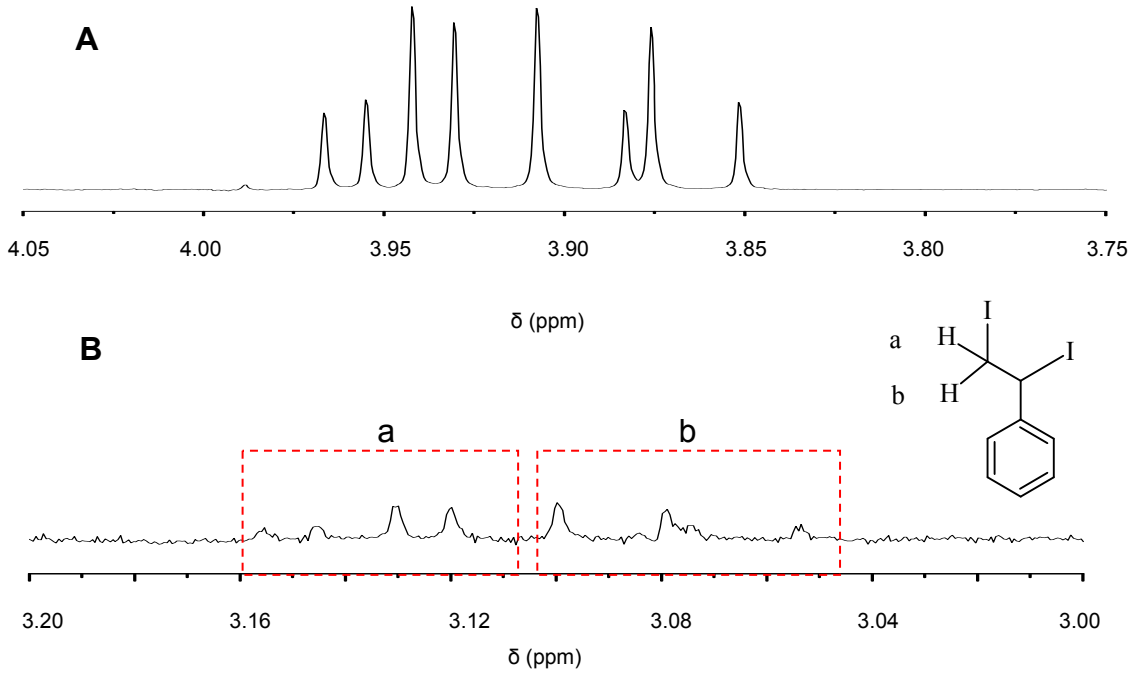
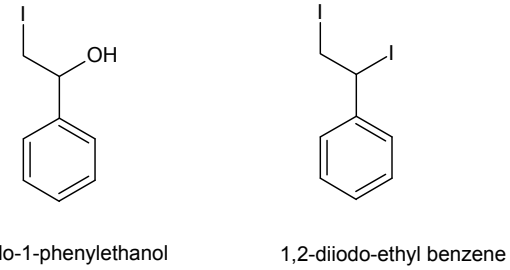


Figure 4.7: Enlarged portions of the ^{1}H NMR spectra of (A) 1,2-diiodo-ethyl benzene formed from a mixture of styrene and iodine in $CDCl_3$ and (B) styrene polymerised by RITP in toluene-d_8 at 70°C for 23 hours ([styrene] = 3.70 M, [toluene] = 5.44 M, [AIBN] = 0.12 M and $[I_2]$ = 6.86 x 10^{-2} M, conversion = 70%, $M_{n, SEC}$ = 2400 g.mol^{-1}, PDI = 1.50), showing the peaks for aliphatic protons of 1,2-diiodo-ethyl benzene.

When an RITP experiment is run at 70°C using AIBN, iodine and styrene in toluene-d_8, the peak assignments are shifted to 3.04 – 3.16 ppm (Figure 4.7 B).The peculiar multiplicity of the CH_2 group is explained as follows; the CH group of 1,2-diiodo-ethyl benzene is an asymmetric centre and thus the CH_2 groups are not in the same chemical environment. The CH_2 protons couple with one another resulting in two doublets. They also couple with the CH proton and the number of signals is doubled, resulting in a total number of eight signals.

Comparable to 1,2-diiodo-ethyl benzene is the compound 2-iodo-1-phenylethanol (Figure 4.8), whose proton signals are observed at 3.25 – 3.45.[15,16]



2-iodo-1-phenylethanol 1,2-diiodo-ethyl benzene

Figure 4.8: Structural similarity between 2-iodo-1-phenylethanol and 1,2-diiodo-ethyl benzene.

The presence of 1,2-diiodo-ethyl benzene in the reaction medium suggests that there should also be 1-PEI (Scheme 4.3). It is assumed that 1-PEI is a chain transfer agent in RITP of styrene. Therefore, kinetic ^{1}H NMR spectra were examined in order to identify the proton signals of 1-PEI, as well as the subsequent phenylethyl end group protons that could transpire. Figure 4.9 shows the signals for the methyl protons of 1-PEI at 1.94 ppm and for the polymer phenylethyl end group at 0.97 ppm in the spectra of styrene polymerised by RITP.

The signal for the methyl protons of 1-PEI are shown as a doublet at 1.93 ppm. The signal for the methyl protons of the phenylethyl chain end group of polystyrene were observed at 1.00 ppm. This is in good agreement with the peak assignments observed by Goto *et. al*.[17] It should be noted that the 1,2-diiodo-ethyl benzene proton signals are observed in ^{1}H NMR spectra of polystyrene samples that are precipitated from methanol.

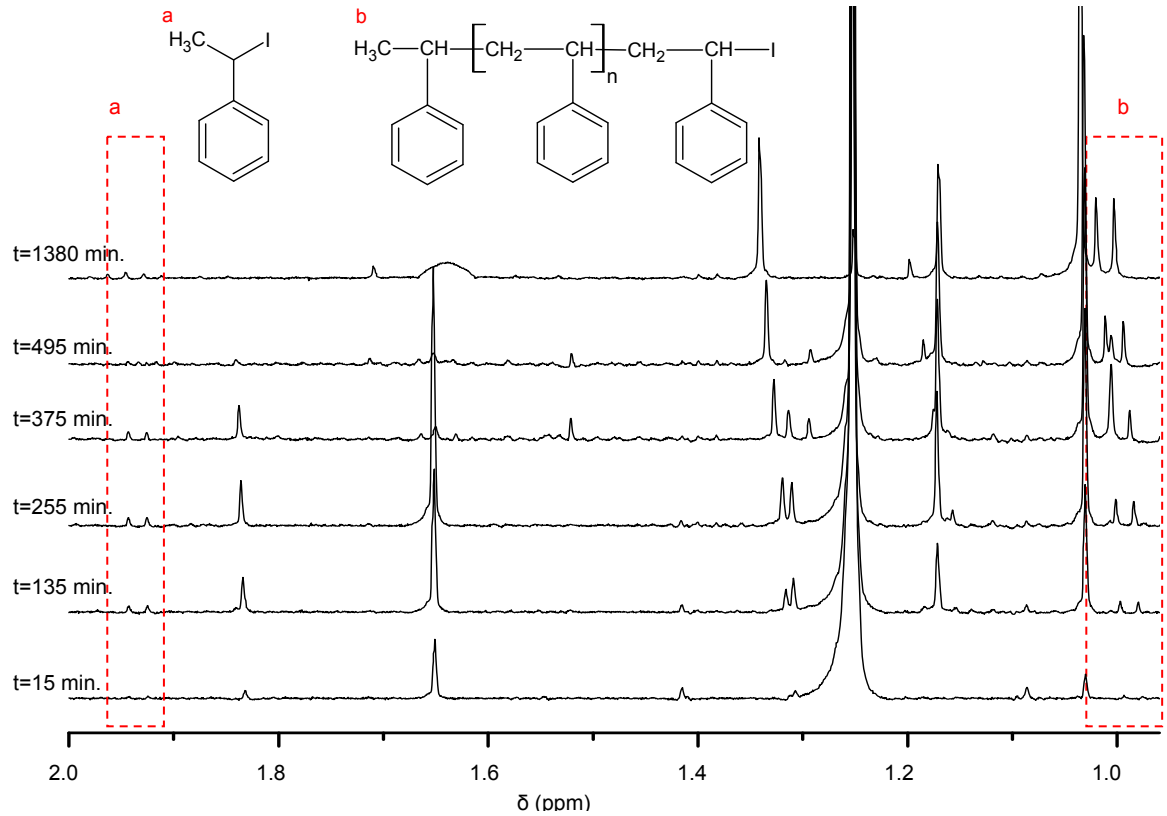
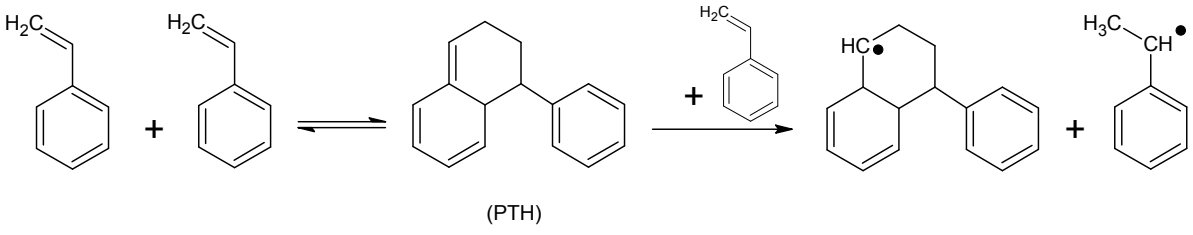


Figure 4.9: An enlarged portion (0.95 – 2.05 ppm) of the ^{1}H NMR spectrum in $CDCl_3$ of styrene polymerised by RITP at 70°C for 23 hours [styrene] = 4.27 M, [toluene-d_8] = 4.82 M, [AIBN] = 0.13 M and [I_2] = 7.91 x 10^{-2} M), showing the signals for the methyl protons of 1-PEI at 1.94 ppm and for the polymer phenylethyl end group at 0.97 ppm.

Auto-initiation of styrene was also considered as a possible mechanism from which 1-PEI could have derived from. The auto-initiation mechanism of styrene is shown in Scheme 4.4.



Scheme 4.4: General mechanism for the Diels-Alder dimerisation reaction of styrene.

Auto-initiation involves the formation of the Diels-Alder dimer 1-phenyl-1,2,3,4-tetrahydronaphthalene (PTH), followed by the transfer of a hydrogen atom to form a phenylethyl and 1-phenyltetralyl radical.[18-20] The ^{1}H NMR spectra for styrene polymerised by RITP showed no proton signals for the 1-phenyltetralyl radical. Thus, it is unlikely that 1-PEI could have formed from auto-initiation of styrene.

4.4.4 Mass spectrometry of polystyrene

MALDI-ToF analysis, run in linear mode, was used to verify the structures identified from ^{1}H NMR spectra of polystyrene synthesised by RITP (Figure 4.10). The terminating ends of these structures would be expected to be iodinated. However, during MALDI-ToF analysis the terminating end is fragmented by the cation of the salt. Also, the C-I bond in PS synthesised by RITP is weak and can fragment easily. Therefore, the expected iodine terminated PS was observed in the ^{1}H NMR spectra, whereas unsaturated structures are observed in MALDI-ToF.[1]

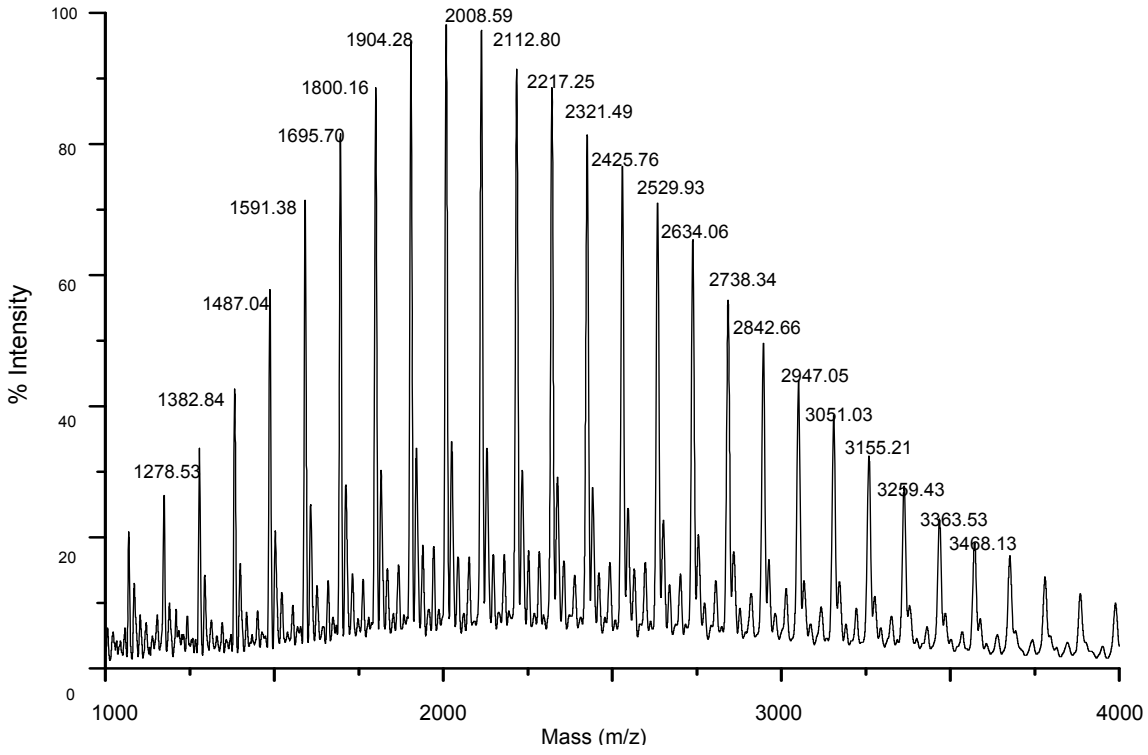


Figure 4.10: MALDI-Tof spectrum (linear mode) of PS synthesised by RITP at 70°C for 24 hours ([styrene] = 3.70 M, [toluene] = 5.44 M, [AIBN] = 0.12 M and [I_2] = 6.86 x 10^{-2} M, conversion = 70%, $M_{n,\,SEC}$ = 2400 g.mol^{-1}, $M_{n,\,NMR}$ = 2500 g.mol^{-1}).

An enlarged portion of the MALDI-ToF spectrum is shown in Figure 4.11. From the spectrum, several populations were identified and shown in Scheme 4.5 and Figure 4.13 respectively.

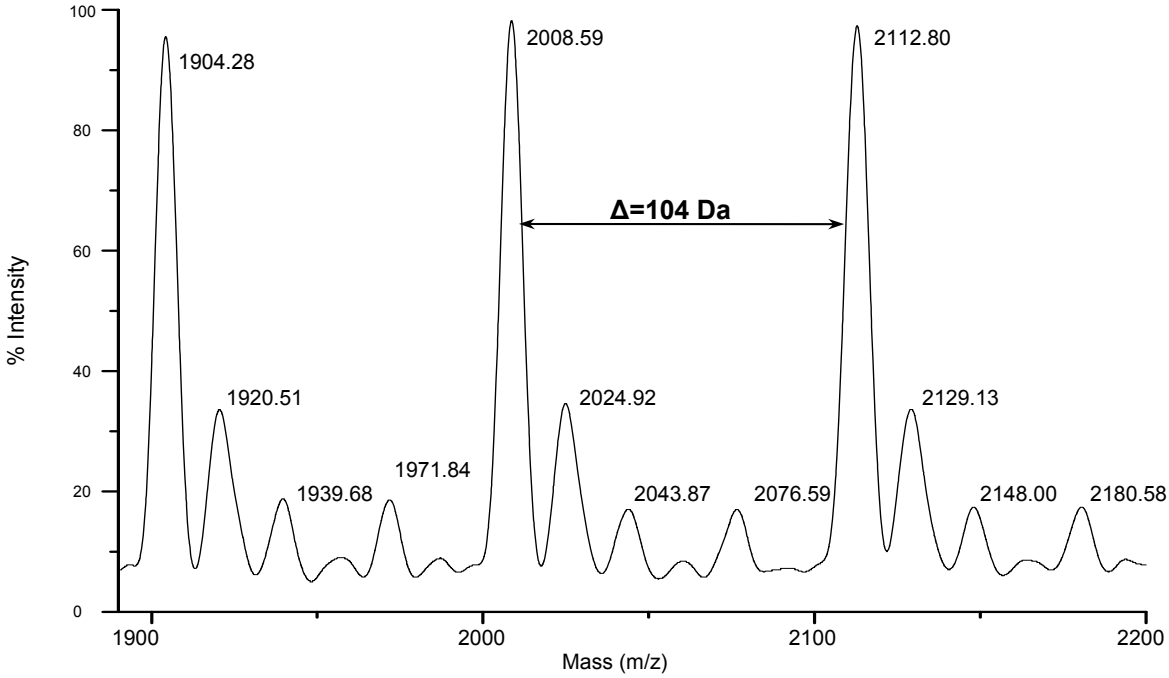


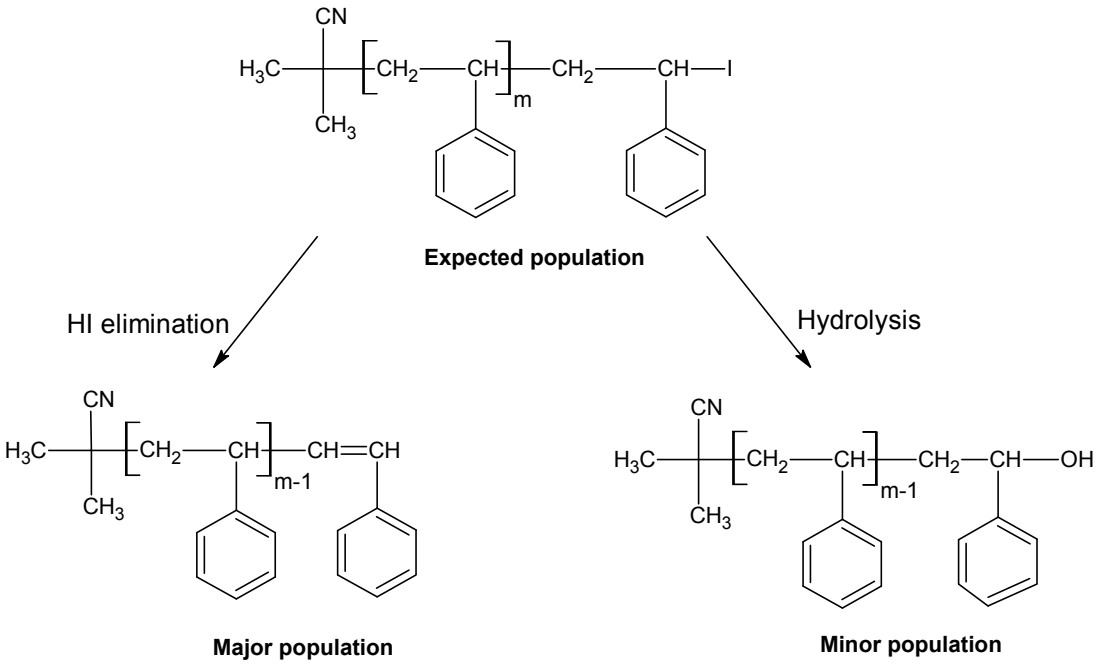
Figure 4.11: Enlarged portion of the MALDI-ToF spectrum (linear mode) of PS synthesised by RITP at 70°C for 24 hours ([styrene] = 3.70 M, [toluene] = 5.44 M, [AIBN] = 0.12 M and [I_2] = 6.86 x 10^{-2} M, conversion = 70%, $M_{n,\,SEC}$ = 2400 g.mol^{-1}, $M_{n,\,NMR}$ = 2500 g.mol^{-1}).

The major population of polystyrene samples is separated by a mass increment of 104 Da, corresponding to the monomer repeat unit. The structures identified in MALDI-ToF are listed in Table 4.2 with their respective predicted masses.

The major population, which appears at 2008.59 Da (Table 4.2), is the structure *A–*M_{m-1}*–CH=C(Ph)H* (Scheme 4.5). A ^{1}H NMR chemical shift for the unsaturated chain end would be expected at around 6.4 – 6.6 ppm. However, since the signal was not observed in ^{1}H NMR, the structure is assumed to form during MALDI-ToF analysis where HI is eliminated from *A–*M_m*–I* due to Cu^+. The unsaturated population has been observed for RITP[1] of styrene as well as for metal–catalysed CRP of styrene.[21]

Table 4.2: Peak assignments for MALDI-ToF analysis (linear mode) of styrene polymerised by RITP for 24 hours at 70°C in toluene.

Structure	m	Experimental mass (m/z)	Theoretical mass (m/z)
A–M_{m-1}–C_8H_7, -HI (Cu^+)	17	2008.59	2005.10
A–M_{m-1}–C_8H_9O, -HI (Cu^+)	17	2024.92	2023.11
C_8H_9–M_{m-1}– C_8H_7, -HI (Cu^+)	17	2043.87	2042.12
A–M_m–A (Cu^+)	18	2076.59	2074.16



Scheme 4.5: The structures identified from the MALDI-ToF analysis of polystyrene synthesised by RITP at 70°C.

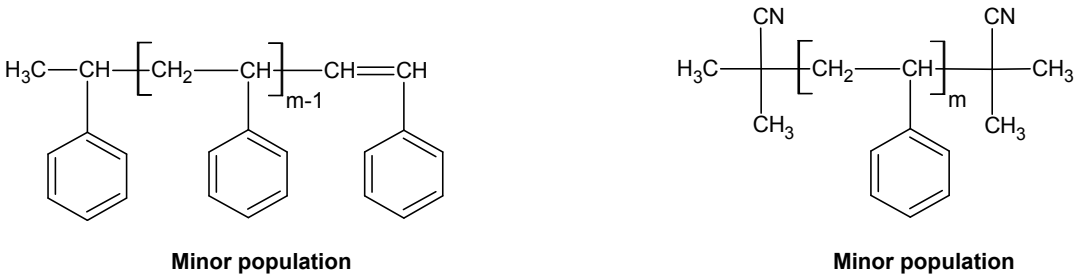


Figure 4.12: Structures identified in MALDI-ToF analysis for the minor populations that do not derive from the A–M_m–I population.

A minor population (Scheme 4.5) is observed at 2024.92 Da. This population is not observed in ^{1}H NMR and might therefore form due to hydrolysis of the halogen end either during storage or during MALDI ToF analysis.

A second minor population is observed at 2043.87 Da (Table 4.2 and Figure 4.12). 1,2-diiodo-ethyl benzene generates 1-PEI, a good transfer agent for CRP. The minor population contains a phenylethyl end group (C_8H_9–M_{m-1}– C_8H_7), which originates from the reaction between styrene and the alkyl iodide chain transfer agent.[4,17] As was the case with the major population, this structure forms during MALDI-ToF analysis due to the elimination of HI.

Another third minor population, appearing at 2076.59 Da (Table 4.2), is that of a direct initiation and termination reaction (combination of the initiator and styrene) (Figure 4.12) to form the structure A–M_m–A. These structures have been reported for iodine mediated polymerisation.[4,6,17,22]

4.4.5 End group functionality of polystyrene

In this section the functionality of polystyrene synthesised by RITP is examined using ^{1}H NMR and SEC. The theoretical iodine functionality ($F^{\text{iodine, theory}}$) can be used as a guideline to compare with the experimental functionality from NMR and SEC. The amount of surplus AIBN that initiates and propagates polymerisation after the inhibition period is given by ΔAIBN.[7] The surplus initiator was calculated using equation 4.5. [7]

$$\Delta AIBN = [\,AIBN\,]_{t,inh} \times (1 - exp(\,k_d \times \tau_{polym.}\,)) \qquad (4.5)$$

where k_d is the rate of dissociation constant, τ_{polym} is the polymerisation time after the inhibition period ($t_{total} - t_{inh,\,exp}$), and the concentration of the initiator in the reaction medium at the end of the inhibition period ($[AIBN]_{t,\,inh}$) was calculated using equation 4.6.[7]

$$[\,AIBN\,]_{t,inh} = [\,AIBN\,]_0 \times exp(-k_d \times t_{inh,exp}\,) \qquad (4.6)$$

The calculated value for the surplus initiator is inserted into equation 4.7 to calculate the $F^{\text{iodine, theory}}$, where $[\text{iodine}]_0$ is the initial concentration of molecular iodine and f is the initiator efficiency.

$$F^{iodine,\ theory} = 2[iodine]_0 \Big/ (2[iodine]_0 + 2f \times \Delta AIBN) \quad (4.7)$$

Due to the fact that the $t_{inh,\ exp}$ of polystyrene synthesised by RITP is much shorter than would be expected, the value of ΔAIBN in eq. 4.5 is impacted heavily. Consequently, the value of $F^{iodine,\ theory}$ is affected and hence the values for theoretical functionality are less than expected.

The integrals from ^{1}H NMR of a polystyrene sample of the α-end group signal and ω-end group signal are used to calculate the experimental iodine functionality (F^{iodine}). In polymers synthesised by RITP, the α-end group usually contains the radical initiator (AIBN) moiety (-C(CN)(CH_3)$_2$), whereas the ω-end group contains an iodine atom next to a methine (-CH-) proton. The protons of the α-end group are situated at 0.90 – 1.10 ppm [9,23] and the methine proton of the ω-end group is at 4.5 – 4.8 ppm (Figure 4.13).[9]

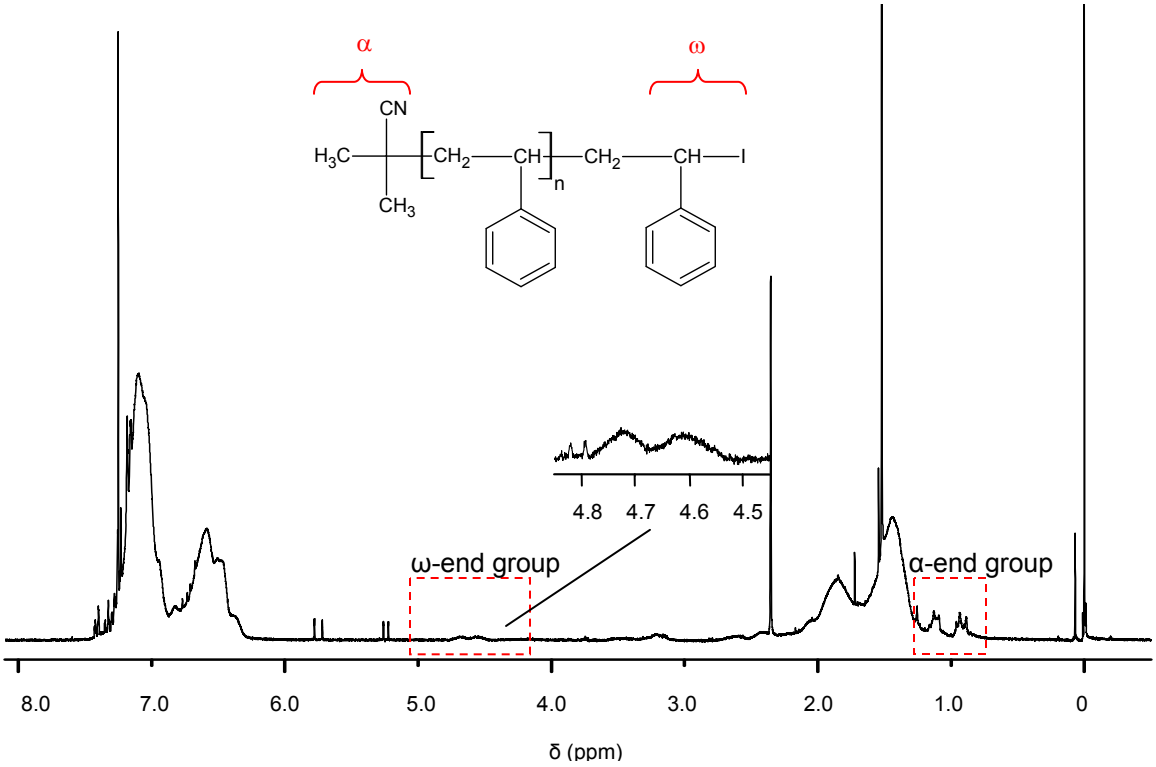


Figure 4.13: ^{1}H NMR spectrum in $CDCl_3$ of styrene polymerised by RITP for 24 hours at 70°C in toluene, showing the regions for the integrals of the α-end group and the ω-end group respectively.

The integrals from 1H NMR are used in equation 4.8 to calculate functionality.

$$F^{iodine} = \int(-CH-) \Big/ \int(-C(CN)(CH_3)_2)/6 \qquad (4.8)$$

Another means of calculating functionality is to consider molecular weights from SEC results and NMR.

With all these calculations considered, the results for end group functionality of polystyrene synthesised by RITP are shown in Table 4.3.

Table 4.3: Results of end group functionality of styrene polymerised by RITP in toluene for 24 hours at 70°C.[a]

Run	[AIBN]/[I_2]	$M_{n,\ target}$ ($g.mol^{-1}$)	$M_{n,\ SEC}$ ($g.mol^{-1}$)[b]	$F^{iodine,\ theory}$ [c]	F^{iodine} [d]
1	1.5	8000	4600	0.68	0.63
2	1.7	1500	700	0.68	0.61
3	1.7	3000	2400	0.62	0.68
4	1.7	5500	3600	0.55	0.61
5	1.7	8000	4850	0.41	0.49
6	2.0	8000	5300	0.43	0.45

[a] Polymerisation of styrene ([styrene] = 3.70 M) in toluene ([toluene] = 5.44 M) at 70 °C with AIBN and molecular iodine.

[b] Calibrated using polystyrene standard.

[c] Calculated by $F^{iodine,\ theory} = 2[iodine]_0 / (2[iodine]_0 + 2f \times \Delta AIBN)$

[d] Calculated by $F^{iodine} = \int(\text{-CH-}) / \int(\text{-C(CN)(CH}_3)_2)/6$

In CRP systems such as RITP, the initiation is quick with no termination and therefore the resulting polymer remains living, usually with a low percentage of dead chains (<10%).[24,25] During the inhibition period, there is almost no polymerisation taking place and consequently the number of dead chains formed during this time is minimal.

The majority of dead chains are formed during the polymerisation period. Also, the amount of dead chains increases after a high monomer conversion (>95%) is obtained.[26]

Since the monomer conversion in these experiments never exceeds more than about 70%, the experiments could be run for 24 hours without concern for limiting the amount of dead chains. Table 4.3 shows that the theoretical functionality of polystyrene is in reasonable agreement with the experimental functionality calculated from NMR. The experimental functionality values calculated from NMR are below the expected functionality for CRP systems, as there are a large proportion of dead chains present. The explanation for the below expected functionality, from NMR, is perhaps attributed to two factors: (1) the shorter than expected experimental inhibition time and (2) the presence of polystyrene populations containing the phenylethyl end group. A plot of iodine functionality *versus* monomer conversion is shown in Figure 4.14.

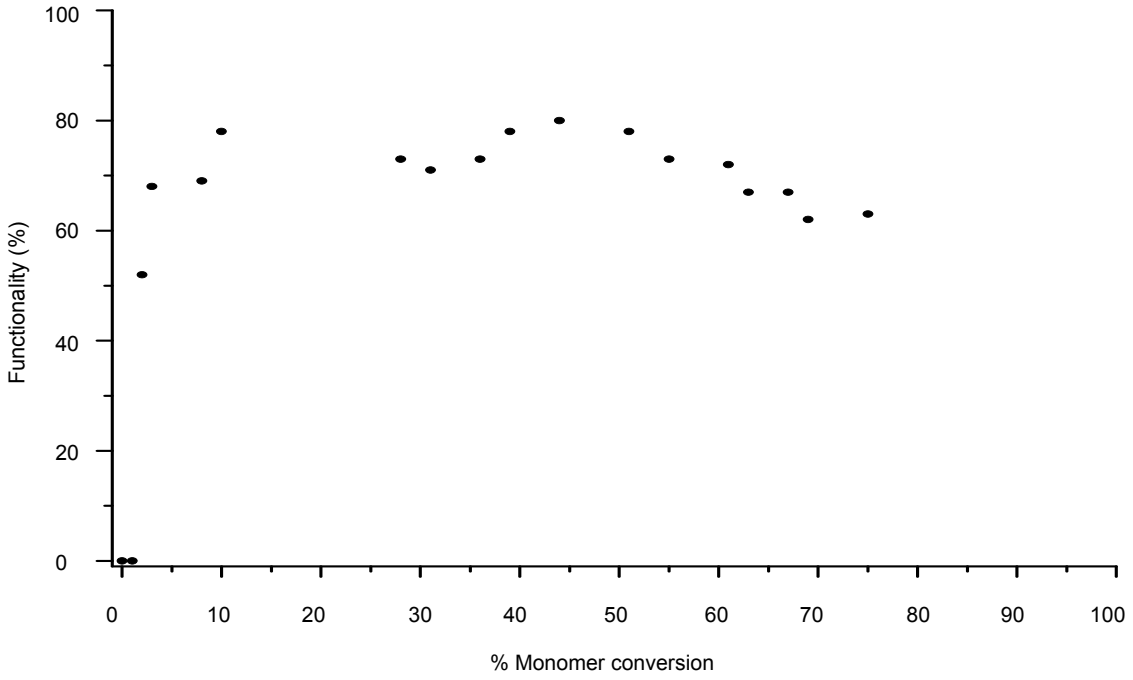


Figure 4.14: Evolution of the iodine functionality (F^{iodine}) of the polystyrene synthesised by RITP in toluene-d_8 for 24 hours at 70°C ([styrene] = 4.27 M, [toluene-d_8] = 4.82 M, [AIBN] = 0.13 and [I_2] = 7.91 x 10^{-2} M).

The plot is constructed using eq. 4.8 at various monomer conversions in the kinetic array of ^{1}H NMR spectra for styrene polymerised by RITP. The functionality increases sharply in the early stages of polymerisation, followed by a gradual decrease in the functionality towards the higher monomer conversion.

Jakubowski *et al*.[27] also observed this loss in halide chain end functionality for polystyrene prepared by ATRP. The decrease in functionality doesn't seem to compromise the ability of polystyrene to form block copolymers. Enríquez-Medrano[28] showed that poly(styrene)-*b*-poly(butyl acrylate) could be synthesised from styrene polymerised by RITP.

4.5 Conclusions

The mechanism of styrene polymerisation by RITP is significantly different to that of acrylates and methacrylates.[7,8] The inhibition period is the feature of its mechanism that makes it so different to that of acrylates and methacrylates. Throughout the inhibition period, iodine reacts with initiator radicals to form chain transfer agents (*A*–*I* and *A*-M_n-*I* adducts). The inhibition period is marked by the disappearance of a brownish colour from the reaction mixture. Iodine not only reacts with the initiator, but also reacts with styrene to form 1,2-diiodo-ethyl benzene. This period is significantly reduced due this side reaction. For RITP, this compound has not been reported. We found evidence of 1,2-diiodo-ethyl benzene in ^{1}H NMR, which consequently reacted with styrene to form a chain transfer agent, 1-PEI. This compound, commonly used in degenerative transfer mediated polymerisation,[4] has not been identified in literature for RITP. The evolution of 1-PEI was followed by *in situ* ^{1}H NMR and the resulting polymer containing phenylethyl end group was confirmed by MALDI-ToF analysis. Although iodine is liberated from 1,2-diiodo-ethyl benzene throughout the polymerisation period of RITP, the monomer conversion is often limited (~65%) due to the shortage of initiator radicals towards the end of polymerisation. The functionality of PS increases very quickly once polymerisation commences, followed by a gradual decrease with time. This decrease in functionality does not prevent the use of PS for block copolymerisation, as shown by Enríquez-Medrano *et al*.[28]

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5 COMPARATIVE STUDY OF STYRENE AND N-BUTYL ACRYLATE POLYMERISED BY REVERSE IODINE TRANSFER POLYMERISATION

5.1 Introduction

In the following sections, the RITP mechanisms of styrene and n-butyl acrylate and the structures generated by each system shall be compared. A brief discussion of the effect of temperature on the inhibition period is also mentioned. Comparisons were made from concentration profiles of the *A–I* adduct formed before polymerisation, the consumption of AIBN throughout the reaction the conversion of monomer to polymer.

Several studies have been reported where *in situ* ^{1}H NMR was used to investigate some aspect of a CRP system.[1-3] The reaction mechanism, kinetics and structures can be studied for CRP systems by constructing concentration profiles. In particular, *in situ* ^{1}H NMR studies of methyl methacrylate[4,5] and styrene[6] synthesised by RITP have been reported. By constructing several concentration profiles, these *in situ* ^{1}H NMR studies help to develop an understanding of the evolution of several species (CTAs and polymer molecules) during polymerisation. The inhibition period can be monitored as well as the monomer conversion.

In this study, styrene and n-butyl acrylate were polymerised separately by RITP. The experiments were run at 70°C for 22 hours by *in situ* ^{1}H NMR, using an [AIBN]/[I_2] ratio of 1.7 and targeting a molecular weight of 3000 g.mol^{-1}.

5.2 Experimental

5.2.1 Materials

Styrene (Sigma-Aldrich) and n-butyl acrylate (Sigma-Aldrich) were washed with an aqueous solution sodium hydroxide and then washed with distilled de-ionised water. The monomers were dried with anhydrous magnesium sulphate over night and distilled under vacuum and stored in a refrigerator at – 5 °C.

2,2'-azobis(isobutyronitrile) (AIBN, Riedel de Haën) was recrystallised from methanol, dried under vacuum and stored in a refrigerator at – 5 °C. Deuterated benzene (C_6D_6, Cambridge Isotope Laboratories, 99%), dimethyl formamide (DMF, Aldrich) and iodine (I_2, ACROS Organics) were used as received.

5.2.2 ^{1}H NMR in situ polymerization of styrene and n-butyl acrylate

Styrene and *n*-butyl acrylate homopolymerisations were followed by *in situ* ^{1}H NMR at 70 °C at in benzene-d_6. The ^{1}H NMR spectra were obtained on a Varian Unity INOVA 400 MHz spectrometer, with a pulse width of 3 μs (40°) and a 4 second acquisition time. The sample NMR tube was inserted into the NMR spectrometer and a reference spectrum was acquired at 25°C. The temperature of the NMR spectrometer was then equilibrated at 70°C for 30 minutes before the NMR tube was reinserted into the spectrometer. The first spectrum was acquired 8 – 15 minutes after the sample was reinserted. Thereafter, spectra were obtained by taking 15 scans every 15 minutes for 22 hours. The same procedure was also performed for 22 hours using n-butyl acrylate.

All NMR spectra were processed using ACD Labs 10.0 ^{1}H NMR processor®. The spectra were phased automatically, whereas baseline correction and integration were done manually. From the processed spectra it was possible to construct concentration profiles relative to an insert of a DMF reference.

In a typical polymerisation reaction, styrene (2.00 g, 19.2 x 10^{-3} mol), AIBN (99.5 mg, 6.06 x 10^{-4} mol), iodine (90.5 mg, 3.57 x 10^{-4} mol) were weighed carefully and mixed thoroughly in a glass vial. The mixture (0.25 mL) was introduced into a J Young NMR Tube, followed by the addition of 0.25 mL of toluene-d_8. An internal reference of 20 μL DMF was inserted into the J Young NMR tube. The sample in the NMR tube was degassed by three successive freeze-pump-thaw cycles and then filled with UHP argon gas.

5.3 Analyses of polymer samples

5.3.1 SEC analysis

SEC was carried out using a SEC instrument equipped with a Waters 717plus Autosampler, Waters 600E system controller and a Waters 610 fluid unit. For detection, a Waters 2414 differential refractometer was used. Two PLgel 5 µm Mixed-C columns and a PLgel 5 µm guard column were used. Polymer samples of 2 mg were weighted and dissolved in 2 mL of THF. The sample volume injected into the column was 100 µL, with the oven temperature kept at 30 ºC. The eluent that was used was THF (HPLC grade, BHT stabilised) at a flow rate of 1mL/min. Calibrations were done using narrow polystyrene standards with a molecular range of 800–2 x 10^6 g.mol^{-1}. Data obtained from SEC is reported as polystyrene equivalents.

5.3.2 NMR analysis

^{1}H NMR spectra were obtained on a Varian Unity INOVA 400 MHz spectrometer. Samples analysed by on-line kinetic ^{1}H NMR were dissolved in benzene-d_6.

5.4 Results and discussion

5.4.1 Chain transfer agents formed during the Inhibition period

Following on from chapters 3 and 4, we can assess the vastly different inhibition periods from a comparative point of view.

During the inhibition period, CTAs are generated *in situ*. Typically, molecular iodine reacts with initiator radicals to form *A-I* and *A-*M_n*-I* adducts. However, it is also possible for iodine to react with with monomers containing a double bond to form 1-2 disubstituted olefins.[5,7,8] The formation of such a compound would lead to a premature conclusion of the inhibition period, and a polymer with an *I-*M_n*-I* structure might be expected. However, this type of compound would inevitably be very unstable and its existence difficult to identify by analysis with chromatographic and spectroscopic techniques.

Nevertheless, the formation of 1,2 disubstituted olefins is a reversible process and therefore could release iodine again once the inhibition period has concluded.

The end of the inhibition period is marked by the change in colour of the reaction medium from brown to colourless. This is due to the complete consumption of iodine when forming CTAs. The *A-I* adduct concentration profile provides a visual representation of this feature (Figure 5.1), where the decrease in concentration signifies the complete consumption of iodine and hence the end of the inhibition period.

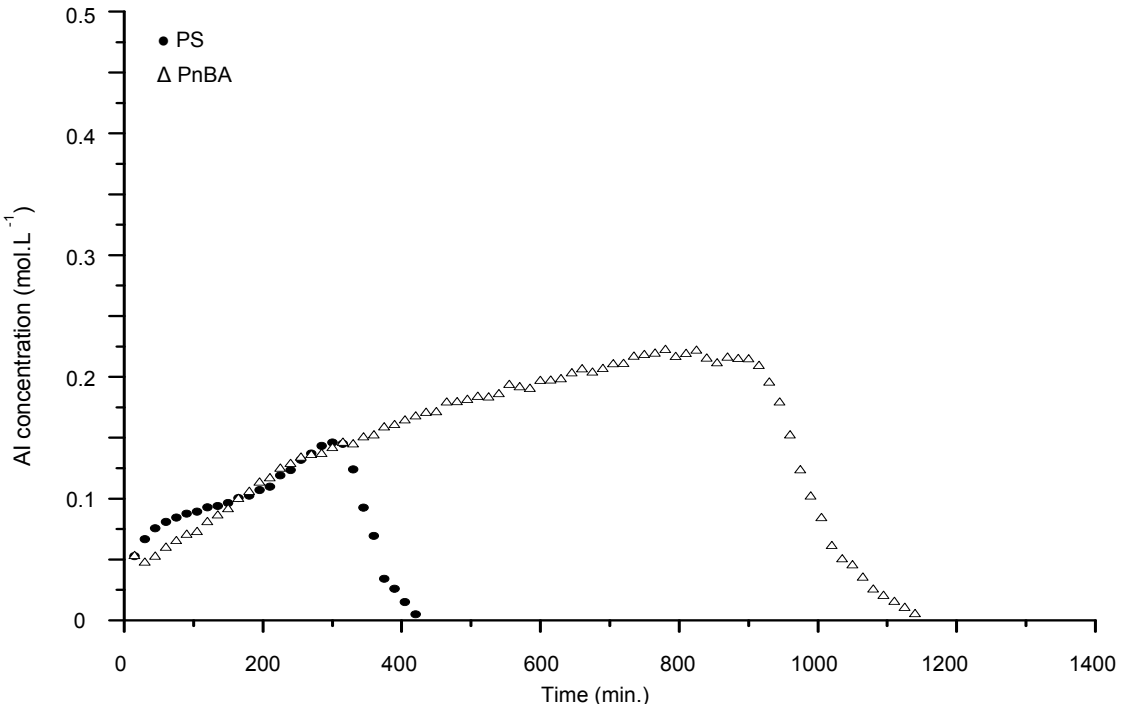

Figure 5.1: The evolution of the concentration of A-I adducts as a function of time for the polymerisation of styrene and n-butyl acrylate in benzene-d_6 at 70 °C.

Similarly, the monomer conversion profile in Figure 5.2 shows the end of the inhibition period with the sudden increase in monomer conversion. From literature, the reported CTAs formed during RITP of methyl methacrylate[4] and methyl acrylate[5] are the typical *A-I* adduct and *A-*M_n*-I* adduct. In our studies there were no 1,2-disubstituted structures observed in the ^{1}H NMR spectra of PnBA.

The parameters that control the duration of the inhibition period differ between n-butyl acrylate and styrene. T_{inh} of n-butyl acrylate is generally influenced by temperature, [AIBN]/[I_2] ratio and molecular weight,[5] whereas t_{inh} of styrene is affected by temperature and molecular weight.[6] In essence, for acrylates, the inhibition period is reduced at elevated temperatures (side reactions could occur). Also, the inhibition period decreases when high [AIBN]/[I_2] ratios are used or when high molecular weights are targeted. Similarly for styrene, the inhibition period is reduced at elevated temperatures, although auto-initiation could occur at very high temperatures. The results for styrene polymerised by RITP at different temperatures are shown in Table 5.1 and for n-butyl acrylate in Table 5.2.

Table 5.1: Results for styrene polymerised by RITP at different temperatures.

Run	[AIBN]/[I_2]	Temp. (°C)	$M_{n,\ target}$ (g.mol^{-1})	$t_{inh,\ theory}$ (h)[a]	$t_{inh,\ exp}$ (h)	Conv (%)[b]	$M_{n,\ theory}$ (g.mol^{-1})[c]	$M_{n,\ GPC}$ (g.mol^{-1})[d]	PDI
1	1.7	70	3000	14	6	71	2200	2400	1.50
2	1.7	80	3000	4	4	78	2350	2500	1.60

[a] Calculated by $t_{inhibition,\ theory} = (-\ln((1-[iodine]_0)/f[initiator]_0))/k_d$ where k_d = 3.71 x 10-5 s^{-1} and f = 0.7.

[b] determined by ^{1}H NMR in $CDCl_3$ by conversion = $(1-(I_1/I_2)) \times 100$ where I_1 is the integral of the vinylic protons (($\int CH_2{=}C$)/2) of styrene at 5.1 ppm and 5.6 ppm, and I_2 is the integral of the aromatic protons (($\int C_6H_5$)/5) of styrene and polystyrene.

[c] Calculated by $M_{n,\ theory} = ((m_{monomer} \times conversion)/(2 \times n_{iodine})) + M_{chain\ ends}$.

[d] Calibrated using polystyrene standard.

Table 5.2: Results for n-butyl acrylate polymerised by RITP at different temperatures.

Run	[AIBN]/[I_2]	Temp. (°C)	$M_{n,\ target}$ (g.mol^{-1})	$t_{inh,\ theory}$ (h)[a]	$t_{inh,\ exp}$ (h)	Conv (%)[b]	$M_{n,\ theory}$ (g.mol^{-1})[c]	$M_{n,\ GPC}$ (g.mol^{-1})[d]	PDI
1	1.7	65	3000	27	>24	99	2950	3200	2.08
2	1.7	70	3000	14	16	98	2950	3300	2.02

[a] Calculated by $t_{inhibition,\ theory} = (-\ln((1-[iodine]_0)/f[initiator]_0))/k_d$ where k_d = 3.71 x 10-5 s^{-1} and f = 0.7.

[b] determined by ^{1}H NMR in $CDCl_3$ by conversion = $(1-(I_1/I_2)) \times 100$ where I_1 is the integral of the vinyl protons (($\int CH_2{=}CH$)/3) of n-butyl acrylate at 5.8 ppm, 6.1 ppm and 6.4 ppm. I_2 is the integral of the methyl protons (($\int CH_3$)/3) of butyl acrylate units at 0.9 ppm.

[c] Calculated by $M_{n,\ theory} = ((m_{monomer} \times conversion)/(2 \times n_{iodine})) + M_{chain\ ends}$.

[d] Calibrated using polystyrene standard.

The inhibition period is reduced for both monomer systems with an increase in temperature, while maintaining good control over molecular weight. In the case of n-butyl acrylate, however, the extent to which one can increase the temperature of the experiment is limited due to the formation of MCRs at temperatures greater than 80 °C. For styrene and n-butyl acrylate polymerised by RITP under the same conditions, the results are compared in Table 5.3.

Table 5.3: Comparative results of styrene *versus* n-butyl acrylate polymerised *in situ* by RITP for 22 hours at 70°C.

Run	[AIBN]/[I_2]	$M_{n,\ target}$ ($g.mol^{-1}$)	$t_{inh,\ theory}$ (h)[a]	$t_{inh,\ exp}$ (h)	Conv (%)	$M_{n,\ theory}$ ($g.mol^{-1}$)[c]	$M_{n,\ GPC}$ ($g.mol^{-1}$)[d]	PDI
PS	1.7	3000	14	6	71[b]	2200	2400	1.50
PnBA	1.7	3000	14	16	98[b']	2950	3300	2.02

[a] Calculated by $t_{inhibition,\ theory} = (-\ln((1-[iodine]_0)/f[initiator]_0))/k_d$ where $k_d = 3.71 \times 10\text{-}5\ s^{-1}$ and $f = 0.7$.

[b] and [b'] determined by ^1H NMR in $CDCl_3$ by conversion = $(1-(I_1/I_2)) \times 100$

[b] I_1 is the integral of the vinylic protons (($\int CH_2{=}C$)/2) of styrene at 5.1 ppm and 5.6 ppm, and I_2 is the integral of the aromatic protons (($\int C_6H_5$)/5) of styrene and polystyrene.

[b'] I_1 is the integral of the vinyl protons (($\int CH_2{=}CH$)/3) of n-butyl acrylate at 5.8 ppm, 6.1 ppm and 6.4 ppm. I_2 is the integral of the methyl protons (($\int CH_3$)/3) of butyl acrylate units at 0.9 ppm.

[c] Calculated by $M_{n,\ theory} = ((m_{monomer} \times conversion)/(2 \times n_{iodine})) + M_{chain\ ends}$.

[d] Calibrated using polystyrene standard.

The inhibition period of PS is much shorter than that of PnBA. This is attributed to the formation of a 1,2-disubstituted compound, namely 1,2-diiodo-ethyl benzene, during the inhibition period. The proton signals for 1,2-diiodo-ethyl benzene are observed in ^1H NMR, but there were no proton signals observed for the expected *I-*M_n*-I* structure, nor was it observed in MALDI-ToF analysis.

Furthermore, 1,2-diiodo-ethyl benzene reacts with styrene during the inhibition period to form 1-PEI. Therefore, the inhibition period for styrene is shortened due to the formation of a few CTAs that are not formed with n-butyl acrylate.

5.4.2 Monomer conversion

In RITP, the CTAs generated during the inhibition period may have a key role in the monomer conversion and PDI. The final conversion is usually influenced by the concentration of the transfer agent in the system. The chain transfer rate constant (k_{ex}) affects the PDI of the resulting polymer (high k_{ex} value gives low PDI value).[9-11] Transfer rate constants are always dependant on temperature.[12,13]

Upon complete consumption of all the molecular iodine during the inhibition period, the polymerisation commences. This part of the process is governed by a DT mechanism and the propagation is controlled by the propagation rate constant (k_p).

Together with the difference in the inhibition periods of PS and PnBA, the monomer conversion profiles of these two polymers look very different. Most notably there are differences in (1) the shape of the profiles and (2) the rate of polymerisation.

It has been reported in literature that the rate of polymerisation of styrene is slower than that of acrylates for NMP[14] and DT governed polymerisation.[15] The shape of the PS conversion plot (Figure 5.2) shows a gradual increase followed by a downward curvature. The downward curvature is somewhat characteristic for styrene polymerised with AIBN as an initiator. Under thermal initiation with AIBN, the curvature may result from chain transfer to the initiator and primary radical termination (PRT). PRT occurs when primary radicals (from the initiator) terminate growing polymer chains instead of initiating chain growth by attaching to the monomer.[16] The effects of PRT are reportedly not that significant for styrene polymerisation initiated by AIBN.[17,18] However, there is a clear downward curvature in the conversion profile of PS. Additionally, the downward curvature indicates a reduction in the rate of polymerisation, due to the low concentration of AIBN (Figure 5.3) at the end of polymerisation.

The shortage of initiator radicals to consume the iodine that is liberated from 1,2-diiodo-ethyl benzene limits final monomer conversion to around 70 %. The conversion profile of PnBA (Figure 5.2) differs from that of PS with respect to the rate of polymerisation. There is a sharp increase in the curvature of the monomer conversion profile which has been observed for acrylates[5] and methacrylates[4] polymerised by RITP.

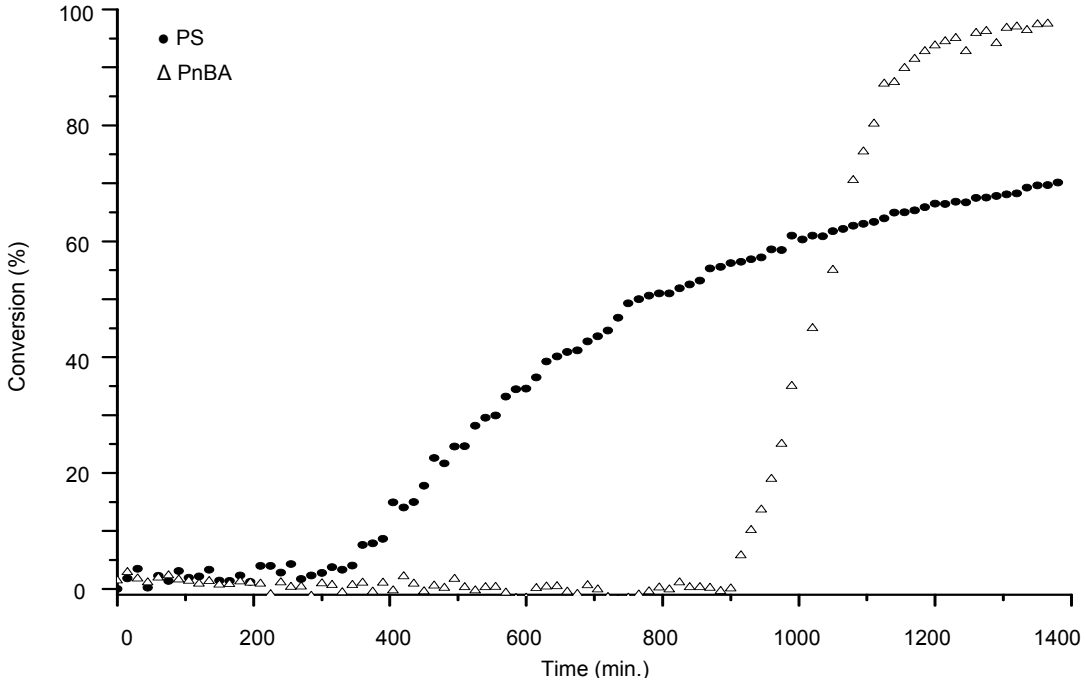

Figure 5.2: : The evolution of monomer conversion for styrene and n-butyl acrylate polymerisations in benzene-d_6 at 70 °C.

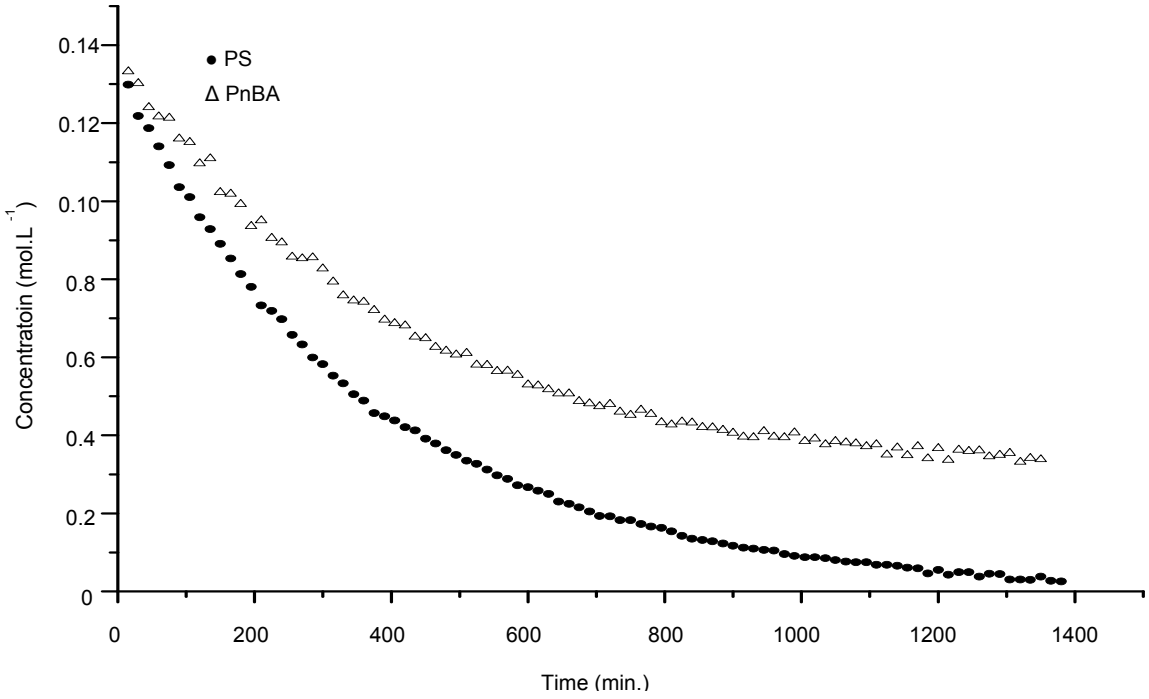

Figure 5.3: The Evolution of AIBN with time during the homopolymerisations of styrene and n-butyl acrylate at in benzene-d_6 at 70 °C.

Table 5.3 shows that the conversion of PS is limited whereas PnBA is close to complete monomer conversion. This is apparent in Figure 5.2 as well and illustrates how different the conversion rates are for styrene and n-butyl acrylate. There is also a significant difference in the PDI values for the two different polymers. The PDI value for PS is comparatively low with respect to PnBA. This is because of a few factors. The slow polymerisation of styrene could contribute to the low PDI value, as well as the presence of 1-PEI.

When comparing the AIBN concentration profiles (Figure 5.3) of styrene and n-butyl acrylate, it is clear that there are differences with regard to the concentration of AIBN after 22 hours. For styrene, almost all the initiator has been consumed whereas there is some excess initiator present at the end of polymerisation of n-butyl acrylate. This is interesting, considering the fact that only 65% of styrene is converted into polymer, whilst n-butyl acrylate is almost completely converted. For both systems, an equal quantity of monomer (2.00 g) and AIBN (99.5 mg) were used with an initiator-to-iodine ratio of 1.7. However, the MALDI-ToF spectra of PS showed a minor population with the structure $A–M_m–A$ that forms from a direct combination of the initiator and styrene. Presumably the formation of this population contributes to the low concentration of AIBN at the end of polymerisation. This $A–M_m–A$ population is not present in the MALDI-ToF spectra of PnBA.

5.5 Conclusions

The RITP mechanisms of styrene and n-butyl acrylate are clearly different. During the polymerisation of styrene by RITP, several CTAs are formed throughout the inhibition period. In contrast, the *A-I* and *A-*M_n*-I* adducts which are formed for all monomer systems during RITP, are formed in n-butyl acrylate polymerisation. The inhibition times for acrylates are therefore somewhat predictable, whereas inhibition times for styrene are not. Due to the potential of RITP industrially, shorter inhibition times would be beneficial. The inhibition period can be shortened by increasing the temperature of the reaction. For styrene, the temperature can be raised without losing too much control over the molecular weight and polydispersity values. For n-butyl acrylate, an increase in the reaction temperature also reduces the inhibition period while maintaining good control over molecular weight and polydispersity. However, the degree by which the temperature can be increased is limited due to the possible formation of MCRs. The conversion of styrene slows down as polymerisation progresses. The reduction in the rate of polymerisation is due to the effects of PRT and the low concentration of initiator radicals in the latter stages of polymerisation. The rate of polymerisation of n-butyl acrylate by RITP exhibits a behaviour that was observed for other acrylates before. The formation of an *A*–M_m–*A* population in RITP of styrene results in more initiator being consumed than for n-butyl acrylate, despite only a 65% conversion of styrene to polymer.

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6 SUMMARY, CONCLUSIONS AND FUTURE WORK

6.1 Summary

In Chapter 3, n-butyl acrylate was polymerised by RITP at 70°C using different initiator to iodine ratios. Molecular weights in the range of 1500 – 8000 g.mol^{-1} were targeted at the different initiator to iodine ratios. Using ^{1}H NMR and SEC, the molecular weight of the polymers was determined. The inhibition period was studied by *in situ* ^{1}H NMR and it was found that transfer agents *A-I* and *A-*M_n*-I* are formed during this period, as seen for other acrylates polymerised by RITP.[1,2] Polymers with the general structure *A-*M_m*-I* are formed during the polymerisation period. The structure was confirmed using MALDI-ToF analysis, where an unsaturated population was formed due to fragmentation of the labile end group. Studies on the functionality of PnBA were not viable using NMR due to the end group signals being overlapped by polymer signals.

The work in Chapter 4 was a study of styrene polymerised by RITP, with a similar approach to that of Chapter 3 being implemented. PS was synthesised by RITP at 70°C at various initiator to iodine ratios and a molecular weight range 1500 – 8000 g.mol^{-1} was targeted. Molecular weight was determined by SEC and ^{1}H NMR. The inhibition period was studied using *in situ* ^{1}H NMR. As was the case with n-butyl acrylate, the transfer agents *A-I* and *A-*M_n*-I* are formed. However, the inhibition period, whose duration is dictated by the concentration of iodine, is much shorter than the theoretical inhibition time. This is attributed to the side reaction where styrene reacts with iodine to form 1,2-diiodo-ethyl benzene. The reaction is reversible and iodine is liberated throughout the polymerisation period. Nevertheless, 1,2-diiodo-ethyl benzene reacts with styrene to form a chain transfer agent, 1-PEI. The polymers formed were confirmed using MALDI-ToF. The experimental iodine functionality of PS was investigated by ^{1}H NMR and compared to calculated theoretical values. The study shows that the functionality of PS increases very quickly once polymerisation commences and then gradually decreases as the reaction proceeds. This decrease in functionality does not seem to prevent PS from being used for block copolymerisation, as shown by Enríquez-Medrano *et al*.[3]

Chapter 5 was a brief comparative study between styrene and n-butyl acrylate polymerised by RITP.

For the study, styrene and n-butyl acrylate were polymerised separately at 70°C for 22 hours by *in situ* ^{1}H NMR. A brief study of the effects of temperature on inhibition times was also done. The results for n-butyl acrylate are comparable to literature,[2] with a clear decrease in inhibition time with an increase in temperature. The same result was obtained for styrene. The increase in temperature does not seem to affect the control over molecular weight and polydispersity. The monomer conversion profiles for styrene and n-butyl acrylate differ significantly. The profile of n-butyl acrylate is similar to other acrylates, whereas that of styrene shows a gradual decrease in the rate of polymerisation with a downward curvature. The reduction in the rate of polymerisation was attributed to the effects of PRT and the low concentration of initiator radicals towards the end of polymerisation. With regards to the initiator concentration of the two systems, more initiator is consumed for styrene polymerisation than for n-butyl acrylate due to the formation of an $A–M_m–A$ population in RITP of styrene.

6.2 Conclusions

There are no significant side reactions taking place during the inhibition period of n-butyl acrylate polymerisation, leading to predictable experimental inhibition. Polymers with the general structure $A\text{-}M_m\text{-}I$ are formed during the polymerisation stage, with an unsaturated structure observed in MALDI-ToF analysis due to fragmentation of the labile iodinated end group.

For styrene polymerised by RITP, iodine reacts with initiator radicals to form chain transfer agents ($A–I$ and $A\text{-}M_n\text{-}I$ adducts) throughout the inhibition period. Iodine also reacts with styrene to form 1,2-diiodo-ethyl benzene. The inhibition period is significantly reduced due this side reaction. Evidence was found in ^{1}H NMR that 1,2-diiodo-ethyl benzene forms during RITP of styrene, which subsequently reacts with styrene to form the 1-PEI chain transfer agent, not observed for acrylates.

The evolution of 1-PEI was followed by *in situ* ^{1}H NMR and a polymer species containing phenylethyl end group was observed in MALDI-ToF analysis. The functionality of PS increases very quickly during polymerisation and decreases over time. The RITP mechanisms of styrene and n-butyl acrylate are clearly different.

The inhibition periods produce different CTAs and the inhibition times for acrylates are more predictable than for styrene. The inhibition time can be reduced by increasing the temperature whilst maintaining control over molecular weight and polydispersity values.

The rate of polymerisation of n-butyl acrylate by RITP is similar to other acrylates whereas the conversion of styrene slows down as polymerisation progresses. This is due to the effects of PRT and the low concentration of initiator radicals in the latter stages of polymerisation. The formation of the $A–M_m–A$ population in RITP of styrene results in more initiator being consumed than for n-butyl acrylate, despite only a 65% conversion of styrene to polymer.

6.3 Future work

After studying styrene and n-butyl acrylate polymerisation by RITP, there is still some future work that can be done. It would be interesting to compare the evolution of PDI values throughout the inhibition period and polymerisation for styrene *versus* n-butyl acrylate.

There are some aspects to n-butyl acrylate polymerisation by RITP that can still be investigated. The functionality of n-butyl acrylate must still be established. Elemental analysis can be used to determine the weight percentage of iodine in a polymer. This technique can be applied to styrene as well. The formation of MCRs in RITP has not been reported in literature. The long inhibition times for n-butyl acrylate are not ideal industrially, and a study of how far the temperature range can be stretched before MCRs become significant may prove useful.

The construction of predicted concentration profiles using PREDICI® software could be useful in a number of ways. For instance, to compare experimental results with predicted scenarios as well as to determine the duration of polymerisation that would limit the amount of dead chains.

Finally, a study of block copolymers formed between PS and PnBA would be interesting to establish the livingness of both polymerisation systems.

References

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