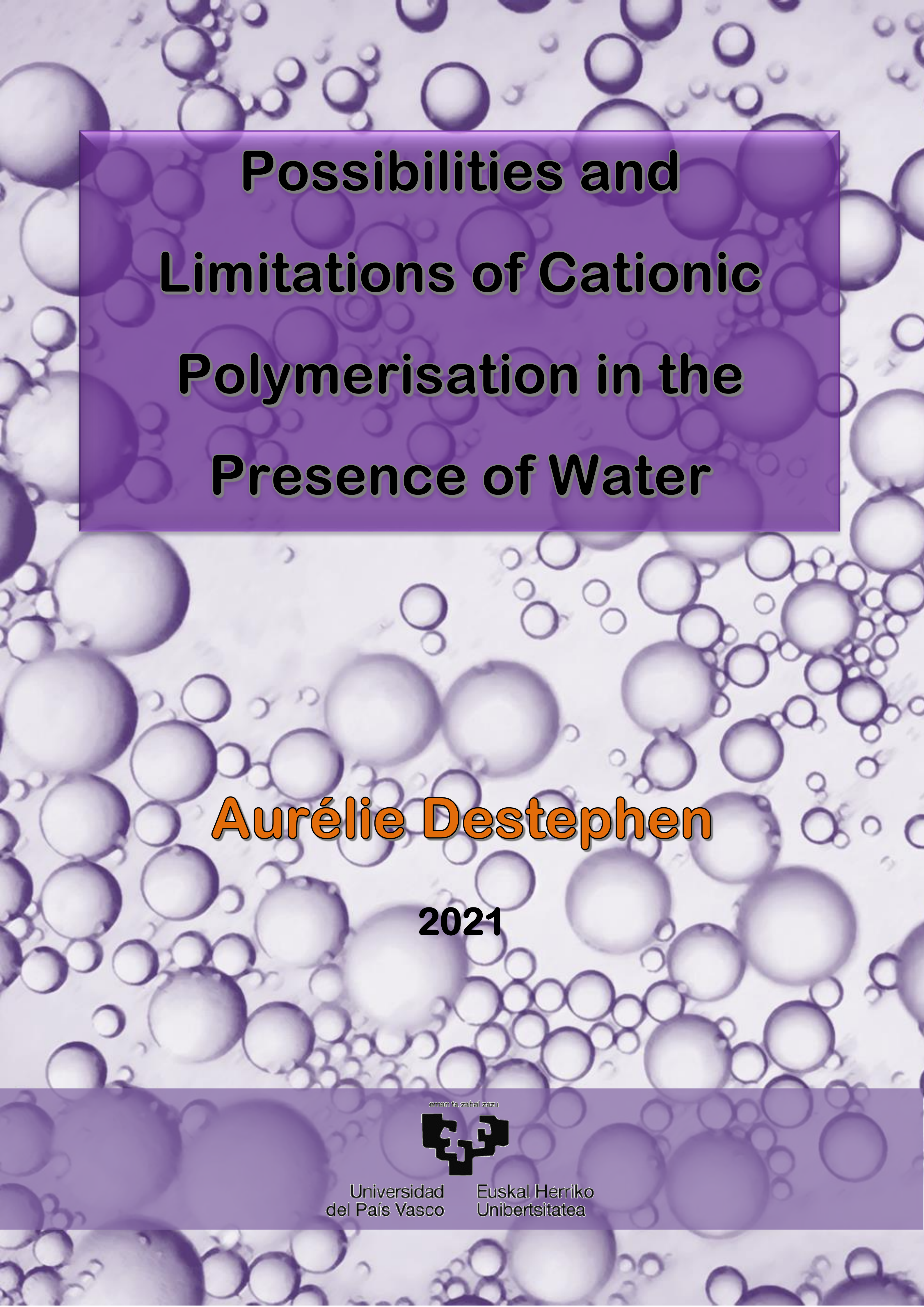

Possibilities and Limitations of Cationic Polymerisation in the Presence of Water

Aurélie Destephen

2021

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POLYMAT

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Chapter 1: Introduction and Objectives

1.1. Introduction

The development of synthetic polymers in the early 20th century led to a rapid change in the design and manufacture of an immense range of products, and today polymers are an essential part of day-to-day life. Behind this revolution in materials has been the development of a range of synthetic techniques capable of producing different macromolecular structures from distinct monomer families. In general, there are two main types of polymerisation techniques, step-growth and chain-growth. Step-growth polymerisation involves the stepwise reaction between reactive functional groups (*e.g.* carboxylic acid-alcohol or amine-isocyanate) present in the monomers[1,2] and is used commercially to produce a wide range of polymers including polyamides,[3] polyurethanes,[4–6] polyesters[7] and polycarbonates.[8] Due to the stepwise reaction mechanism, the molecular weight is built up slowly during the reaction and high molecular weight polymers are only generated towards the end of the polymerisation when the conversion is very high (see **Figure 1-1**).

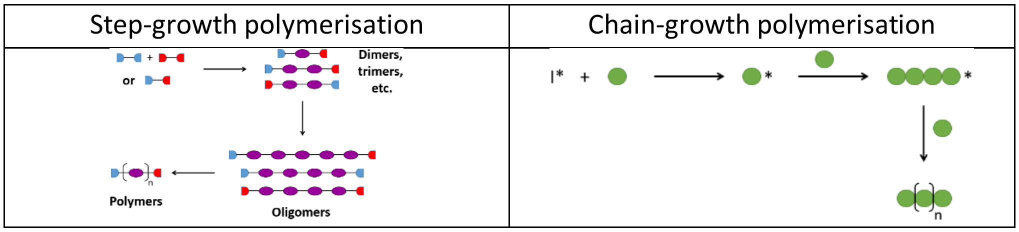


Figure 1-1: *Step-growth* vs. *chain-growth polymerisation mechanisms.*

In contrast to the step-growth mechanism, chain growth polymerisation involves the rapid addition of the monomer molecules to a small number of active centres[9] (**Figure 1-1**). As a result of this chain growth mechanism, high molecular weight chains are obtained from the beginning of the reaction. Depending on the nature of these centres, chain growth polymerisation can be divided in three different groups: coordination, radical and ionic polymerisations. Coordination polymerisation occurs by insertion reactions of vinylic species that are coordinated to a metal centre and is used extensively in the production of polyethylene and polypropylene.[10–12] Radical polymerisation proceeds with the propagation of a radical centre and allows the use of a large variety of vinylic monomers, such as styrene and (meth)acrylics. The versatility with regards to monomer family and relative insensitivity to impurities has made radical polymerisation one of the most widely used industrial techniques in the synthesis of polymers for applications such as coatings, adhesives, packaging and polymeric fibres.[13] The mechanism of ionic polymerisation is similar to that of radical polymerisation but occurs *via* ionic propagating species, either anions or cations. In this case, the monomers suitable for these techniques are more limited as they need to bear groups that are able to stabilise the negative or positive charge created on the molecule.

The major focus of this thesis is cationic polymerisation, particularly reactions that are performed under mild conditions in the presence of water. In this chapter, following a brief introduction to the uses of cationic polymerisation, the mechanistic details of cationic polymerisation are described. Subsequently, an outline of the historical development of catalysts capable of inducing cationic polymerisation in the presence of water is given. After that, we provide an overview of the current state-of-the-art with regards to cationic polymerisations conducted directly in aqueous media. Finally, an outline of the general aims and scope of the thesis is given.

1.2. Cationic Polymerisation

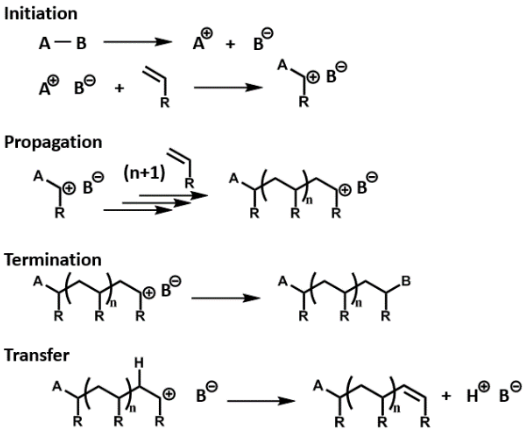
Cationic polymerisation is an ionic chain growth technique that proceeds *via* carbocationic propagating species. Due to the need to stabilise the carbocation centre, cationic polymerisation is limited to the polymerisation of vinyl monomers containing electron-donor groups, such as alkyl vinyl ethers,[14] isobutene,[15–18] styrene and its substituted derivatives,[19–23] and many derivatives of the terpene family,[24–26] but can also polymerise heterocycles from lactone,[27,28] lactam[29] and amine[30] families with high ring strain (5 and less-membered rings). Unlike radical polymerisation, cationic polymerisation of vinylic monomers offers the potential to obtain well-controlled polymer microstructures[31–33] (*i.e.* tacticity, stereoselectivity) and thus allows for the tuning of the final physical properties of polymer materials.[34,35]

Industrially, cationic polymerisation is used to produce poly(butene)s, hydrocarbon resins based on vinyl aromatics or poly(terpene)s, and poly(vinyl ethers).[36] These polymers have different applications depending on their final molecular weights (M_n) and composition. In the case of poly(butane) for example, low molecular weight poly(butene)s (M_n < 3,000 g.mol^{-1}) find use as adhesives[37,38] and lubricants,[39] while higher molecular weight poly(butane)s are used in sealants[40,41] and caulking applications. By copolymerisation of isobutylene with isoprene (0.5 to 2.5%), a highly resilient rubber known as butyl rubber is obtained, which is applied as inner tubes for tires,[42,43] electrical cable insulations,[44] protective gloves,[45,46] chemical tank liners[47] and pharmaceutical stoppers.[48]

Poly(vinyl ether)s are also produced by cationic polymerisation and can be synthesised as viscous oils, tacky resins or elastomeric solids depending on the initial monomer and their final molecular weights. The vinyl ethers are employed as non-migrating tackifiers,[49] plasticisers[50] and viscosity index improvers for lubricants.[51,52] Hydrocarbon resins, made of low M_n polymers by cationic polymerisation (M_n < 3,000 g.mol^{-1}) such as polystyrene and its derivatives, and poly(terpene)s (*i.e.* poly(pinene), poly(limonene), etc.), have applications in adhesives,[53,54] holt-melt systems,[55,56] inks and rubber additives.[57–59] In the case of terpene polymers, this is particularly significant as these polymers cannot be homopolymerised by radical polymerisation techniques.

1.3. The Mechanism of Cationic Polymerisation

Similar to other chain-growth polymerisation systems, cationic polymerisation proceeds in three different steps:[9] (i) the initiation step, in which the initiator/monomer is generally activated by a catalyst to create a cationic species and its counterion; (ii) the propagation step, corresponding to the reaction of the propagating cation with monomer units; and (iii) the termination step, which can occur through reaction of the cationic growing polymer chain with an anion or by transfer reactions (**Scheme 1-1**). In the following sections, the key stages in cationic polymerisation will be discussed.



Scheme 1-1: Mechanism of cationic polymerisation.

1.3.1. Initiation

Various initiators can be used to generate the propagating cation, including protic acids,[60] Lewis acids,[61,62] halogens,[63,64] photoinitiators,[65–67] electroinitiators[68–73] and ionising radiation.[66,74,75] This thesis will largely focus on the initiation by protic and Lewis acids. The initiation by a protic acid consists of the addition of a proton to the olefin. The nature of the acid plays a significant role in the rate of polymerisation. On one hand, the acid has to be strong enough to generate the carbenium ion centre. On the other hand, the anion should not be too nucleophilic to avoid instantaneous combination with the growing chain.[76] As an example, hydrogen halides are very strong acids that are able to produce a large quantity of protonated species, but the halide anions are too nucleophilic and rapidly terminate the polymerisation by combination.[9] Hydrogen iodide is the only one able to polymerise the most reactive monomers (*e.g.* vinyl ethers, *N*-vinylcarbazole).[64,77] Even in this case, only polymers of maximum a few thousand g.mol^{-1} can be obtained.

Higher molecular weight polymers are achievable when using Lewis acids, which is why this is the most common way to (co)initiate a cationic polymerisation.[78–80] In this case, a proton or carbenium ion donor, also called cationogen (*e.g.* hydrogen halide, alcohol, carboxylic acid, alkyl halide, ester, ether) is usually used in conjunction with a Lewis acid (*e.g.* metal halide, mainly $AlCl_3$, BF_3, $SnCl_4$, $TiCl_4$, and their organometallic derivatives).[24,79,81] The cationogen plays then the role of initiator as it generates the cationic species (proton or carbenium ion) that initiates the polymerisation, and the Lewis acid is called the co-initiator, or catalyst. This allows the creation of less nucleophilic anions, which have a lower tendency to combine with the propagating carbenium ion, so the propagation of a chain lasts longer, inducing the synthesis of high molecular weight polymers.[82,83] In the absence of any initiating species, the presence of trace amounts of water allows for generation of protons that can initiate the polymerisation. Though water can be detrimental to the polymerisation due to transfer reactions, when no initiator is used, traces amounts of water (up to 1:1 ratio with the catalyst) are essential in order to initiate the polymerisation.[21,84,85]

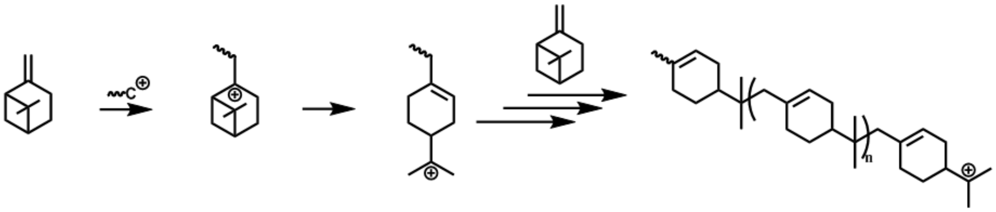
1.3.2. Propagation

High molecular weight polymers can be obtained only if the ions live long enough to propagate, which means that the propagating centres should be stabilised by solvation. Although high polarity solvents have a high solvation ability, many cannot be used in cationic polymerisation, as highly polar protic solvents such as water or alcohols can react with the propagating cation.[84] For this reason, low or moderately polar aprotic solvents, such as dichloromethane (DCM),[77] toluene[86] or *n*-hexane,[77] are usually employed. In these solvents, the propagating species are considered to exist in different forms that are in equilibrium; the covalent species (**a**), the contact ion pair (**b**), the loose ion pair (**c**) and the completely free ions (**d**).

$\sim\sim AB$	$\sim\sim A^{+}B^{-}$	$\sim\sim A^{+}\|B^{-}$	$\sim\sim A^{+} + B^{-}$
a	**b**	**c**	**d**

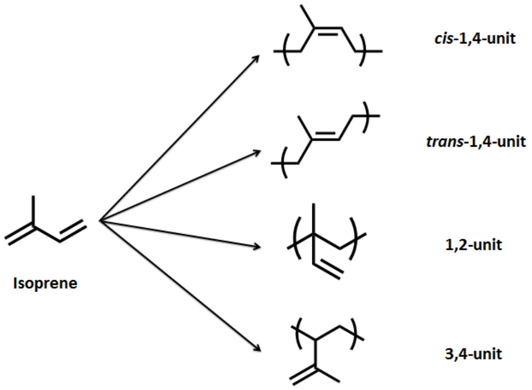
The covalent species is generally ignored, as it is usually non-reactive. For the contact ion pair, the propagating cation and its negatively charged counterion are close to each other and the ionic species are not separated by the solvent. In the loose ion pair, the solvent molecules partially solvate the different species, while in the case of free ions the ionic species are completely solvated by the solvent.[87] The presence of species **b** or **c** depends on the solvent, but generally the loose ion pair (**c**) is present for cationic propagating centres as their counterions are rather large, leading to lower attractive electrostatic forces between the two charges. The concentration of these different species in the reaction media depends significantly on the polarity of the solvent, and plays an important role on the kinetics of the polymerisation. For this reason, solvent choice has a strong influence on the kinetics of cationic polymerisation.[88]

In most cases, the carbenium ions formed by each propagation reaction are stable enough to polymerise directly, but in some cases the molecule undergoes a rearrangement in order to obtain a more stable carbenium ion, which has implications for the polymer structure. This rearrangement is particularly common in the polymerisation of α-olefins, which undergo hydride shifts to give more stable carbenium ions and in monomers that can relieve ring strain by rearrangement such as β -pinene[24] (**Scheme 1-2**).



Scheme 1-2: *Rearrangement of β-pinene during the propagation step.*

Cationic polymerisation, unlike radical polymerisation, has the advantage of allowing some control over the stereo- and regioselectivity of vinylic and diene monomers during the polymerisation. For example, isoprene is a diene that can create four different microstructures during the polymerisation (**Scheme 1-3**) and can be polymerised *via* several mechanisms (radical, coordination, anionic, cationic). Although its reactivity is lower in cationic polymerisation compared to other techniques, Richardson *et al.*[89] showed in 1954 that polyisoprenes obtained using metal halides contained more than 90% of *trans*-1,4-units. Similarly, later work has demonstrated that *trans*-1,4 units are almost exclusively obtained in cationic polymerisation of most 1,3-dienes.[78,90,91]



Scheme 1-3: *Different microstructures obtained from isoprene.*

Various vinyl ethers have also been polymerised with high selectivity *via* cationic polymerisation. In the early 2000s, Ouchi *et al.* studied the influence of the structure of the Lewis acid used as catalyst,[92] as well as the influence of the vinyl ether structure[32] (structures in **Figure 1-2**) on the stereochemistry during the polymerisation. Using catalysts bearing non-bulky substituents, it was shown that the polymerisation became more stereoselective and highly isotactic poly(vinyl ether)s were obtained. Moreover, they observed that the vinyl ethers bearing branched alkyl chains, such as isopropyl vinyl ether (IPVE), *tert*-butyl vinyl ether (TBVE) and isobutyl vinyl ether (IBVE), could polymerise much faster than those with linear alkyl chains. The stereoselectivity during the polymerisation was also found to be dependent on the pendant chain. Indeed, when the alkyl chain was branched close to the ether group, the polymer obtained was highly isotactic (meso diads between 88 and 90%) whereas the vinyl ethers having linear or highly bulky alkyl chains (*e.g.* TBVE) gave polymers that were more atactic.

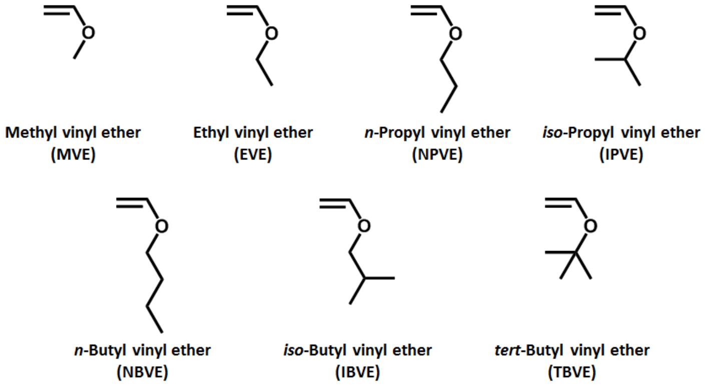
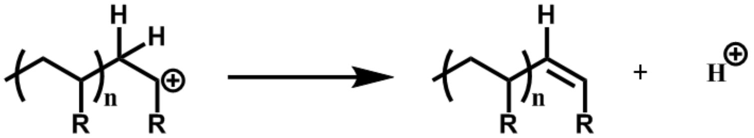


Figure 1-2: *Structures of the vinyl ethers studied by Ouchi* et al..

1.3.3. Termination and Transfer

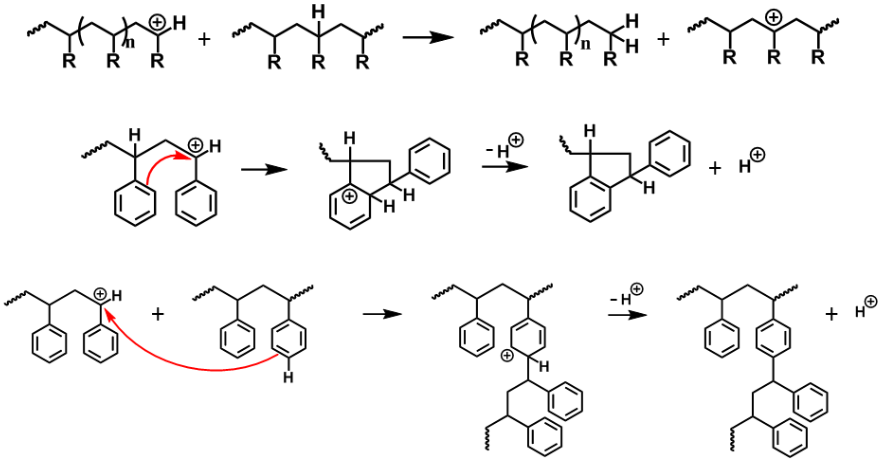
One major advantage of cationic polymerisation over alternative chain-growth techniques, such as radical polymerisation, is that it allows for polymerisation at high concentrations of propagating species without any bimolecular termination, as two cations cannot react together. However, cationic polymerisations readily undergo alternative termination and transfer reactions with various species.

One of the most important termination reactions occurring in cationic polymerisation is the β-hydrogen elimination reaction.[21,93] This reaction arises because although carbocations are drawn with the charge centred on the carbon atom, in reality the charge is dispersed and a significant fraction can be localised on the β-hydrogen atoms. This hydrogen atom is therefore relatively easily abstracted by any basic component (monomer, counterion, water, *etc.*) present in the reaction,[94] leading to a polymer chain ended by a double bond (**Scheme 1-4**). This mode of termination does not necessarily imply a decrease in the rate of polymerisation as the number of propagating chains does not change, but limits the molecular weight of the polymer. Since the activation energy of β-H elimination is higher than that of propagation, cationic polymerisations are often conducted at very low temperatures, typically between -40 and -100 °C, where the effects of β-H elimination (and other transfer reactions) are reduced.[95–98]



Scheme 1-4: *β-Elimination process in cationic polymerisation.*

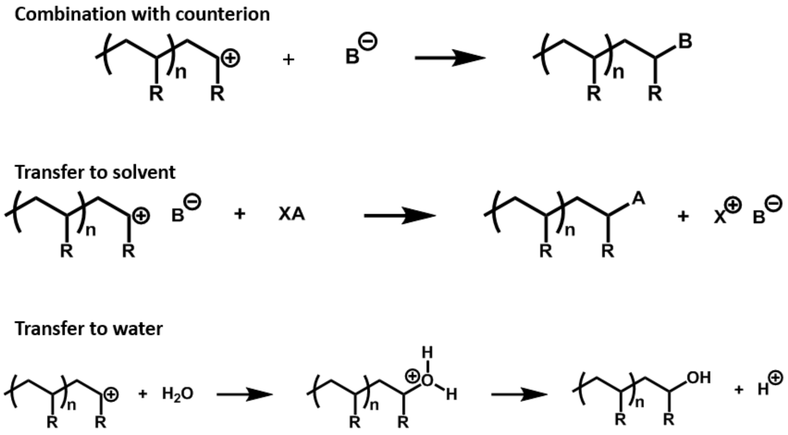
Chain transfer to polymer can also occur in cationic polymerisation.[99,100] This transfer reaction can arise through both inter and intramolecular substitution reactions, respectively, leading to branching or a rearrangement of the chain end (**Scheme 1-5**). In the cationic polymerisation of monomers containing aromatic rings, such as styrene, transfer to polymer commonly occurs through a Friedel-Crafts reaction leading to substitution on the aromatic ring.[100]



__Scheme 1-5:__ Possible transfer reactions to polymer in cationic polymerisation.

Propagating cations can also combine with the counterion,[85] which leads to a decrease in the concentration of propagating species. This reaction is particularly influenced by the nature of the solvent and recombination is enhanced in non-polar solvents where the ions are not stabilised. Chlorinated solvents such as dichloromethane (DCM), which are relatively polar but non-reactive, are therefore considered ideal for the cationic polymerisation.[98]

Due to the high reactivity of the carbocation, cationic polymerisation is very sensitive to nucleophilic impurities, which play the role of retardants or transfer agents in the system, limiting the final molecular weight of the polymers. Nucleophiles can interact with the Lewis acids, which can result in a retardation of the reaction due to the decreased acidity of the Lewis acid complex. Another common effect of nucleophiles is reaction with the carbocation leading to the formation of onium species.[101,102] For example, in the case of alcohols an initial onium species is formed that can subsequently release protons to leave an ether end group and represents a chain transfer reaction. To avoid these side reactions with nucleophilic impurities, all reactants are generally purified and dried before use. One common nucleophilic impurity is water. In the presence of water, transfer reactions to water (**Scheme 1-6**) can become important, causing termination of the propagating chains and limiting the molecular weights.[84,103,104] In order to minimise these transfer reactions, cationic polymerisations are usually performed under dry conditions.



Scheme 1-6: Different termination and transfer reactions occurring in cationic polymerisation.

1.3.4. Living Cationic Polymerisation

One of the major developments in the field of cationic polymerisation arose during the 1980s, when “living” cationic polymerisation systems were developed. The main conceptual difference between a normal cationic polymerisation and a living polymerisation, is that reaction conditions are targeted such that termination and transfer reactions are suppressed. In an ideal living polymerisation, after a fast and quantitative initiation, transfer and termination reactions do not take place, leading to a system in which only propagation occurs until all the monomer is consumed, which allows the addition of fresh monomer and thus the possibility to create block copolymers.[98,105] In this case, the molecular weights (M_n) increase linearly with the conversions and narrow dispersities are obtained. However, as detailed above, transfer/termination readily occurs in most cationic polymerisations and propagation is very fast, making quantitative initiation a great challenge. In this case, such systems display many of the characteristics of true living polymerisations (narrow molecular weight distributions, linear evolution of molecular weight with conversion, *etc.*) but are better described as "pseudo-living" or controlled.[106] In order to proceed in a pseudo-living fashion there are three fundamental requirements that must be met: (i) Initiation should be fast and quantitative; (ii) termination of the propagating carbocation should be reversible; (iii) transfer reactions should be suppressed.

The first of these requirements ensures that the initiation stage occurs early in the reaction, such that polymerisation occurs evenly across all chains. This can be achieved by using functionalised initiators which can be activated to give carbocation structures that are similar to the monomers considered, readily ionise and subsequently propagate in the presence of the activating Lewis acid (examples in **Figure 1-3**).[107]

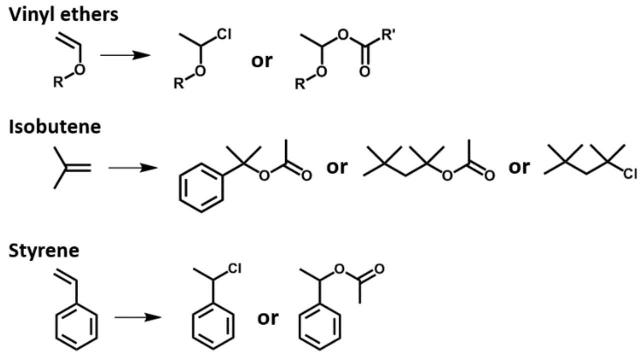
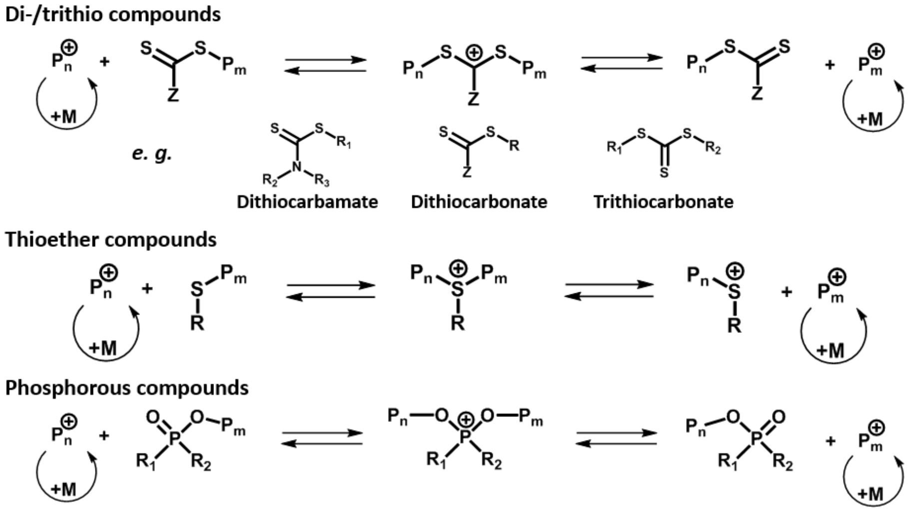


Figure 1-3: *Examples of typical initiators for different monomers in living cationic polymerisation.*

The second key aspect is ensuring an equilibrium between active and dormant chains. This is commonly achieved by using a Lewis acid that can reactivate the chain end following ion recombination. The strength of the Lewis acid and the nature of the counterion dictate the balance between active and dormant chains and are therefore critical for achieving a well controlled, living system.[60,61,108] In many cases, Lewis acid strength alone is not sufficient to induce control and therefore additives must be included that shift the equilibrium in favour of the dormant species. This can be achieved by addition of a nucleophilic compound which interacts either with the Lewis acid or the carbocation itself.[109–114] An example of this is through the addition of species that react with carbocations to give dormant onium species such as sulphides and ethers. In this case an additional equilibrium is set up and the concentration of propagating cationic species is lowered.[101] Alternatively, the equilibrium can be shifted towards the dormant species by addition of a salt to the catalytic system, which can lead to improved control over the polymerisation.[81,115,116] For instance, Higashimura and co-workers showed in the early 1990s that the addition of tetrabutylammonium halides ($n\mathrm{Bu}_4\mathrm{NX}$; X = Cl, Br, I) to different halogen adducts of styrene (St-X) coupled with tin tetrachloride ($SnCl_4$) led to a more controlled cationic polymerisation of styrene than without salt.[22,117]

The final key aspect of suppressing transfer reactions is perhaps the most challenging. Although many publications in this area suggest that transfer reactions occur less frequently in living cationic systems, evidence for significant reduction in the rate of chain transfer is scarce. In fact, most "living" cationic polymerisations are simply conducted at low temperatures (to minimise transfer) and at relatively low initiator/monomer ratios, which minimises the number of dead chains in the system.[118] As an example, one of the first "living" cationic polymerisation systems was reported by Faust and Kennedy who presented the living cationic polymerisation of isobutylene (IB) employing esters/boron trichloride (BCl_3) as catalytic systems at -30 °C.[95] The use of 2,4,4-trimethylpentyl-2-acetate (TMPOAc) and cumyl acetate (CuOAc) led to very fast initiation and propagation. The counteranions associated to these species avoided substantial amounts of chain transfer and termination events, shown by the absence of double bond-terminated species, characteristic of β-hydrogen elimination reactions. Moreover, a linear increase of the molecular weight with conversion was observed, even after several monomer additions. Furthermore, there was a decrease of the dispersity with the subsequent additions, clearly demonstrating the living character of the polymerisation.

This example, and other "living" cationic polymerisations detailed above, proceed by a reversible termination mechanism in which a Lewis acid activates a functional end group. More recent work has demonstrated the possibility to conduct controlled cationic polymerisations by a mechanistically distinct, degenerative chain transfer route. In these systems, a very small amount of protic initiator is added to the system and the molar mass is controlled by the presence of chain transfer agents that undergo degenerative chain transfer. These reactions are proposed to take place *via* an intermediate cationic species as shown in **Scheme 1-7** and has been demonstrated for a number of chain transfer agents (CTAs) from different families, such as phosphorous coumpounds,[119] thioethers,[120] dithiocarbamates,[121,122] dithiocarbonates[123,124] and trithiocarbonates.[121,124–128] Using the same reversible addition-fragmentation chain transfer (RAFT) agents in controlled radical and cationic polymerisation allows the production of new block copolymers, such as block copolymers of vinyl ethers and (meth)acrylates,[120,121,126,127] that are not possible to synthesise solely by radical or cationic polymerisation.



Scheme 1-7: Structures of the different families of RAFT agents available for cationic RAFT polymerisation.

1.4. Towards Water Tolerant Initiator Systems

As has been highlighted above, the presence of water can be problematic in cationic polymerisations as water acts as a chain transfer agent and can limit the molecular weights of polymers obtained. However, given that many of the most common catalysts used in cationic polymerisations are based on metal halides and other water sensitive Lewis acids, water poses an additional problem in that it can also inhibit polymerisation through decomposition of the catalyst. While metal halides are still commonly employed industrially, the high sensitivity of these catalysts to water is a major drawback. As a result, there has been a significant amount of interest directed at moving towards catalyst systems that are tolerant to the presence of water. In the next section, the historical development of catalyst systems used in cationic polymerisation will be detailed, with a particular focus on those systems for which the presence of water does not drastically influence the polymerisation.

1.4.1. Development of Initiator and Co-initiator Systems

1.4.1.1. Bronsted acids

Most hydrogen halides do not make good initiators of cationic polymerisation as the highly nucleophilic halides tend to result in the formation of a covalent bond between the carbenium ion and the halide anion, thus preventing polymerisation.[9,76] However, it is possible to initiate polymerisation using Bronsted acids that generate less nucleophilic anions such as perchlorates[21,87,129] and triflates.[130,131] Even in these cases, except when highly reactive monomers are used, the molecular weights are limited due to recombination of the ion pairs and β-hydrogen elimination reactions that occur due to the relatively high basicity of the counterions. For example, Pepper and Reilly employed perchloric acid in the cationic polymerisation of styrene, at temperatures ranging from 25 to -70 °C in various chlorinated solvents such as 1,2-dichloroethane and carbon tetrachloride but observed low molecular weights ($M_n <$ 6,000 $g.mol^{-1}$).[21,87]

While the recombination of halides with the propagating carbenium ion was looked upon in a negative light in early work, the later discovery of living type reactions has shown that in many cases, in the presence of a Lewis acid, the dormant terminal bonds can be reactivated.[77,86] In these cases, protic acids are generally used to form an initiator in-situ by direct reaction with the double bond of the monomer. The resulting alkyl halide (or ester in the case of carboxylic acid initiators) adducts can then be activated with a Lewis acid to reversibly generate the propagating cationic species. For example, Miyamoto *et al.* used a combination of hydrogen iodide and molecular iodine for the living polymerisation of isobutyl vinyl ether (IBVE), which led to polymers of low dispersity ($Đ < 1.1$). They later used the same system to polymerise different vinyl ethers (VEs) (structures in **Figure 1-4**) and make block copolymers of a combination of VEs as well as VE with *p*-methoxystyrene (pMOS) in the same conditions.[86]

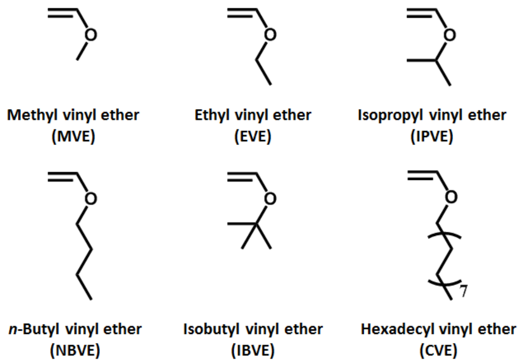


Figure 1-4: *Structures of the different vinyl ethers studied with non-metal halide initiators.*

1.4.1.2. Metal Halide Lewis Acids

As highlighted above, Lewis acids are often used to catalyse cationic polymerisations, but in most cases the Lewis acid itself does not strictly act as an initiator but serves as a co-initiator when some cation generating species are present. One of the most common initiating species arises from the presence of trace amounts of water.[132] It is also fairly common to add initiating species (also known as cationogens), which are ionised in the presence of the Lewis acid and lead to a more controlled initiation process.[107] Common cationogens include alkyl halides, esters, ethers and alcohols. In these systems, protic initiation arising from adventitious water can be at least partially suppressed by the addition of proton traps, such as di-tert-butyl pyridine.[133,134]

In the presence of a cationogen and Lewis acid, the polymerisation rate depends significantly on the Lewis acid strength and the nature of the counterion.

Stronger Lewis acid tend to give higher concentrations of propagating cationic species and therefore the rate of polymerisation is higher as Lewis acid strength increases. Thus, for the equivalent ligands, polymerisations conducted with aluminium based Lewis acids would be expected to be faster than boron based Lewis acids.[135] The choice of Lewis acid is also dependent on the monomer that is to be polymerised. For example, titanium chloride with one alkoxy group is capable of polymerising styrene, methyl styrene and vinyl ethers. When it has two alkoxy groups, it is too weak to initiate polymerisation of styrene but is capable of polymerisation of methyl styrene and vinyl ethers. When it has three alkoxy groups, the Lewis acidity is low and can only polymerise vinyl ethers.[98]

In the presence of water, most Lewis acid catalysed polymerisations result in at first an increase with increasing [H_20]/[Lewis acid] before reaching a maximum, after which the increase in water concentration results in a decrease in the polymerisation rate.[84,136] This shift arises because initially the increase in water concentration results in higher number of propagating chains but later reaction with water results in the formation of inactive species. Coupled with the decrease in rate is a decrease in the molar mass of the polymer, which is the result of transfer reactions to water. At particularly high water concentrations, or in aqueous media, most metal halides decompose and have negligible catalytic activity.[137,138] However, as detailed below, there are a number of Lewis acid catalysts that are less sensitive to water that have been proposed for cationic polymerisations conducted in aqueous media.

1.4.1.3. Rare Earth Metal Triflates

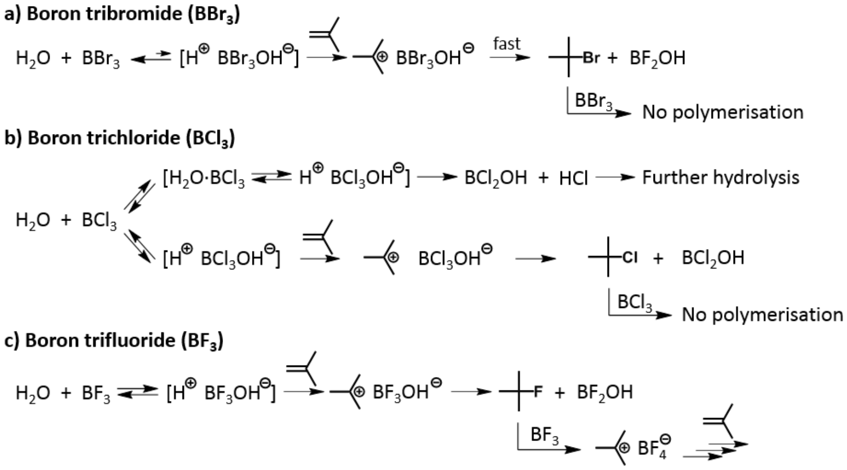
The Lewis acids used to catalyse cationic polymerisations are largely similar to those used to catalyse many common reactions in organic chemistry such as Friedel-Crafts, Diels-Alder, Aldol or Michael reactions. The evolution of these reactions towards water-containing systems led to the discovery of novel water-resistant catalysts, based mainly on lanthanides[139–142] and scandium[142,143] triflates. Building on these discoveries, in 1997 Satoh *et al.* attempted the use of ytterbium triflate ($Yb(OTf)_3$; OTf = OSO_2CF_3) as a catalyst with the adduct of IBVE and HCl as initiator for the cationic polymerisation of IBVE at -15 °C in DCM.[144] This catalytic system alone led to an almost instantaneous uncontrolled polymerisation. The addition of amine nucleophiles such as pyridine and its substituted analogues as well as trimethylamine allowed for a living polymerisation, obtaining polymers which molecular weight increased linearly with the conversion and low dispersities. It was demonstrated that the amines had an electron-donating effect on the $Yb(OTf)_3$ that decreased the Lewis acidity of the catalyst, making it more suitable for living cationic polymerisation. However, the most remarkable feature of this new catalyst was the possibility to recover it by extraction in water and subsequently reuse it. Thus, unlike most Lewis acid catalysts, despite the treatment in water, $Yb(OTf)_3$ was not deactivated. This discovery later inspired the same group to translate this catalyst to use directly in aqueous media as will be described in Section 1.5.2.

1.4.1.4. Boron-based Lewis Acids

Boron-based catalysts are another family of catalysts employed for the cationic polymerisation of different monomers. Unlike most Lewis acids used in cationic polymerisation, certain boron-based Lewis acids have some degree of tolerance to water and several generations of this type of catalysts have been developed with a progressive improvement in water tolerance.

- Boron Halides (BX_3)

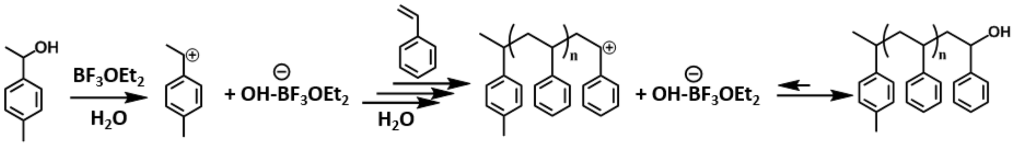
The first generation of boron-based catalysts that was developed, boron halides, have similar sensitivity to water as the Lewis acids detailed in Section 1.4.1.2., with complete degradation in the presence of water in the medium. For instance, the cationic polymerisation of isobutylene[85] was studied in the late 1970s by Kennedy and co-workers using different boron halides (BCl_3, BF_3, BBr_3) as catalysts. Each of the catalysts resulted in different behaviour of the polymerisations. Indeed, boron tribromide (BBr_3) failed to catalyse the polymerisation, with final conversions below 10%. Although the reasons could not be experimentally proven, several possibilities were proposed: (i) the hydrolysis of BBr_3 giving rise to inactive products; (ii) the BBr_3OH^- anion that would be formed by the reaction of the catalyst with water was so unstable that it could not be formed or would immediately be converted to *tert*-butyl bromide (*t*-BuBr) and BBr_2OH, which cannot further react (**Scheme 1-8a**). Boron trichloride (BCl_3) was a good catalyst for the polymerisation of isobutylene only in the presence of a large amount of polar solvents such as DCM and at very low temperature (T < -50 °C). Trace amounts of water were crucial in order to initiate the polymerisation. However, direct contact of BCl_3 with water led to fast hydrolysis that made the polymerisation impossible (**Scheme 1-8b**). Almost full conversion could be obtained adding BCl_3 last to the water/isobutylene/DCM mixture and molecular weights up to 200,000 $g.mol^{-1}$ could be achieved. As for boron trifluoride (BF_3), its hydrolysis is much slower and the reaction of water with this catalyst leads to the formation of protonating agents (**Scheme 1-8c**). The polymerisation of isobutylene catalysed by BF_3 was successful in polar and non-polar solvents, and contrary to BCl_3, the final conversion decreased with the decrease of temperature. Nevertheless, the maximum molecular weight reached were lower than those obtained with BCl_3, probably due to stronger interaction of the carbenium ion of the propagating chain and the fluoride-based counteranion, inhibiting the ionisation.



Scheme 1-8: *Mechanisms of hydrolysis and initiation for the cationic polymerisation of isobutylene encountered with water/boron halides catalysts systems.*

- Boron Trifluoride Diethyl Etherate (BF_3OEt_2)

The second generation of catalysts containing boron centred is the use of boron trifluoride diethyl etherate (BF_3OEt_2). BF_3OEt_2 is tolerant to water, which allows it to be used even in the presence of residual or small amounts of water in the medium, but it still undergoes hydrolysis that limits its utility. This is demonstrated in the work of Satoh *et al.,* who published several articles on the cationic homo- and copolymerisation of St and derivatives (*p*-hydroxystyrene – pHS, *p*-methoxystyrene – pMOS) and β-methylstyrene derivatives (anethole and isoeugenol) using BF_3OEt_2 in conjunction with alcohols as initiating systems at 0 °C in dichloromethane or acetonitrile.[20,145–147] They successfully synthesised homopolymers and copolymers of high molecular weights in a controlled manner in the presence of water in the medium (up to $[H_2O]_0 = 200$ mM). However, a further increase of water content led to a loss of control in the polymerisations. They concluded that using BF_3OEt_2, water acts as a reversible chain transfer agent accelerating the interconversion of the active species (cations) into the dormant ones (C-OH) (**Scheme 1-9**). Later work by Radchenko *et al.* has shown that in the presence of large excess of water, BF_3OEt_2 catalysed polymerisations suffer from dramatic drops in the polymerisation rate and results in low molecular polymers with broad molecular weight distributions. This has been attributed to the hydrolysis of the Lewis acid in the presence of excess water.[148]

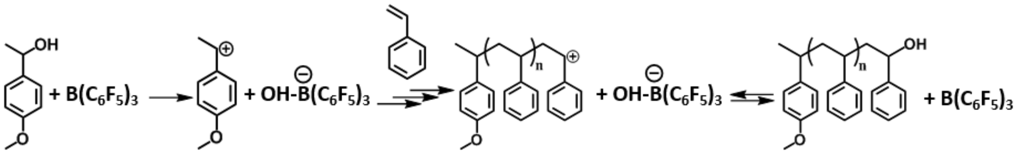


Scheme 1-9: *Proposed mechanism for the living cationic polymerisation of styrene using BF_3OEt_2.*

- Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$)

Following on from the use of BF_3OEt_2, a significant amount of work has been conducted using tris(pentafluorophenyl)borane ($B(C_6F_5)_3$). Unlike the overwhelming majority of systems that have been used in cationic polymerisation, $B(C_6F_5)_3$ is tolerant to water,[149,150] which allows the cationic polymerisation to be performed even in a large amount of water. This characteristic allows for an efficient catalyst without the need of extremely dry conditions.

Kostjuk *et al.* were one of the first to study the use of $B(C_6F_5)_3$ and reported the cationic polymerisation of St in DCM[151] and pMOS in acetonitrile[152] at 20 °C under air atmosphere using water or pMOS-OH as initiator. For the polymerisation of St initiated by water, almost complete conversion was obtained after 24h and the molecular weight decreased while the dispersities increased along the reaction, probably due to transfer reactions. In contrast, using pMOS-OH as initiator, significant conversion could be achieved in only 6h, the experimental M_n increased with conversion and at the later stage of the polymerisation were close to the theoretical values calculated in the assumption that each molecule of initiator creates one polymer chain. The higher M_n than the calculated ones at the beginning of the reaction was attributed to the fast monomer addition in comparison to the reversible terminated species (**Scheme 1-10**). In the case of pMOS, the cationic polymerisation was much faster using pMOS-OH as initiator than water and the reaction could be controlled at high initiator concentration ($[pMOS\text{-}OH]_0 = 0.02$ mol.L^{-1}), with a linear evolution of the M_n with conversion, close to the theoretical values, narrow molecular weight distributions (MWDs) and efficient chain extension with fresh feeds of pMOS.



Scheme 1-10: *Proposed mechanism of the cationic polymerisation of St using $B(C_6F_5)_3$.*

Radchenko *et al.* also studied the influence of the concentration of water for the polymerisation of pMOS in a 1:1 (v/v) mixture of acetonitrile and dichloromethane at 22 °C using pMOS-OH/$B(C_6F_5)_3$ as catalytic system.[153] They observed a decrease of the rate of polymerisation with the increase of water concentration, with an induction period of several hours for a water concentration of 0.52 M as well as a lowering of the molecular weight, due to a competitive initiation by water at high concentrations. However, the dispersity decreased with the increase in water content, which they attributed to the role of water as chain transfer agent that leads to a higher concentration of inactive chains compared to propagating carbenium ion and results in a better control of the molecular weight distribution.

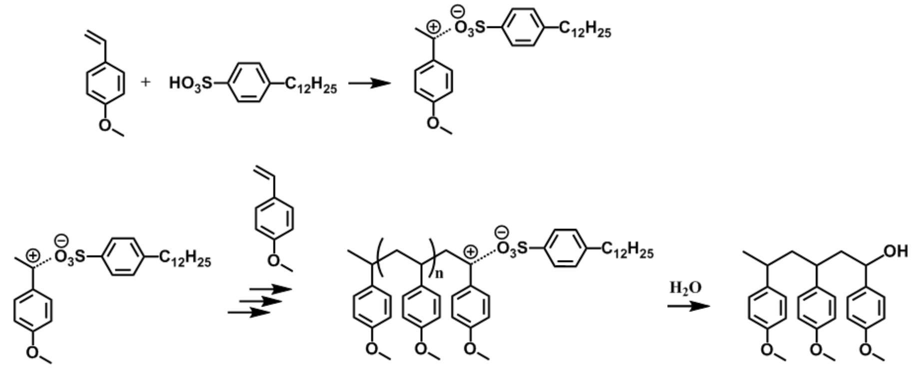
1.5. Cationic Polymerisation in Aqueous Media

All current commercial cationic polymerisation processes utilise catalysts which have high sensitivity to water. With the development of water-tolerant and water-resistant catalysts for the cationic polymerisation, there have been a number of attempts to move away from these catalysts and work towards systems that allow cationic polymerisation to be performed in aqueous media (suspension, emulsion and miniemulsion). Conducting the polymerisation in dispersed systems using water would overcome the use of halogenated toxic solvents and would therefore be highly beneficial with respect to the sustainability of the process. However, as should be clear from the content of this chapter so far, there are a number of obvious challenges that arise from conducting cationic polymerisations in the presence of water.

First, as seen previously, cationic polymerisations are often performed at very low temperatures (typically between -40 and -100 °C), at which water is in the solid state. Unless conducted at high salt concentration, where colloidal stability would be an issue, cationic polymerisation in aqueous media must be performed at temperatures above 0 °C. This increase in temperature will then make the propagating chains more subject to transfer reactions. Moreover, as described in section 1.3.3, cationic polymerisation is very sensitive to water due to the transfer reactions easily occurring directly with water. Despite these challenges, since 2000 there have been a number of apparently successful attempts to conduct cationic reactions directly in aqueous media. To date, the major challenge has been to find an initiating system that promotes a relatively fast rate of reaction and also leads to high molecular weights in the presence of water. In this section, the development of various catalyst systems for cationic polymerisation in dispersed media will be described.

1.5.1. Bronsted Acids

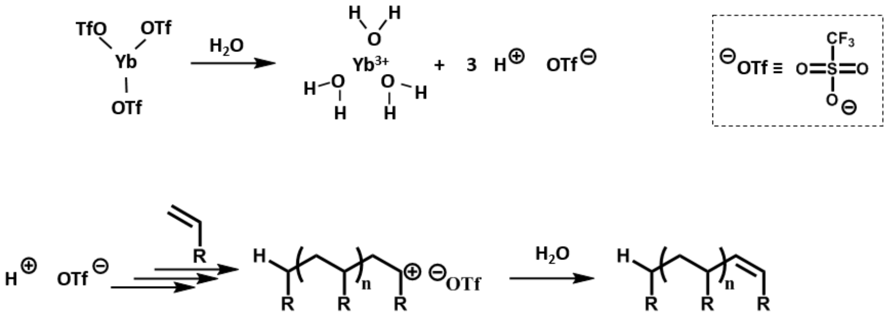
As described in Section 1.4.1.1., Bronsted acids can be used to initiate cationic polymerisation in the event that the anion formed is not too nucleophilic. In aqueous dispersed media, an additional challenge arises in that the acid will tend to partition towards the aqueous phase and the concentration in the dispersed monomer phase will be low. One way to overcome this issue is the use of so-called INISURFs (initiator and surfactant combined), such that the acid adsorbs to the water/monomer interface. For example, using dodecylbenzenesulfonic acid (DBSNa) as INISURF, Cauvin *et al.* have reported the cationic polymerisation of *p*-methoxystyrene (pMOS) in miniemulsion (**Scheme 1-11**).[154,155] DBSNa is a strong Bronsted acid that is able to initiate the cationic polymerisation. However, using this type of INISURF only oligomers could be obtained (M_n < 1,500 $g.mol^{-1}$) and the timescale for the polymerisation was long (up to one week). In the same way, Touchard *et al.*[156] performed the cationic polymerisation of pMOS in miniemulsion using sodium dodecyl sulfate (SDS). The acidic medium led to the surfactant existing in its sulphuric acid form. This enabled the formation of protons to initiate the polymerisation and obtained oligomers of around 1,400 $g.mol^{-1}$.



__Scheme 1-11:__ Mechanism of the cationic polymerisation of pMOS using DBSNa as INISURF.

1.5.2. Rare Earth Metals

Unlike the majority of metal based Lewis acids reported in Section 1.4.1.2., rare-earth metal halides and triflates have reduced sensitivity to water. Taking advantage of this difference in reactivity, Satoh *et al.* developed the use of lanthanide triflates as co-catalysts for the cationic polymerisation of pMOS[157–159] as well as isobutyl vinyl ether (IBVE),[157] initiated by the adducts of the monomer and hydrochloric acid (pMOS-HCl or IBVE-HCl) in suspension and emulsion. Among the lanthanides, ytterbium triflate ($Yb(OTf)_3$) was one of the most efficient to perform these polymerisations. However, in all cases, limited molecular weights were obtained with a maximum molecular weight of *ca*. 3,000 $g.mol^{-1}$. Furthermore, very large quantities of the ytterbium triflate salts were required in order to achieve a reasonable polymerisation rate. Using similarly high quantities of ytterbium chloride ($YbCl_3$) as a co-catalyst, Storey *et al.*[160] reported relatively high molecular weight polymers (M_n < 20,000 g.mol^{-1}) using phenylphosphonic acid initators. Cauvin *et al.*[161,162] proposed a mechanism for the lanthanide triflate mediated polymerisation process, involving catalyst dissociation in water to give Yb^{3+} and $(OTf)^-$ ions (**Scheme 1-12**). The triflate anions can then capture protons which would initiate the cationic polymerisation, with the lanthanide triflate acting as counterion.



Scheme 1-12: Mechanism for the cationic polymerisation using $Yb(OTf)_3$ as a catalyst.

Central to the proposal of Cauvin *et al.* was the idea that due to the polarity of the catalyst molecules, the polymerisation took place primarily at the interface between the organic and the aqueous phases. As the polymer chains grew, they became more hydrophobic until eventually the chains would enter inside the organic particles and stop propagating (**Figure 1-5**). As a result, a so called "critical degree of polymerisation (DP)", calculated to be around 10 monomer units, was expected, regardless of the monomer considered.[154,155]

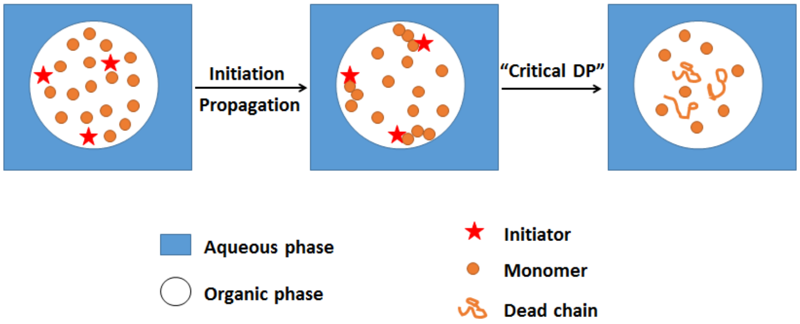


Figure 1-5: *Mechanism of the so-called "critical DP".*

1.5.3. Lewis Acid-Surfactant Combined Catalysts (LASCs)

In order to try to displace the polymerisation from the interface to the inside of the particles and avoid the "critical DP" effect, Lewis acid-surfactant combined catalysts (LASCs) were developed. Using this technique, Cauvin *et al*.[163] reported the synthesis of poly(*p*-methoxystyrene) (poly(pMOS)) in an emulsion polymerisation with high molecular weights (several thousand g.mol^{-1}). In their work, Disponil FES32 ($C_{12}H_{25}(O\text{-}CH_2\text{-}CH_2)_8OSO_3Na$, 30% water solution) was used as the surfactant and $YbCl_3$ as the Lewis acid to generate the LASC. However, the reaction was observed to occur in two distinct steps (**Figure 1-6**). During the first step, the polymerisation rate was very low and polymers with molecular weight in the range of that considered to be characteristic of cationic polymerisations conducted in water (< 5,000 g.mol^{-1}) were observed. This was proposed to be the result of the polymerisation occurring at the water/monomer interface. In the second step, after approximately 100h of polymerisation, polymers of significantly higher molecular weight were obtained (up to 43,000 g.mol^{-1}), which was attributed to the shifting of the polymerisation to the interior of the particles.

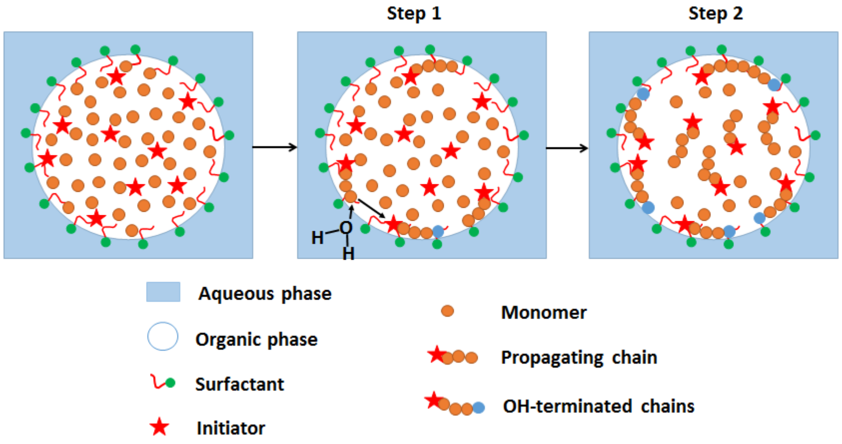
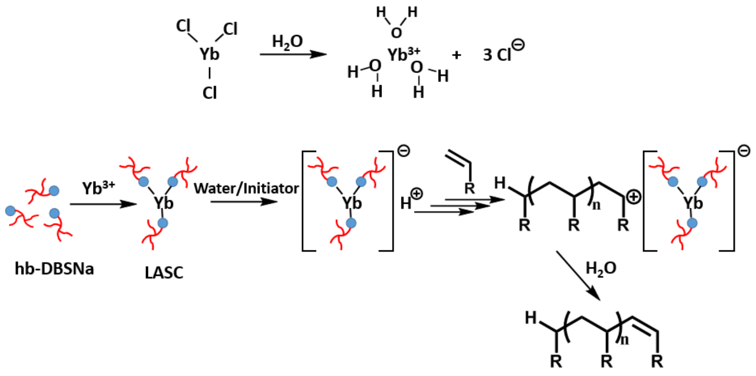


Figure 1-6: *Mechanism proposed by Cauvin* et al. *for the cationic polymerisation in emulsion in two steps.*

Building on this work, Vasilenko *et al.* presented groundbreaking results on the use of LASCs for the synthesis of high molecular weight polymers in emulsion. They demonstrated the synthesis of poly(pMOS),[164,165] as well as poly(styrene) (PS), poly(isoprene) (PI) and their copolymers,[164] and poly(β-myrcene)[166] using LASCs made from a combination of lanthanide salts and hyper-branched dodecylbenzene sulfonic acid (hb-DBSNa). Reasonably high solid content latexes were obtained (≈ 30 wt-%) although large quantities of the LASC was used (≈ 60 wt-% based on monomer). They demonstrated the synthesis of polymers with high molecular weights (up to 150 kg.mol^{-1}) and suggested a mechanism to explain these surprising results (**Scheme 1-13**). They proposed that ytterbium triflate dissociated completely and, subsequently, the metal ion formed a hydrate. Slow hydrolysis of the hydrated metal complex would then result in the formation of a Bronsted acid that initiates the polymerisation. The Yb^{3+} cation also complexes with the surfactant to form a micellizable LASC. Upon addition of monomer, a two phase system is generated, consisting of a continuous aqueous phase and a dispersed phase of monomer droplets stabilised by the LASC. As initiation takes place inside the monomer droplets, it was proposed that the rate of polymerisation should be dependent on the Bronsted acid concentration within the particles, a result which was demonstrated experimentally using different ytterbium salts. Slow initial rates of polymerisation were observed which was attributed to the low amount of hydrolysis of the hydrated metal complex and the limited partitioning of the Bronsted acid into the monomer droplets. It was proposed that once initiated, propagation took place rapidly in the monomer droplets with the LASC acting as counterion, until the carbenium ion undergoes chain transfer to either water molecules or monomer. This proposed mechanism agreed qualitatively with the experimental observations.



Scheme 1-13: Mechanism of the cationic polymerisation performed in aqueous media using the LASC system proposed by Vasilenko et al..

1.5.4. Boron Based Catalysts

In parallel to the development of the LASC type systems, the new generation of water tolerant boron-based Lewis acids, such as tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), were further investigated in aqueous media. Kostjuk *et al.* studied the polymerisation of pMOS[152] and St[151] in suspension at 20 °C under air atmosphere using pMOS-OH/$B(C_6F_5)_3$ as initiator system. They used a surfactant-free formulation, which gave dispersions with only limited colloidal stability. In solution, the polymerisation of pMOS led to a reasonable control over the molecular weight and dispersity. However, when the equivalent reactions were performed in a suspension polymerisation, they obtained lower molecular weights (M_n), with almost no increase with conversion during the reaction, and broad molecular weight distributions (MWDs). They discovered that the use of acetonitrile in the system (water:acetonitrile 3:2 v/v) was necessary in order to obtain a controlled polymerisation with an increase of M_n up to 3,000 $g.mol^{-1}$ and keep the MWDs relatively narrow.

Extending this work further, Kostjuk *et al.* also compared the cationic polymerisation of isoprene in dichloromethane (DCM) and in aqueous dispersed systems (suspension, emulsion) using the same pMOS-OH/$B(C_6F_5)_3$ initiating system.[167] It was observed that the molecular weights in aqueous media were lower than the ones obtained in DCM (M_n < 1,000 $g.mol^{-1}$ and M_n > 10,000 $g.mol^{-1}$, respectively). They explained this difference by the polymerisation taking place at the interface between the aqueous and oil phases, until reaching the "critical DP", from which the chains enter the droplets and cannot propagate any more. It was notable that the polymerisation in aqueous media had increased regioselectivity of the polymerisation, with 96.4% of *trans*-1,4 units (against 92.9% in DCM). Furthermore, the double bond content in the final polymers (96-99% in aqueous media, 88% in DCM) showed that the polymerisation in aqueous media reduced the extent of side reactions (cyclisation, branching) observed in solution.

1.6. Objectives

The objective of this thesis is to outline the potential and limitations of conducting cationic polymerisation in the presence of water and in dispersed media. Although cationic polymerisation is performed on a large scale industrially, the high water sensitivity of the process does not lend itself to being conducted in the presence of large amounts of water. Despite this, and as summarised in **Table 1-1**, there are numerous reports in the literature that molecular weights in excess of 10,000 g.mol^{-1} are achievable by emulsion polymerisation-like procedures, and this appears to offer an opportunity to produce high molecular weight polymers directly in aqueous dispersed media. Furthermore, with the development of catalysts that are water tolerant, there is scope to work towards cationic processes that have limited sensitivity to water.

Table 1-1: *Summary of polymers obtained* via *cationic polymerisation in aqueous media present in the literature.*

Monomer	Maximum reported M_n (g/mol)	Catalyst system	Reference
Isobutyl vinyl ether (IBVE)	2,100	$YbCl_3$	168
	4,500	$AlPW_{12}O_{40}$	169
	8,600	BF_3OEt_2	170
Isoprene	1,000	$B(C_6F_5)_3$	167
	97,000	**$YbCl_3$/hb-DBSNa**	164
pMOS	4,380	$B(C_6F_5)_3$	152
	10,600	$Yb(OTf)_3$	160
	2,900	$Yb(OTf)_3$	104
	1,230	DBSNa	171
	2,900	$Yb(OTf)_3$/DBSNa	162
	1,500	$Yb(DS)_3$	156
	35,000	**$YbCl_3$/hb-DBSNa**	165
	43,200	**$YbCl_3$/Disponil FES 993**	163
Styrene	3,400	$B(C_6F_5)_3$	172
	2,300	$B(C_6F_5)_3$	151
	3,900	$Yb(OTf)_3$	173
	117,200	**$YbCl_3$/hb-DBSNa**	164
	182,700	**$BMI.Fe_2Cl_7$**	174
	1,940,000	**$BMI.Fe_2Cl_7$**	175

1.7. Outline of the Thesis

The central aim of this thesis is to explore to what extent cationic polymerisation can be conducted in aqueous media. Following this introductory chapter, in **Chapters 2** to **4** we outline the limitations of conducting cationic polymerisations directly in water. In **Chapters 2** and **3**, a number of the cases shown in **Table 1-1**, in which exceedingly high molecular weights are reported in cationic (mini)emulsion polymerisation systems are revisited. It is demonstrated that these reactions are in fact radical polymerisation processes, which explains the unusually high molecular weights achieved. Using these reactions as case studies, in **Chapter 4** we demonstrate that cationic polymerisations conducted in excess water will necessarily lead to lower molecular weight polymers than the corresponding polymerisation in dry conditions. An outline of the features that limit the molecular weight in cationic polymerisations conducted in water is given and we conclude that for most common monomers there exists a limiting molecular weight of around 10,000 $g.mol^{-1}$. In the subsequent chapters of the thesis, we look towards the synthesis of such low molecular weight polymers in cationic polymerisation conducted in non-anhydrous solution, using the water tolerant catalyst $B(C_6F_5)_3$. In **Chapter 5**, we explore the cationic polymerisation of β-pinene and the successful application of the resulting polymers as tackifier in the formulation of pressure-sensitive adhesives based on commercial triblock copolymers. In **Chapter 6**, we focus on the understanding of the mechanisms occurring during the controlled cationic polymerisations of styrene and *p*-methoxystyrene, mediated by reversible addition-fragmentation chain-transfer (RAFT) agents in wet solution. Finally, in **Chapter 7** we summarise the most relevant conclusions obtained during this work.

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Chapter 2: A Re-evaluation of the Lewis Acid-Surfactant Complex Catalysed Polymerisation in Aqueous Dispersed Media

2.1. Introduction

As explained in **Chapter 1**, although cationic polymerisation is very sensitive to water,[1–3] the development of new catalysts has led to a number of reports of cationic polymerisation performed in aqueous media (suspension, emulsion, miniemulsion).[4–7] While in many cases relatively low molecular weights (M_n) have been obtained, there are a number of examples where values of M_n well in excess of 10,000 g.mol^{-1} have been reported. In particular, as detailed in Section 1.5.3, it has been shown that the use of Lewis acid-surfactant combined catalysts (LASCs) can lead to the production of very high molecular weight polymers, up to 100,000 g.mol^{-1},[8–10] which had previously been thought to be impossible in aqueous media. The central idea behind these systems is that the Lewis acids by themselves tend to catalyse polymerisation at the interface and at a critical degree of polymerisation the propagating centre migrates away from the interface, thus preventing further polymerisation. By formation of a LASC, it was suggested that polymerisation within the monomer droplets can be promoted and higher molecular weights can be obtained.

There are two main LASC systems that have been reported. The first reported uses ytterbium triflate in combination with an electrosteric surfactant (sodium polyoxyethylene (8) lauryl sulfate).[8] The second, which has been used more extensively, involves Lewis acids based on lanthanides and a branched sodium dodecyl benzene sulfonate surfactant. This system has been shown to be active for a number of different monomer systems including styrene, p-methoxystyrene, isoprene and β-myrcene. [9–11] In order to try to understand how such high molecular weight polymers could possibly have been obtained by LASC mediated cationic polymerisation in aqueous media, in this chapter we present a fundamental study of the LASC mediated polymerisation of styrene and *p*-methoxystyrene in aqueous media, using these catalyst systems. [8–10]

2.2. Experimental Part

2.2.1. Materials

Styrene (Quimidroga, technical grade) was distilled under reduced pressure prior to use and stored at -22 °C. *p*-Methoxystyrene (pMOS, TCI, > 98.0% purity), methyl methacrylate (MMA, Sigma Aldrich, 99% purity), acrylamide (AM, Sigma Aldrich), ytterbium chloride ($YbCl_3$, Sigma Aldrich, 99.9% purity), sodium dodecyl sulfate (SDS, Sigma Aldrich, > 98.5% purity) and Disponil surfactants ($C_{12}H_{25}(O\text{-}CH_2\text{-}CH_2)_xOSO_3Na$, x = 2, 4, 7, 12, 30, 50, 27.0-34.0% water solution, BASF) were used as received. In this work, three different types of sodium dodecylbenzene sulfonate were used. Most of the work was conducted using a branched form supplied by Sigma Aldrich (hb-DBSNa, technical grade). The branched structure was confirmed by ^1H NMR by comparing the spectrum to that reported by Ganachaud and co-workers.[9] Additional experiments were conducted using a linear DBSNa (l-DBSNa, Sigma Aldrich, technical grade) and a partially branched DBSNa (hard type, TCI, ≥ 95% purity).

2.2.2. Methods

Dynamic light scattering (DLS) was performed using a Zetasizer Nano – ZS. Three measurements were performed at 25 °C, with an equilibration time of 60 sec before the first measurement.

Gel permeation chromatography (GPC) was performed using three columns in series (Styragel HR2, HR4 and HR6) with a refractive index (RI) detector (Waters 2410) and UV detector (Waters 2487). THF was eluted at a flow rate of 1 $mL.min^{-1}$. The samples were prepared at a concentration of 2 $mg.mL^{-1}$ of polymer in THF and filtered using a nylon filter with pores of 45 µm. The molecular weights and dispersities (Đ) of all the polymers were calculated using the RI detector, based on polystyrene standards. Additional experiments using the same series of columns were conducted using a MALS detector (Dawn Heleos II, Wyatt) and viscometer (Viscoton, Wyatt) to obtain the Mark-Houwink-Sakurada plot (see **Figure 2-4**).

Proton nuclear magnetic resonance (^{1}H NMR) was recorded on a Bruker 400 MHz at 25 °C. Samples were prepared in deuterated chloroform ($CDCl_3$) and the signals obtained were calibrated relative to the solvent peak (7.26 ppm).

Carbon nuclear magnetic resonance (^{13}C NMR) was recorded on a Bruker 500 MHz at 25 °C. The samples were prepared in $CDCl_3$ at a concentration of 30 $mg.ml^{-1}$ and the signals obtained were calibrated relative to the solvent peak (77.16 ppm).

X-Band electron spin resonance (ESR) spectroscopy measurements were performed on a Bruker ELEXSYS 500 spectrometer at 340 K with frequencies about 9.492 GHz, microwave power of 2 mW, 100 KHz modulation frequency and 1 G modulation amplitude. The spectra were recorded in 83.89 sec (sweep-width 100 Gauss). First, a solution of a radical trap, *N*-*tert*-butyl-α-phenylnitrone (PBN, 0.01 g) in DMSO (0.5 mL) and phosphate buffered saline (PBS, 4.5 mL) was prepared. Then, a solution of hb-DBSNa (1.114 g) in ultrapure water (5 g) as well as a microemulsion containing St (0.146 g), hb-DBSNa (0.728 g) and ultrapure water (4 g) were made. For each experiment, 1 mL of the PBN solution was mixed with 2 mL of the other solution. Nitrogen was bubbled for 5 min in the mixture and a quartz capillary was refilled with 0.02 mL of the final mixture. Spectra were recorded after 30 minutes at 340 K.

Matrix-assisted laser desorption/ionisation – time of flight mass spectroscopy (MALDI-ToF MS) was performed on a Bruker Autoflex Speed system equipped with a 355 nm NdYAG laser. The matrix was composed of *trans*-2-[3-(4-*tert*-butylphenyl)-2-

methyl-2-propenylidene] malonitrile (DCTB, Fluka) dissolved in THF to obtain a concentration of 10 mg.mL^{-1}. Around 0.5 µL of the premixed mixture matrix:salt:polymer (10:1:1) was hand spotted on a ground steel target plate. For each spectrum, 8,000 laser shots were accumulated. External calibration of the spectra was made with a mixture of different polyethylene glycol standards (PEG, Varian).

The microemulsions for the Galvinoxyl detection of radicals was performed by adding a 3.22 mM solution of Galvinoxyl in styrene (0.1752 g) to a solution of hb-DBSNa (0.8736 g) in deionised water (4.9512 g). The microemulsion was stirred for 10 min at room temperature. Then a glass cuvette was filled with 1 mL of the microemulsion and the solution was heated for 1 hour at 60 °C.

2.2.3. Procedures

The reaction conditions used in the experiments are summarised in **Table 2-1**. In a typical polymerisation, the metal salt, the surfactant and deionised water were first mixed together in a 25 mL round bottom flask at 400 rpm, until a clear solution was obtained. The monomers were then added and the emulsion was stirred for 5 min. In experiments conducted under a nitrogen atmosphere, nitrogen was bubbled for 15 min prior to the reaction and the reactions were performed under nitrogen flow. The round bottom flask was then placed into an oil bath to reach the reaction temperature of 60 °C. After predetermined times, the polymerisation was quenched by adding a hydroquinone solution of 1% concentration. The final polymers were precipitated into an excess of methanol and dried in an oven at 60 °C. Monomer conversions were determined gravimetrically.

Runs 2-9 and 2-10 were performed following the protocol described by Storey and Scheuer.[12] Phenylphosphonic acid (0.02 g), ytterbium chloride (0.50 g) and deionised water (1.00 g) were stirred for 5 min in a 25 mL round bottom flask. Then the monomers (1.00 g of pMOS or 0.80 g of pMOS and 0.20 g of MMA, respectively) were added to the round bottom flask and the reaction was performed at room temperature under atmosphere. The reaction was quenched with aqueous solution of potassium hydroxide ([KOH] = 1 M) and the final polymer was precipitated in an excess of methanol and dried in an oven at 60 °C. Monomer conversions were determined gravimetrically.

For the radical polymerisation (Run 2-11) ytterbium chloride (0.03 g), sodium persulfate (0.06 g), Disponil FES 993 (0.80 g), styrene (3.00 g) and deionised water (11.55 g) were stirred at 400 rpm in a 25 mL round bottom flask. Nitrogen was bubbled for 15 min prior to the reaction, then the round bottom flask was plunged into an oil bath at 60 °C. The reaction was performed under nitrogen flow. After predetermined times, the polymerisation was quenched by an excess of hydroquinone (1% concentrated solution). Monomer conversions were determined gravimetrically.

Table 2-1: *Summary of the experimental conditions of all the experiments.*

Run	Surfactant type (wt-%)	YbCl$_3$ (wt-%)	M1[a]	M1 (wt-%)	MMA (wt-%)	Gas	T (°C)	Time (h)	X (%)
2-1[e]	hb-DBSNa (13.0)	3.5	St	25.2	-	Atm.[b]	60	4	91
2-2	l-DBSNa (7.1)	1.9	St	27.3	-	Atm.[b]	60	6	0
2-3[f]	Disponil FES 993 (18.7)	2.5	St	30.0	-	Atm.[b]	60	22.5	-
2-4[g]	hb-DBSNa (13.0)	3.5	pMOS	25.1	-	Atm.[b]	60	23.5	41
2-5	hb-DBSNa (13.0)	3.5	pMOS	25.1	-	N$_2$[c]	60	8	91
2-6	hb-DBSNa (13.0)	3.5	pMOS	25.1	-	N$_2$[c]	40	18	0
2-7	hb-DBSNa (12.8)	3.4	pMOS	25.6	-	N$_2$[c]	rt[d]	18	0
2-8	hb-DBSNa (13.0)	3.5	pMOS	20.2	5.0	Atm.[b]	60	24	62
2-9[h]	-	19.6	pMOS	39.4	-	Atm.[b]	rt[d]	96	> 99
2-10	-	19.4	pMOS	31.4	8.2	Atm.[b]	rt[d]	96	80
2-11	Disponil FES 993 (5.1)	0.2	St	19.5	-	N$_2$[c]	60	4	78
2-12[i]	hb-DBSNa (12.7)	3.4	St	26.2	-	Atm.[b]	60	24	0
2-13	hb-DBSNa (13.2)	3.5	β-pinene	24.9	-	N$_2$[c]	60	47.5	0
2-14	hb-DBSNa (13.0)	3.5	-	-	25.1	N$_2$[c]	60	6	-[j]
2-15	hb-DBSNa (12.7)	3.7	AM	25.3	-	N$_2$[c]	60	0.05	-[k]
2-16	hb-DBSNa (13.5)	-	AM	26.0	-	N$_2$[c]	60	1	-[k]
2-17	-	4.0	AM	28.8	-	N$_2$[c]	60	8	0
2-18	hb-DBSNa (12.5)	3.4	St	23.3	4.9	N$_2$[c]	60	6	76
2-19	hb-DBSNa (13.1)	-	St	20.0	5.0	N$_2$[c]	60	8	63
2-20	-	3.5	St	20.0	5.1	N$_2$[c]	60	23.5	5
2-21	l-DBSNa (13.1)	3.5	St	20.1	5.0	N$_2$[c]	60	24	0
2-22	l-DBSNa (13.0)	-	St	20.0	5.0	N$_2$[c]	60	24	64

[a]M1: Monomer 1. [b]Atm.: Performed in air. [c]N$_2$: Nitrogen. [d]rt: room temperature. [e]Reaction performed following ref [9]. [f]Reaction performed following ref [8]. [g]Reaction performed following ref [10]. [h]Reaction performed following ref [12]. [i]Reaction performed with 1.5 wt% 2,6-di-tert-butyl-4-methylphenol. [j]Conversion not measured due to coagulation of reaction mixture. [k]Conversion not measured due to highly viscous reaction media that prevented sampling.

2.3. Results and Discussion

2.3.1. Influence of the Surfactant

The polymerisation of styrene in dispersed aqueous media was performed using a hyper-branched sodium dodecylbenzene sulfonate (hb-DBSNa) and ytterbium chloride ($YbCl_3$) as a Lewis acid surfactant catalyst in air in a sealed flask (Run 2-1), following the work of Vasilenko *et al.* described in ref [9]. The kinetic plot for the experiment and the molecular weight distribution of the final polymer are shown in **Figure 2-1** and summarised in **Table 2-3**. It can be seen that the reaction was effectively complete after 30 minutes with a conversion (X) in excess of 90% and a final molecular weight (M_n) of 96.6 $kg.mol^{-1}$. These results are in reasonable agreement with those reported in ref [9] ($M_n = 117.2$ $kg.mol^{-1}$, X = 0.94 after 2.5 h at 50 °C).

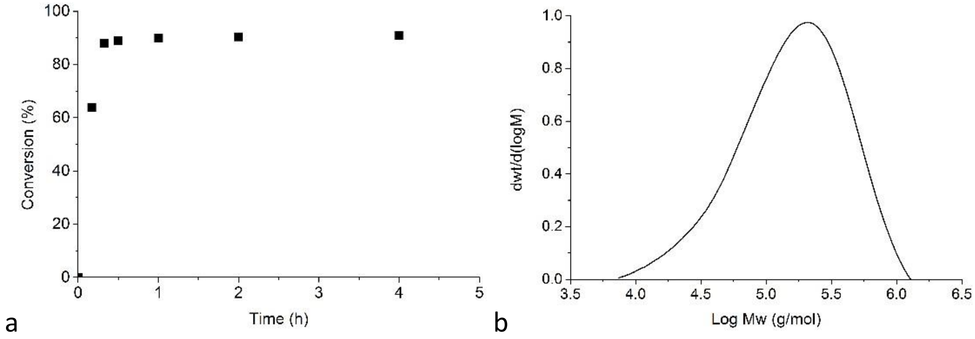


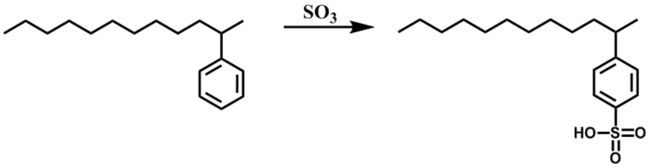
Figure 2-1: *(a) Evolution of the conversion with time and (b) molecular weight distribution of the final polymer obtained by GPC for Run 2-1.*

In order to gauge the importance of the surfactant in the polymerisation, a number of alternatives were tried. Another experiment, replacing hb-DBSNa by its linear analogue (l-DBSNa) was attempted, but a precipitate of the surfactant with the metal was formed and no polymerisation occurred (Run 2-2, **Table 2-3**). As reported previously,[9] a number of different types of DBSNa obtained from different sources also resulted in precipitation of the surfactant complex and an absence of polymerisation (**Table 2-2**).

Table 2-2: *Different sodium dodecylbenzene sulfonate tested.*

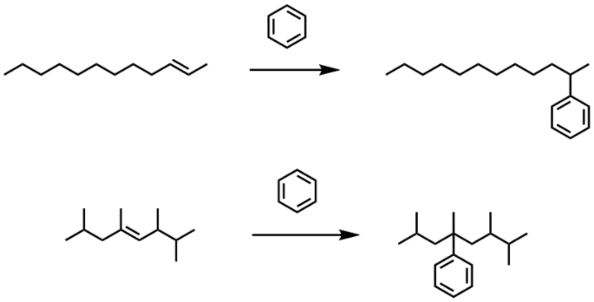
Surfactant	Provider	Purity	Polymerisation
Hyper-branched dodecylbenzene sulfonic acid, sodium salt	Aldrich	Technical grade	Yes
Sodium dodecylbenzenesulfonate (hard type) (mixture)	TCI	≥ 95%	No, precipitate forms
Dodecylbenzenesulfonic acid, sodium salt	Aldrich	Technical grade	No, precipitate forms

These differences can be understood by the varying nature of commercial sources of sodium dodecyl benzene sulfonate. Alkyl benzene sulfonates are typically made industrially by sulfonation of the alkyl benzene with sulphur trioxide (see **Scheme 2-1**). This yields the target alkyl benzene sulfonic acid, which is then neutralised to give the salt. Due to the commercial importance of these compounds as surfactants, the side products arising from this reaction are reasonably well known and are limited to sodium sulphate, sodium chloride, non-sulfonated alkyl benzenes and trace amounts of metals,[13] none of which would be expected to induce polymerisation.



Scheme 2-1: *Sulfonation of phenyldodecane.*

The main difference between the surfactants used in this work is in the alkyl chains. Branched dodecyl benzene sulfonates have historically been produced using tetrapropylene while linear benzene sulfonates use linear olefins (see **Scheme 2-2**). Due to the poor biodegradation of tetrapropylene based DBSNa, alternative branched olefins have been developed, leading a large range of potential structures for any given commercial DBSNa sample. In addition, regardless of the extent of branching, the starting products can also have a distribution of chain lengths so that the product also has a distribution of alkyl chain lengths. Different isomers (*i.e.* 2-phenyldodecane, 3-phenyldodecane, *etc.*) are also formed with the relative abundance dependent on the catalyst used in the alkylation.[13]



Scheme 2-2: *Alkylation of benzene using linear olefins to produce linear alkylbenzenes or with branched olefins to give branched alkylbenzenes.*

These structural differences can be seen in the NMR spectra of the different sources of DBSNa used in this work, as shown in **Figure 2-2** and **Figure 2-3**. Although the large number of isomers present in all samples makes precise structural elucidation incredibly challenging, there are several regions in the NMR spectra where clear differences can be observed. In the ^{1}H NMR spectra, the two branched forms of DBSNa (hb-DBSNa and DBSNa (hard type)) display multiple peaks in the region around 7 ppm whereas the linear DBSNa only shows two (**Figure 2-2**). The peak at ~7.7 ppm can be attributed in all cases to the C-*H* on the aromatic ring that is located closest to the sulfonate group. The other peaks can be attributed to the C-*H* on the aromatic ring that is closer to the alkyl group. As the alkyl group differs between the different samples and have a broad distribution of structural isomers, these signals are also substantially shifted going from the linear to branched structures.

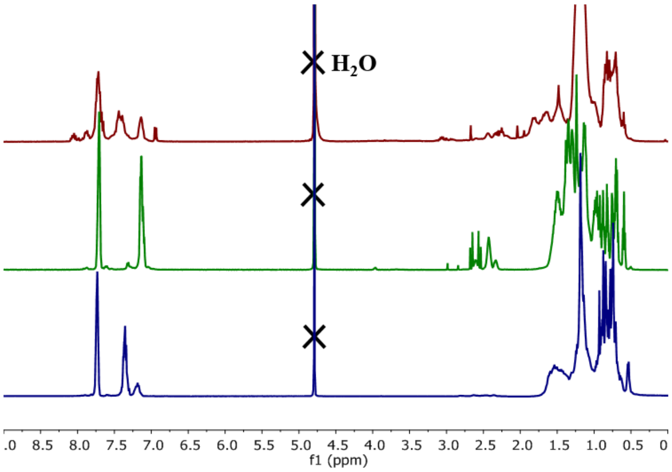


Figure 2-2: *^{1}H NMR spectra of the three forms of DBSNa used in this work; hb-DBSNa (top, red), linear DBSNa (middle, green) and DBSNa (hard type) (bottom, blue).*

Although the differences between peaks associated with the alkyl chain of the ^{1}H spectra (1-2.5 ppm) show substantial overlap, clearer differences in the shifts of alkyl groups can be observed in the ^{13}C NMR spectra of the different samples, where in the region 10-50 ppm it can be seen that there is limited overlap between different spectra showing that they are composed of alkyl chains with different structures (**Figure 2-3**).

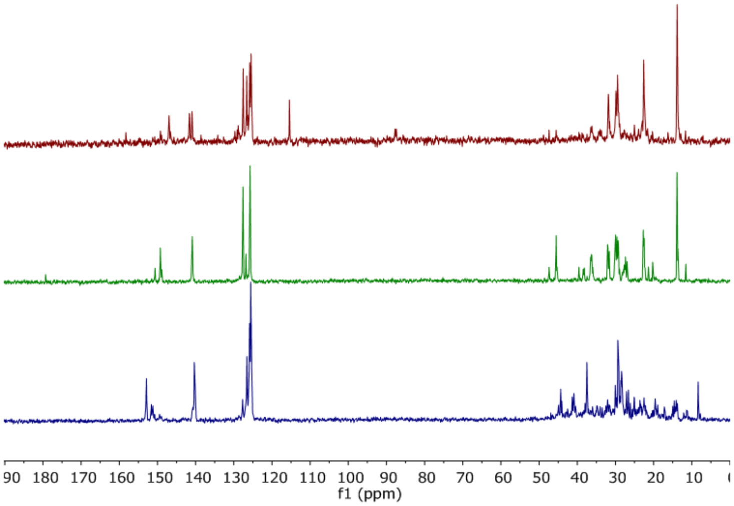


Figure 2-3: *^{13}C NMR spectra of the three forms of DBSNa used in this work; hb-DBSNa (top, red), linear DBSNa (middle, green) and DBSNa (hard type) (bottom, blue).*

Thus, the differences in the alkyl chain of the DBSNa result in different solubility in the presence of Yb^{3+} and therefore different polymerisation behaviour. It is important to emphasise that the ^{1}H and ^{13}C NMR spectra of the hb-DBSNa used throughout the work are very similar to that presented by Vasilenko *et al.,*[9] to which the present results are compared.

Attempts to polymerise with electrosteric surfactants in the LASC were also performed following the work of ref [8]. Using Disponil FES 993, a fatty alcohol polyglycol ether sulphate containing 12 ethylene oxide (EO) units (Run 2-3), successful polymerisation was achieved (see **Table 2-3**). The molecular weights in these experiments were in excess of 10^6 g.mol^{-1}, an unprecedented value for cationic polymerisation. It may be noted that the use of Disponil surfactants having different numbers of EO groups resulted in no polymerisation or the formation of a gel when the surfactant and $YbCl_3$ were mixed (**Table 2-4**). A similar surfactant containing less oxide units (8 instead of 12) has also been previously studied for the formation of a Lewis acid surfactant combined catalyst (LASC) for the polymerisation of *p*-methoxystryrene.[8]

Table 2-3: *Summary of experiments using different surfactants.*

Run	Surfactant	Monomer	Time (h)	Conversion (%)	M_n (g/mol)	Đ
2-1	hb-DBSNa	St	4	91	96,600	2.4
2-2	l-DBSNa	St	8	0	-	-
2-3	Disponil FES 993	St	23.5	91	1,448,900	2.9

Table 2-4: *Different Disponil surfactants tested, provided by BASF, with Disponil/$YbCl_3$ molar ration of 3.*

Surfac-tant	Number of EO units	Active matter (wt-%)	Surfac tant (wt-%)	$YbCl_3$ (wt-%)	St (wt-%)	Water (wt-%)	Polymerisa-tion
Disponil FES 27	2	27.9	8.6	2.5	29.9	59.0	Gel
Disponil FES 32	4	31.2	11.1	2.5	29.8	56.6	< 10%
Disponil FES 147	7	27.1	13.6	2.5	30.3	56.6	< 10%
Disponil FES 993	13	30.7	18.7	2.5	30.0	48.7	Yes
Disponil FES 77	30	34.0	22.4	2.5	30.0	46.1	Gel
Disponil FES 61	50	32.2	23.2	0.9	29.9	45.9	Gel

2.3.2. Study of the Mechanism

It was noticed during the initial studies that even in the case where polymerisation occurred, there was often variability in the kinetics of the reactions. In order to probe this further, some reproducibility experiments were performed for both hb-DBSNa and Disponil FES 993 surfactants (Runs 2-1.1 to 2-1.4 and Runs 2-3.1 to 2-3.5, final conversion and molecular weights shown in **Table 2-5**). In both cases, significantly different kinetics were observed for different runs with the same nominal mixtures (see **Figure 2-4**). Moreover, for the experiments using Disponil FES 993 as a surfactant, a widely variable inhibition period was observed. From this point, in order to focus on understanding the mechanism of the polymerisations, all the experiments were performed using the hb-DBSNa surfactant, unless stated otherwise.

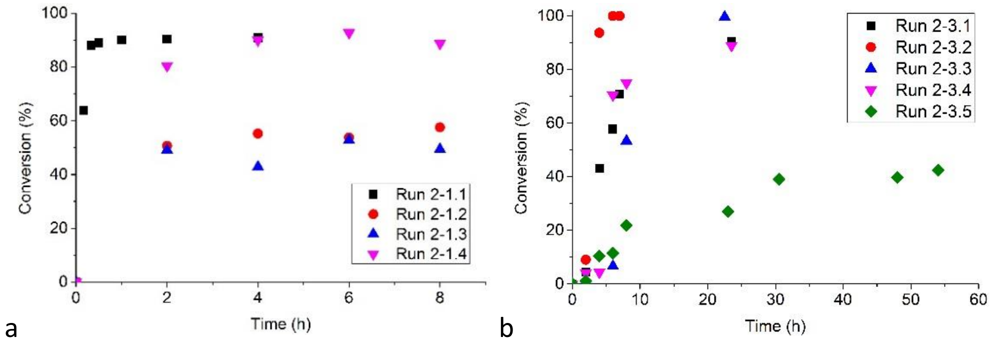


Figure 2-4: *Reproducibility of the same experiment comparing the evolution of the conversion with time using (a) hb-DBSNa and (b) Disponil FES 993 as surfactant.*

Table 2-5: *Summary of the reproducibility experiments.*

Run	Surfactant	Monomer	Time (h)	Conversion (%)	M_n (g/mol)	Đ
2-1.1	hb-DBSNa	St	4	91	96,600	2.4
2-1.2	hb-DBSNa	St	8	58	64,400	4.0
2-1.3	hb-DBSNa	St	8	46	67,300	3.5
2-1.4	hb-DBSNa	St	8	89	-	-
2-3.1	Disponil FES 993	St	23.5	91	1,448,900	2.9
2-3.2	Disponil FES 993	St	8	> 99	1,995,000	2.3
2-3.3	Disponil FES 993	St	22.5	> 99	587,200	3.6
2-3.4	Disponil FES 993	St	23.5	89	-	-
2-3.5	Disponil FES 993	St	28	43	-	-

With the suspicion that the cause of inhibition/retardation in these experiments may arise from conducting the reactions in air, two reactions using *p*-methoxystyrene (pMOS) were conducted using similar conditions as those reported by Vasilenko *et al.*[10] under either an air (Run 2-4) or a nitrogen (Run 2-5) atmosphere (results shown in **Table 2-6** and **Figure 2-5**). In the case of the reaction conducted in air, an inhibition period was observed and a relatively low final conversion of 41.4% was obtained in 24h, with a final M_n of 16.7 kg.mol^{-1}. In contrast, it can be seen from **Figure 2-5** that in the presence of nitrogen, the inhibition period completely disappeared, and the conversion was almost complete in 8h. It may be noted that the experiment under nitrogen (Run 2-5) is in good agreement with those reported by Vasilenko *et al.* with 90.6% conversion in 8h (against 95% in 17h) and a final M_n of 21.5 kg.mol^{-1} and M_w of 70.3 kg.mol^{-1} (as compared with M_n = 29.7 kg.mol^{-1} and M_w = 62.4 kg.mol^{-1}).[9] The effect of the atmosphere on the reaction is surprising in that in the present conditions, where the reaction mixture is in contact with water, performing the reaction under inert conditions should have little effect on the polymerisation process, assuming a cationic process. This effect is more reminiscent of a radical polymerisation in which oxygen acts as an inhibitor for the polymerisation. Attempts to polymerise pMOS at lower temperatures of 40 and 25 °C (Runs 2-6 and 2-7 respectively) resulted in no polymerisation.

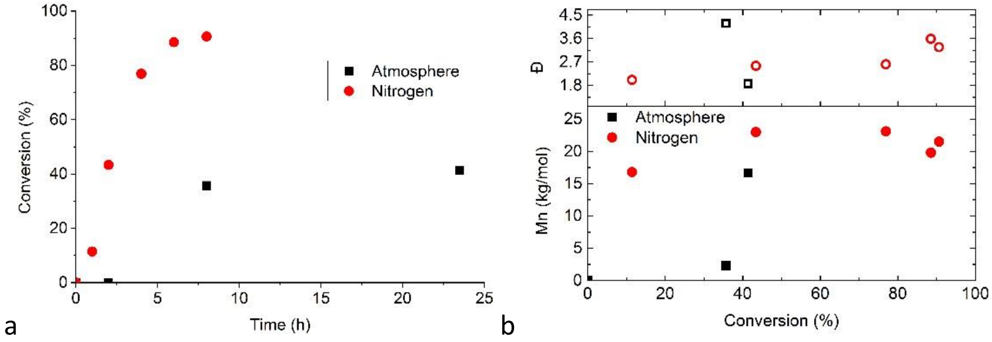


Figure 2-5: *(a) Evolution of the conversion with time and (b) evolution of the molecular weights (full symbols) and dispersities (empty symbols) with conversion for the experiments conducted under atmosphere (Run 2-4, black squares) and nitrogen (Run 2-5, red spheres).*

Aside from the sensitivity of the reaction to air, a second feature of the reactions conducted that is strange assuming a cationic reaction mechanism is the molecular weight of the polymers obtained. Even assuming that transfer to water is not occurring, which under the water-saturated conditions seems unlikely, in a cationic polymerisation process chain transfer to monomer/polymer typically results in a relatively low limiting molecular weight, even at reduced temperatures where such reactions are suppressed.[14] For example, in the case of styrene, the ratio of the rate coefficient of chain transfer to monomer constant to the rate coefficient of propagation ($k_{tr,M}/k_p$) has been calculated to be 1.7 x10^{-2} at -30 °C.[15] For cationic polymerisation, the degree of polymerisation is proportional to the rate of propagation divided by the rate of chain termination arising from transfer events (equation 1).

$$DP \approx \frac{k_p[M]}{k_{tr,M}[M]+k_{tr,P}[P]+k_{tr,H_2O}[H_2O]} \tag{2-1}$$

Thus, even neglecting transfer to water and transfer to polymer events, taking the value of $k_{tr,M}/k_p$ above leads to a limiting molecular weight *ca.* 6,000 g.mol^{-1} in the case of dry conditions and low temperatures (-30 °C). At elevated temperatures, the relative rate of transfer to propagation increases and therefore the molecular weight would be expected to be significantly lower than this value at 60 °C. Although it is certainly possible that there is a degree of error in the value of $k_{tr,M}/k_p$, that molecular weights in excess of 100,000 g.mol^{-1} (or 1,000,000 g.mol^{-1} in the case of Disponil FES 993) are achieved suggests such a huge decrease in chain transfer, so as to raise questions about the possibility of a cationic process occurring. It should be noted that measurement of molecular weight by SEC/MALS confirmed the molecular weight and also that there was no branching in these samples ($0.5 \le a \le 0.8$ in Mark-Houwink-Sakurada plot) (**Figure 2-6**).

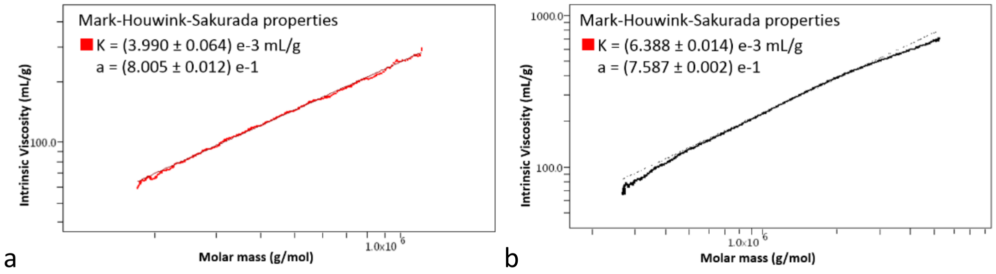


Figure 2-6: *Mark-Houwink-Sakurada plots from SEC/MALS analysis of (a) Run 2-1.2 and (b) Run 2-3.3.*

With the results shown above suggesting that cationic polymerisation was not occurring, we undertook an additional pair of experiments which sought to determine the capacity of methyl methacrylate (MMA) to polymerise in these conditions, by adding 20% of MMA compared to the total amount of monomers in the formulation (Run 2-8). MMA cannot be polymerised by a cationic mechanism due to the instability of the MMA based carbocation and therefore if MMA is detected in the polymer then this gives further evidence that the reaction is not a cationic polymerisation. Indeed, it has been shown in some examples performing dual cationic/radical reversible addition-fragmentation chain transfer (RAFT) polymerisation in one-pot that (meth)acrylate monomers could not polymerise in the presence of catalysts inducing a cationic polymerisation.[16,17]

Table 2-6: *Summary of the experiments performed to investigate the cationic or radical mechanism implied, using ytterbium as catalyst.*

Run	Surfactant	Monomers	Time (h)	Conversion (%)	M_n (g/mol)	Đ
2-4	hb-DBSNa	pMOS	23.5	41	16,700	1.9
2-5	hb-DBSNa	pMOS	8	91	21,500	3.3
2-8	hb-DBSNa	pMOS + MMA	24	62	28,000	2.5
2-9	-	pMOS	96	71.4	1,300	3.5
2-10	-	pMOS + MMA	96	80	1,800	2.0

It can be seen from **Table 2-6** that similar results were obtained for the Run 2-8, containing 20% MMA compared to the Run 2-4, in which only pMOS was polymerised. **Figure 2-7a** presents the ^{1}H NMR spectra of pure poly(pMOS) (top, blue) and the polymer obtained when 20 wt-% of MMA compared to the total amount of monomers was added (bottom, red). In both spectra, we can find the different peaks corresponding to poly(pMOS). In the spectrum of the experiment in which MMA was added (bottom, red), new peaks were detected, at 0.5-1 ppm and between 2.5-3 ppm, characteristic of poly(MMA). Similarly, analysis by ^{13}C NMR and FTIR, demonstrated additional signals corresponding to poly(MMA) (see **Figure 2-7b and c**). Note that similar experiments using styrene as monomer also led to incorporation of MMA, even when reactions were conducted at lower temperature of 40 °C (see **Figure 2-7d**).

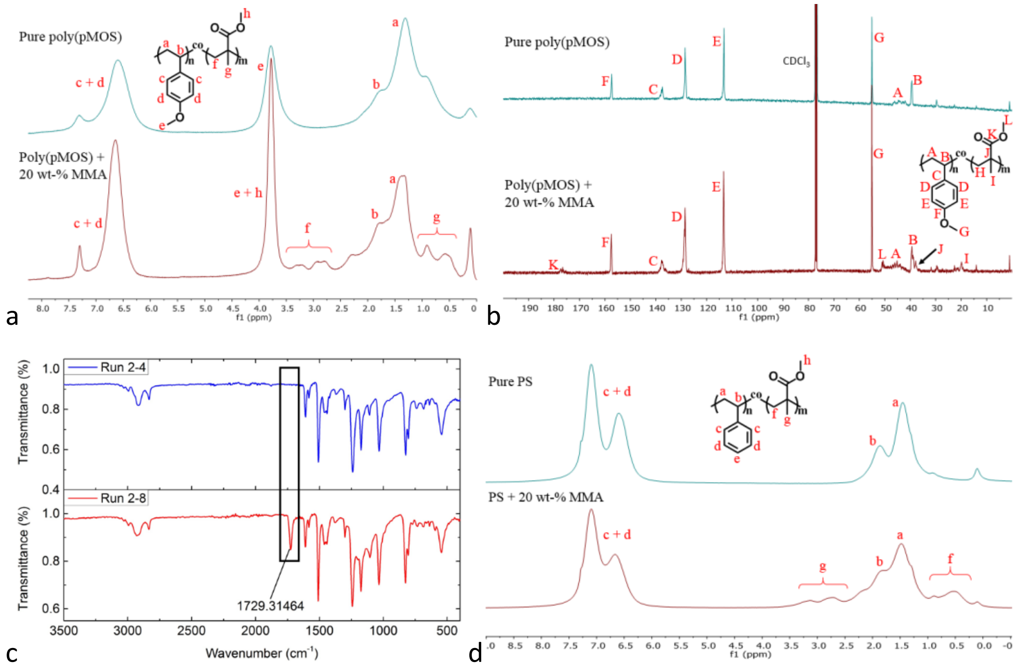


Figure 2-7: *(a) ^{1}H NMR and (b) ^{13}C spectra of pure poly(pMOS) polymer (Run 2-4) (top, blue) and polymer consisting of pMOS + 20 wt-% MMA (Run 2-8) (bottom, red). (c) FTIR spectra of the polymers obtained in Run 2-4 (top, blue) and Run 2-8 (bottom, red). Highlighted region depicts the carbonyl region where signal from the C=O bond of MMA is expected. (d) ^{1}H NMR spectra of the polymers obtained using the formulation of Run 2-1 but at 40 °C in the absence (top, blue) and presence (bottom, red) of 20 wt-% MMA.*

In order to confirm the formation of a poly(pMOS-*co*-MMA) copolymer, as opposed to two poly(pMOS) and poly(MMA) homopolymer distributions, the precipitated copolymer was analysed by GPC using refractive index (RI, detects both monomers) and ultra-violet (UV, only detects pMOS units) detectors. Both traces were almost perfectly overlaid (**Figure 2-8a**), except at very low masses, indicating the formation of copolymer. Moreover, DOSY NMR analysis of the polymer obtained exhibits the formation of a copolymer of poly(pMOS-*co*-MMA) and not two homopolymers since there is only one diffusion coefficient for signals corresponding to pMOS as well as MMA (**Figure 2-8b**).

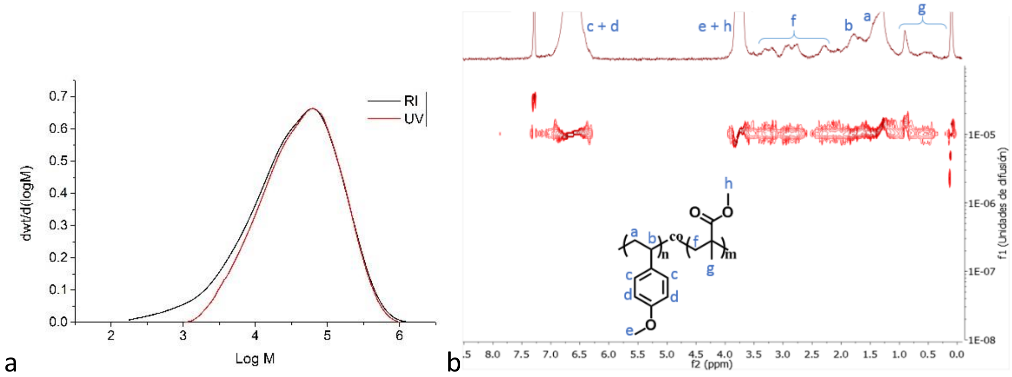


*Figure 2-8: (a) GPC traces of the copolymer poly(pMOS-*co*-MMA) obtained in Run 2-8 using refractive index (black) and UV (red) detectors. (b) DOSY analysis of the polymer obtained for the Run 2-8.*

As further evidence of the presence of a copolymer, ^{13}C NMR showed a clear shift in the carbons in the α methyl position of the MMA unit as well as additional signals arising from the carbons from pMOS that are in the polymer backbone adjacent to MMA units (see **Figure 2-9**). These shifts have previously been documented in poly(MMA-*co*-St) random copolymers produced by radical polymerisation.[18]

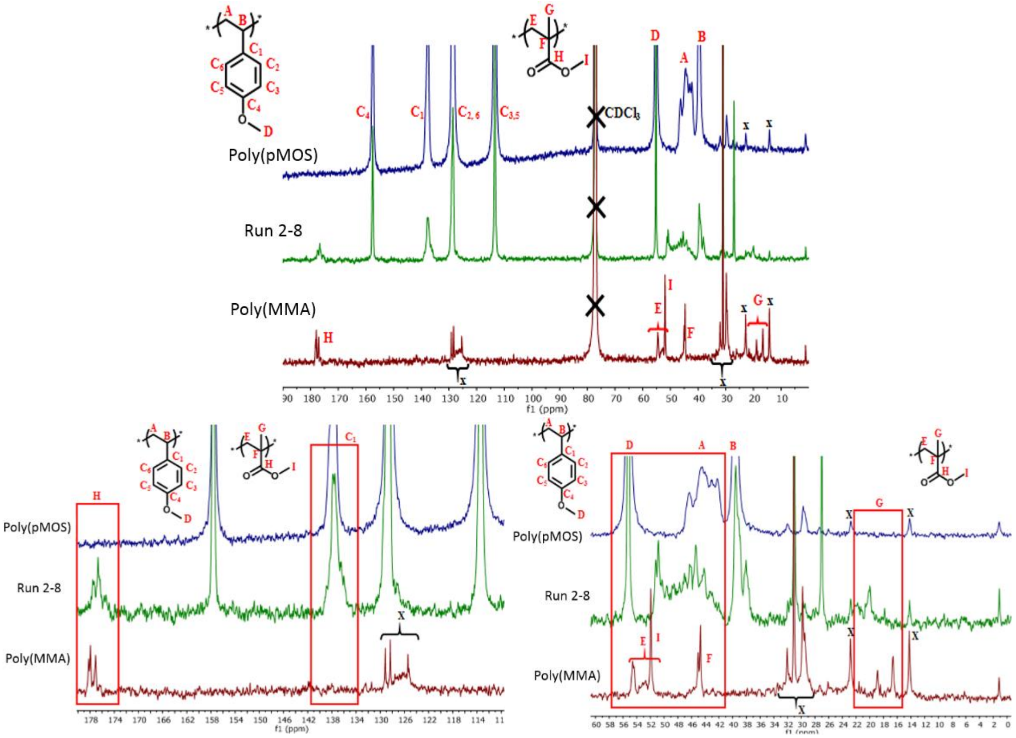


Figure 2-9: *^{13}C NMR spectra of pure polymer made using pMOS + 20 wt-% MMA (compared to the total amount of monomers) (Run 2-8) as compared to pure poly(pMOS) and pure poly(MMA). The peaks arising from the solvent at 77.2 ppm and from residual DBSNa are marked with an X. The zoomed areas below show that the peak around 20 ppm that is related to the α-methyl group of MMA is shifted substantially and that the peaks in the polymer backbone arising from the pMOS units also show a change in the shape of the peaks indicating formation of a random copolymer.*

As a final demonstration that incorporation of MMA in the copolymer indicates a cationic mechanism is not occurring, reactions were conducted in the presence of MMA using a known cationic system as reported by Storey and Scheuer[12] (Run 2-9 and Run 2-10 respectively, **Table 2-6**). In that case, MMA was absent in the ^{1}H NMR spectra (**Figure 2-10**).

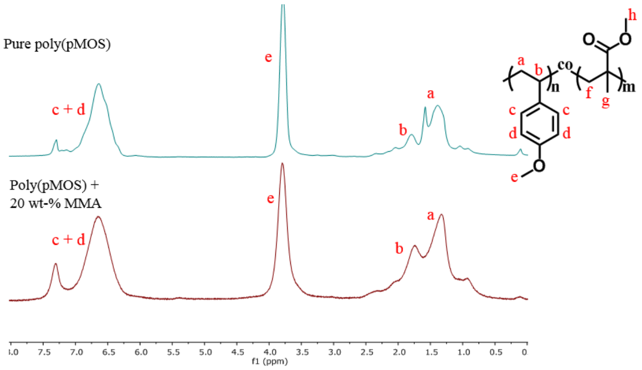


Figure 2-10: *^{1}H NMR spectra of pure poly(pMOS) polymer (top, blue) and final polymer consisting of pMOS + 20 wt-% MMA (compared to the total amount of monomers) (bottom, red) for the experiments based on Storey and Scheuer (Runs 2-9 and 2-10, respectively).*

The incredibly high molecular weights, the incorporation of MMA into the copolymer and the impact of atmospheric oxygen all suggest that the polymerisation mediated by the LASC is not occurring by a cationic process but by free radical polymerisation. To bring further proof of this hypothesis, experiments containing radical or cationic inhibitors were performed. Indeed, it was previously reported that ytterbium may be an inhibitor of radicals,[8,19] so a conventional radical polymerisation of styrene in emulsion was performed using sodium persulfate (NaPS) as an initiator, in the presence of ytterbium chloride (Run 2-11, **Table 2-7**). The polymerisation occurred, obtaining 80.4% conversion in 30 min (**Figure 2-11**). This suggests that the presence of ytterbium ions does not inhibit radical polymerisation under the present conditions, in agreement with other reports in the literature.[20,21] Another experiment was to perform the supposed cationic polymerisation in air in the presence of 2,6-di-tert-butyl-4-methylphenol (BHT), a known radical scavenger (Run 2-12, **Table 2-7**). In this case, no polymerisation occurred in 24h, again indicating a radical mechanism.

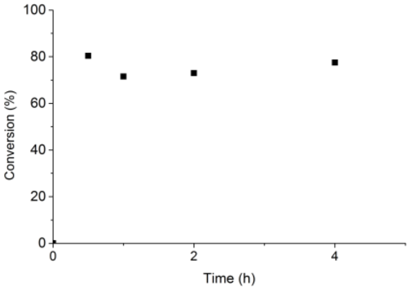


Figure 2-11: *Evolution of the conversion with time for the radical polymerisation of styrene in the presence of* $YbCl_3$.

As an attempt to confirm the radical pathway occurring in our system, we tried to polymerise a terpene monomer, β-pinene, which is known to undergo cationic polymerisation but for which radical homopolymerisation is not possible (Run 2-13). In this case, no polymerisation was observed (**Table 2-7**). In contrast, experiments using only methyl methacrylate (Run 2-14), a monomer that is known to undergo radical polymerisation but cannot undergo cationic polymerisation, showed rapid polymerisation and, despite coagulation of the dispersion, analysis of the solid content revealed near quantitative conversion (see **Table 2-7**).

Table 2-7: *Summary of the experiments performed to prove the radical polymerisation process.*

Run	Monomer	Radical scavenger	Polymerisation
2-11	St	$YbCl_3$	Yes
2-12	St	BHT	No
2-13	β-pinene	-	No
2-14	MMA	-	Yes
2-15	Acrylamide	-	Yes

Polymerisation of acrylamide, a water-soluble monomer that rapidly undergoes radical polymerisation but cannot be polymerised by cationic polymerisation was also attempted (Run 2-15). The polymerisation occurred rapidly with a significant isotherm, forming a gel in only 3 min. The polymerisation of acrylamide was also attempted removing the metal from the formulation (Run 2-16). The polymerisation occurred more slowly than in the presence of metal, forming a gel in 1h. However, when the experiment was performed in the presence of metal but without surfactant (Run 2-17), no polymerisation occurred, even after 8h of reaction. This strongly suggests that polymerisation in these reactions does not polymerise by self-initiation but that radicals are formed by the surfactant.

^{13}C NMR was used to compare the tacticity between poly(pMOS) obtained in conventional cationic and radical polymerisation and the polymers obtained in aqueous media. It can be seen in **Figure 2-12** that the intensity of the mm triads in the case of a cationic polymerisation is slightly inferior to the mr and rr triads, whereas in the radical polymerisation process the mm triads have much lower intensity than the mr or rr triads. The ^{13}C NMR spectrum of the polymer obtained in the Run 2-8 seems to correspond to a polymer obtained by a radical process, as the intensity of the different triads is similar to the polymer obtained by conventional radical polymerisation.

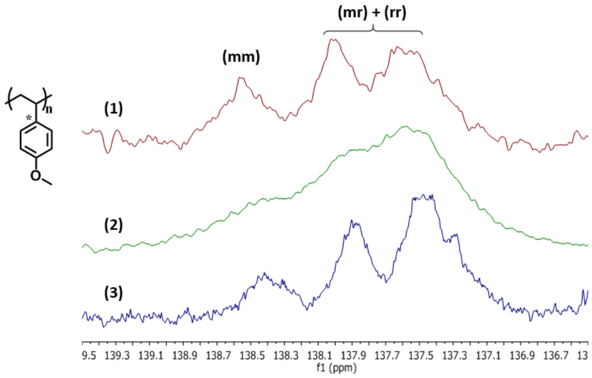


Figure 2-12: *^{13}C NMR spectra of the poly(pMOS) obtained by: (1) cationic polymerisation (Run 2-6), (2) Run 2-8 and (3) radical polymerisation (bulk polymerisation of pMOS initiated by AIBN).*

Further proof for a radical mechanism was obtained from MALDI-ToF spectroscopy of the low molecular weight region of polystyrene polymers obtained using hb-DBSNa (Run 2-1). Note that due to practical limitations, only the low molecular weight region of the polymer can be measured and as such may not be representative of the whole sample. As shown in **Figure 2-13a**, the mass spectra are identical to a polymer produced by a conventional radical emulsion polymerisation of styrene under similar conditions. The signal of highest intensity likely corresponds to chains that are initiated by radical chain transfer to the Diels Alder dimer of styrene that have undergone bimolecular termination by combination. It should be noted that chain transfer to the Diels Alder dimer is recognised to be the dominant termination event in radical emulsion polymerisation of styrene.[22,23] A second peak was assigned to chains similarly initiated by transfer to the Diels Alder dimer but terminated by an unsaturated group. This may occur as a result of intramolecular or intermolecular radical chain transfer to polymer and subsequent β-scission reaction.[24] Indeed, the third peak observed corresponds to chains that bear on one extremity the corresponding structure of β-scission reaction. It should be noted that chain ends that would typically be associated by termination events in cationic polymerisation were not observed. Transfer to water reactions that result in chain initiation by a proton and termination by a hydroxyl group (m/z = 1,063 Da) that have been observed in true cationic polymerisations conducted in water[4] were absent. Similarly, transfer to polymer reactions that result in chain initiation by a proton and termination by an indanyl group (m/z = 1,045 Da) or by β-elimination (m/z = 1,045 Da) were absent. This emphasises that the polystyrene synthesised *via* the LASC system did not undergo cationic polymerisation. In **Figure 2-13b**, the MALDI-ToF mass spectra of the polymer in Run 2-1 between a mass range of 4,000 to 6,000 Da is shown, confirming that this series of products is also present at higher molar masses.

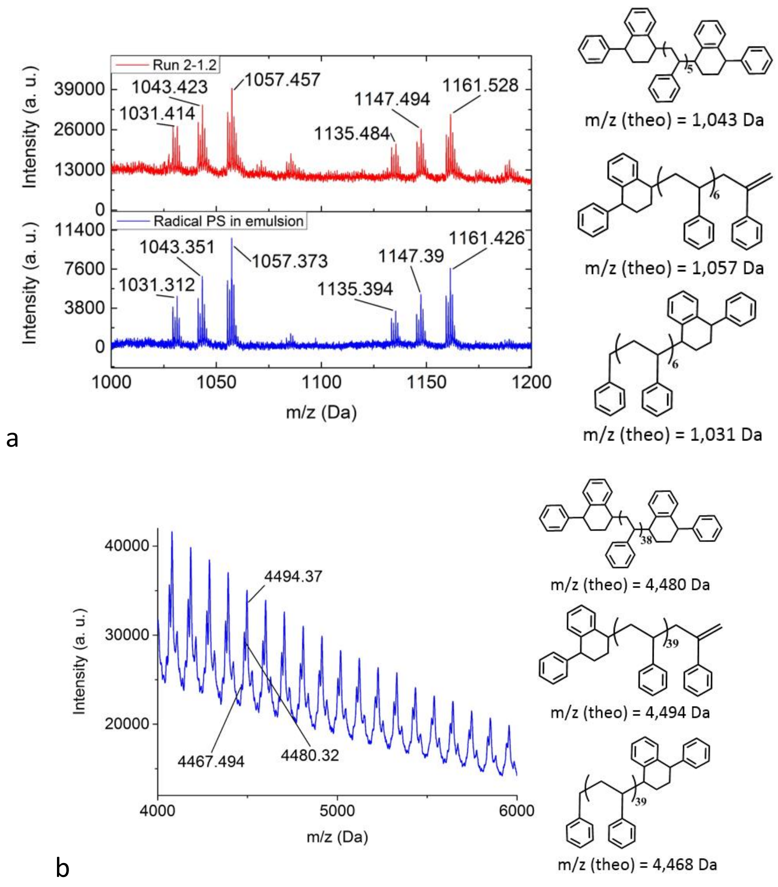


Figure 2-13: *(a) MALDI-ToF mass spectra of the polymers synthesised using the LASC system (Run 2-1) (top, red) and classical emulsion radical polymerisation process (bottom, blue) and (b) MALDI-ToF spectra of the polymer obtained in Run 2-1 at higher range of m/z.*

2.3.3. Determination of the Radical Source

To prove the generation of radicals, an additional pair of experiments was conducted. First, Galvinoxyl was used as a colorimetric detector for the presence of radicals. Galvionxyl is a stable free radical species that undergoes a transition from orange/brown to yellow by reaction with radicals. A styrene microemulsion containing Galvinoxyl was formed using DBSNa as surfactant. After heating at 60 °C for less than 1 hour, the Galvinoxyl had fully reacted and developed the yellow colour characteristic of the presence of radicals (see **Figure 2-14a**). Note a blank experiment of a solution of Galvinoxyl in styrene under similar conditions showed no obvious change in colour. Secondly, electron spin resonance (ESR) experiments were performed. A spin trap, *N*-*tert*-butyl-α-phenylnitrone (PBN), was used to detect the presence of radicals. As a blank experiment, an aqueous PBN solution was analysed and no radicals were detected. In a second experiment, a solution of hb-DBSNa in water in the presence of the spin trap was examined. As shown in **Figure 2-14b**, radicals were detected in the medium when DBSNa was present. Similarly, a microemulsion containing styrene and hb-DBSNa in water also demonstrated the presence of radicals. The spectra could be fit to give the coupling parameters a^N (coupling to the nitrogen) and a_β^H (coupling to the β-hydrogen) (see **Figure 2-14c and d**). The structure of the spectra suggests that the PBN reacts with a carbon centred radical[25] but due to the limited sensitivity of the spectra of PBN adducts towards the attacking radical, the structure of the radical cannot be precisely determined.[26]

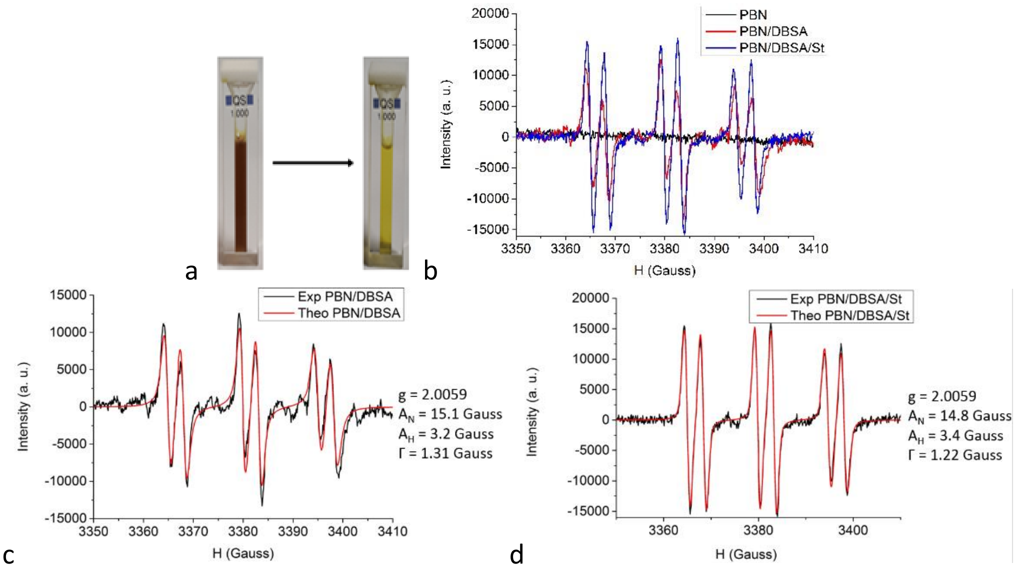


Figure 2-14: *(a) Microemulsion of styrene/water/hb-DBSNa containing Galvinoxyl before and after heating for 1 hr at 60 °C. Note that a blank experiment in which a solution of Galvinoxyl in St presented no change of colour under similar conditions. (b) Electron spin resonance (ESR) spectra of the blank experiment containing only the spin trap PBN (black), the aqueous solution containing the surfactant hb-DBSNa (red) and the microemulsion containing the surfactant and styrene (blue). (c and d) Superimposition of the experimental (black) and calculated (red) spectra for (c) the aqueous solution containing hb-DBSNa and (d) the microemulsion containing hb-DBSNa and St.*

These experiments provide a few vital insights into the potential reaction mechanism and radical source. As the homopolymerisation of both MMA and acrylamide were successful and due to the low temperatures used in these experiments, spontaneous generation of radicals from the monomers themselves can be ruled out. The detection of radicals by ESR in the absence of styrene suggests that the radicals are generated by surfactant molecules. This is further backed up by experiments conducted without $YbCl_3$ in which polymerisation is seen to proceed (Runs 2-18 and 2-19, **Figure 2-15**). In the absence of the surfactant no polymerisation occurred (Run 2-20, **Figure 2-15**). Note that linear DBSNa was also shown to induce polymerisation when the $YbCl_3$ is not present, while when it was present the surfactant precipitated and no reaction occurred (Runs 2-21 and 2-22, **Figure 2-15**). Although the mechanism for the generation of radicals from the surfactants used is unknown, there are precedents in the literature for the generation of radicals from DBSNa. For example, in 2007, Osti et al.[27] tested different surfactants in the presence of *L*-ascorbic acid and established that when this ascorbic acid and DBSNa were together in the reaction medium, radicals were generated that initiated the emulsion polymerisation of styrene. The sonochemical decomposition of DBSNa has also been noted to proceed *via* a radical process.[28]

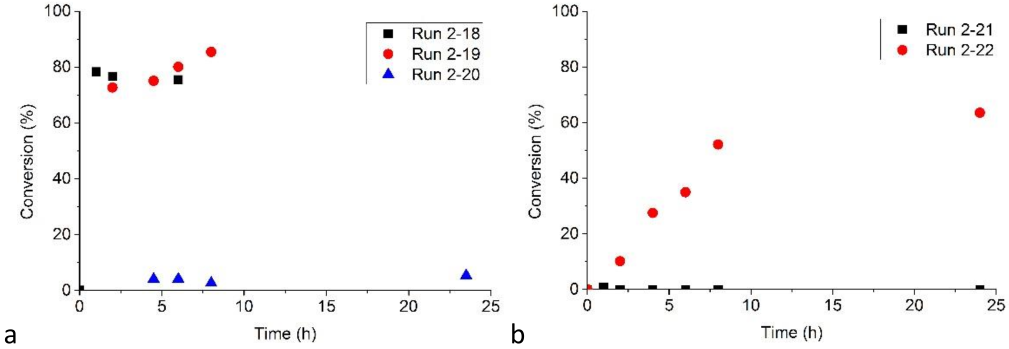


Figure 2-15: *Evolution of the conversion versus time for (a) the Runs 2-18 to 2-20 (all reactants, without metal and without surfactant, respectively) using hb-DBSNa and (b) the Runs 2-21 and 2-22 (all reactant and without metal, respectively) using l-DBSNa as surfactant.*

2.4. Conclusions

In conclusion, we have demonstrated that results reporting polymerisation of vinylic monomers using LASCs based on electrosteric sulphate surfactants and hb-DBSNa likely proceed by radical polymerisation, not cationic polymerisation as previously suggested. The ability to (co)polymerise methyl methacrylate and other monomers not able to be polymerised *via* a cationic mechanism, the strong influence of radical inhibitors such as atmospheric oxygen, the high molecular weights, the observation of products of radical transfer reactions by mass spectroscopy and the detection of radicals in spin trap experiments combined with ESR are the key indicators that a cationic polymerisation is not occurring in this instance. Although the mechanism for the generation of radicals is unknown, electron spin resonance experiments performed to determine the source of radicals confirmed that the radicals were created by the surfactant.

2.5. References

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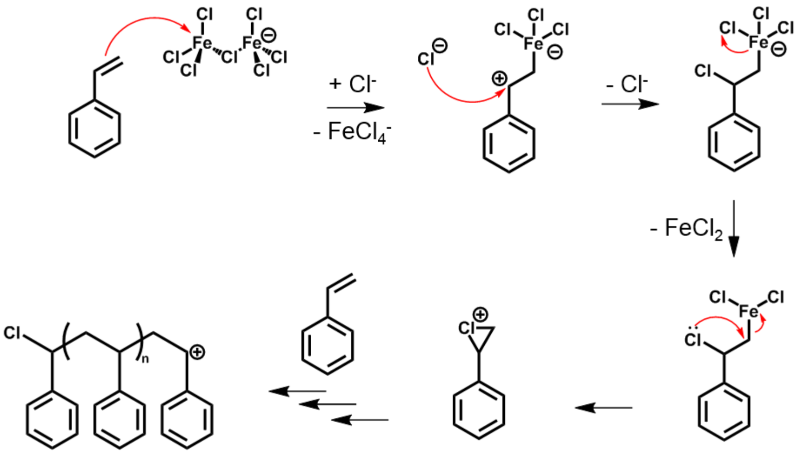
Chapter 3: A Re-evaluation of the Cationic Polymerisation of Styrene Using Ionic Liquids as Catalyst

3.1. Introduction

Ionic liquids (ILs) have been proposed as alternative reaction media to halogenated solvents for polymerisation processes[1,2] thanks to their non-flammable and recyclable nature, in addition to their high polarity, which improves the solubility of a diverse range of organic, inorganic and organo-metallic compounds. Among the ionic liquids, 1,3-dialkyl imidazolium salts, which can act as both hydrogen bond donor (imidazolium cation) and acceptor (anion), are particularly interesting due to their tunable Lewis acidity. This feature allows the use of these ionic liquids as catalysts in different polymerisations.[3,4] Recently, Rodrigues *et al.*[5] employed 1-n-butyl-3-methylimidazolium heptachlorodiferrate (BMI·Fe_2Cl_7) in the cationic polymerisation of styrene in bulk and solution without any additional initiator at 70 °C. When performed in bulk or in ionic liquids solvents, the polymerisations reached conversions above 70% in only 15 min, whereas in toluene the polymerisation was much slower (77h). In all cases, low molar masses polymer were obtained (M_n < 5,000 g.mol^{-1}). They proposed that the polymerisation took place through the formation of a styrene chloronium cation stabilised by ion-pairing (mechanism in **Scheme 3-1**), evidence for which came from mass spectrometry.



Scheme 3-1: *Mechanism proposed by Rodrigues* et al. *for the cationic polymerisation of styrene catalysed by ionic liquids.*

Later on, Alves *et al.* extended the cationic polymerisation of styrene using BMI· Fe_2Cl_7 in miniemulsion.[6] In this system, a temperature of 90 °C was necessary to obtain high conversion after 6h of polymerisation, and much higher molecular weight polymers were synthesised, up to 1,000 kg.mol^{-1}. They postulated a mechanism for the polymerisation, which consists of initiation by the formation of a chloronium cation in the aqueous phase, where the ionic liquids are soluble and a small amount of styrene molecules are present due to the partitioning of the monomer. Upon the addition of styrene units, it was proposed the growing polymer chain becomes hydrophobic enough to enter a particle and then a cationic polymerisation takes place in the organic phase (**Figure 3-1**).

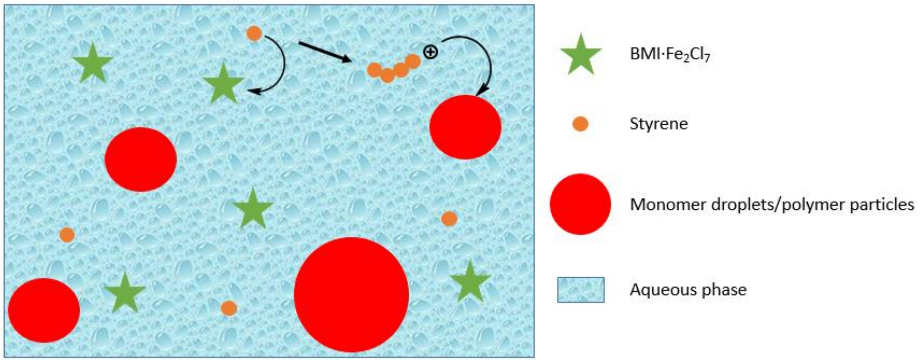


Figure 3-1: *Mechanism proposed by Alves* et al. *for the cationic polymerisation of styrene in miniemulsion using BMI·Fe_2Cl_7 ionic liquid as a catalyst.*

Following this work, Dutra *et al.* explored the miniemulsion polymerisation of styrene using three ionic liquids as catalysts, BMI·Fe_2Cl_7 and two derivatives.[7] They synthesised polystyrenes with even higher molecular weights, up to 1,300 kg.mol^{-1} and dispersities around 2 at 85 °C. They observed that a decrease in the reaction temperature up to 50 °C allowed for the synthesis of polymers with higher molecular weight ($M_n \approx 1{,}900$ kg.mol^{-1}) and narrower dispersity ($Đ = 1.7$), but also led to a decrease in the polymerisation rate.

However, in the light of the results obtained in **Chapter 2**, such high molecular weights seem at odds with the idea of a cationic polymerisation. Therefore, in this chapter we revisit the polymerisation of styrene using BMI·Fe_2Cl_7 as a catalyst/initiator in different media (bulk, solution and miniemulsion) and clarify the potential of this type of catalyst for cationic polymerisation in aqueous media.

3.2. Experimental Part

3.2.1. Materials

Styrene (Quimidroga, technical grade) was distilled under reduced pressure and stored at -22 °C prior to use. Hexadecane (HD, Sigma Aldrich, 99% purity), hexadecyltrimethylammonium bromide (CTAB, Sigma Aldrich), methyl methacrylate (MMA, Sigma Aldrich, 99% purity), β-pinene (Alfa Aesar, 99% purity) and 2,6-di-tert-butyl-4-methylphenol (BHT, Sigma Aldrich) were used as received. 1-n-butyl-3-methylimidazolium heptachlorodiferrate ($BMI{\cdot}Fe_2Cl_7$) was synthesised following reference [8].

3.2.2. Methods

Gel permeation chromatography (GPC) was performed using three columns in series (Styragel HR2, HR4 and HR6) with a refractive index (RI) detector (Waters 2410) and UV detector (Waters 2487). THF was eluted at a flow rate of 1 $mL.min^{-1}$. The samples were prepared at a concentration of 2 $mg.mL^{-1}$ of polymer in THF and filtered using a nylon filter with pores of 45 µm. The molecular weights and dispersities of all the polymers were calculated using the RI detector, based on polystyrene standards.

Proton nuclear magnetic resonance (^{1}H NMR) was recorded on a Bruker 400 MHz at 25 °C. Samples were prepared in deuterated chloroform ($CDCl_3$) and the signals obtained were calibrated relative to the solvent peak (7.26 ppm).

Matrix assisted laser desorption/ionisation – time of flight mass spectrometry (MALDI-ToF MS) measurements were performed on a Bruker Autoflex Speed system equipped with a 355 nm NdYAG laser. Both positive reflectron and linear modes were used to obtain the spectra. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malonitrile (DCTB, Fluka) was used as a matrix, dissolved in THF at a concentration of 20 mg.mL^{-1}. Silver trifluoroacetate (AgTFA) was added as the ionisation agent (10 mg.mL^{-1} dissolved in THF). Polymer samples were dissolved in THF at a concentration of 10 mg.mL^{-1}. The matrix, the salt and the polymer were premixed at a ratio 10:1:1. Around 0.5 µL of the mixture was hand spotted on a ground steel target plate. For each spectrum, 10,000 laser shots were accumulated. The spectra were externally calibrated with a mixture of different polyethylene glycol standards (PEG, Varian).

3.2.3. Procedures

The synthesis of the 1-n-butyl-3-methylimidazolium heptachlorodiferrate ($BMI·Fe_2Cl_7$) ionic liquid was performed following ref [8]. In a round bottom flask, 2.5 g of 1-n-butyl-3-methylimidazolium chloride (BMI·Cl) and 5.643 g of iron (III) chloride

($FeCl_3$) were stirred together and nitrogen was bubbled for 15 min. The round bottom flask was then plunged in an oil bath at 50 °C for 4h under nitrogen conditions.

The experimental conditions of all the experiments performed in this chapter are summarised in **Table 3-1**. For the cationic polymerisation in bulk, 5 mL of styrene and the appropriate amount of $BMI \cdot Fe_2Cl_7$ were stirred together and bubbled with nitrogen in a vial for 15 min. Then, the vial was placed in an oil bath at 70 °C for 6h under nitrogen atmosphere in order to ensure the anion exchange.

Regarding the solution polymerisation, 5 mL of styrene, 0.022 g of $BMI \cdot Fe_2Cl_7$ and 2 mL of toluene were stirred together in a vial and bubbled with nitrogen for 15 min. The vial was then placed in an oil bath at 70 °C for 3h under nitrogen conditions.

In a typical miniemulsion polymerisation, hexadecyltrimethylammonium bromide (0.06 g) and 11 mL of deionised water were stirred for 20 min in a beaker. In parallel, hexadecane (0.15 g) and styrene (3.00 g) were also stirred for 20 min in another beaker. The organic phase was then added to the aqueous phase and the emulsion was allowed to stir for 20 min more before sonication for 1 min (power 70%, cycle 0.8). The ionic liquid solution (0.0144 g of $BMI \cdot Fe_2Cl_7$ in 1 mL of deionised water) was then added to the miniemulsion and nitrogen was bubbled for 20 min. The reaction was finally performed in an oil bath at 90 °C under nitrogen conditions. The conversions were determined gravimetrically.

Table 3-1: *Summary of the experiments performed in this chapter.*

Run	Solvent	M[a]	IL:M[a] (mol-%)	T (°C)	Time (h)	X[b] (%)	M_n (g.mol^{-1})	Đ[c]
3-1	None	St	1:1,000	70	0.25		16,100	1.6
3-2	None	St	1:5,000	70	6	98.5	4,000	4.2
3-3	Toluene	St	1:1,000	70	3	100	1,200	5.4
3-4	Water	St	1:1,000	90	24	50.5	423,200	3.6
3-5	Water	St	-	90	24	49.7	479,600	3.5
3-6	Water	St + MMA	1:1,000	90	24	37.4	219,000	2.8
3-7	Water	β-pinene	1:1,000	90	24	0	-	-
3-8	Water	MMA	1:1,000	90	24	0	-	-
3-9	Water	St	1:1,000	60	24	0	-	-
3-10	Water	St + MMA	1:1,000	90	24	0	-	-
3-11	Water	St (BHT[d])	1:1,000	90	24	0		

[a]Monomer. [b]Conversion. [c]Dispersity. [d]2,6-di-tert-butyl-4-methylphenol radical scavenger.

3.3. Results and Discussion

The cationic polymerisation of styrene (St) was first performed in bulk at 70 °C using 1-n-butyl-3-methylimidazolium heptachlorodiferrate (BMI·Fe_2Cl_7) ionic liquid (IL) as catalyst to compare with Alves *et al.*.[6] Using a 1:1,000 molar ratio of IL:St (Run 3-1) led to a solid in which aggregates of undissolved IL could be observed (**Figure 3-2a**). On the contrary, using a 1:5,000 molar ratio (Run 3-2), a homogeneous viscous liquid was obtained (**Figure 3-2b**), reaching 98.5% conversion in 6 h. The polymer had a molecular weight (M_n) of 4,000 g.mol^{-1} and a dispersity of 4.2 (**Figure 3-3**), which is consistent with the low molecular weights expected in cationic polymerisation performed at elevated temperatures.[9] The relatively broad molecular weight distributions may be the result of intermolecular transfer to polymer occurring *via* electrophilic aromatic substitution reactions. In that case, branched structures will be formed resulting in a broadening of the molecular weight distribution.

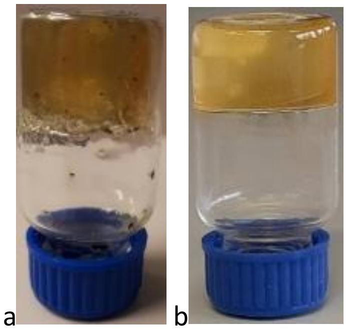


Figure 3-2: *Appearance of the polymer obtained for the polymerisation of styrene in bulk using IL:St molar ratios of (a) 1:1,000 and (b) 1:5,000.*

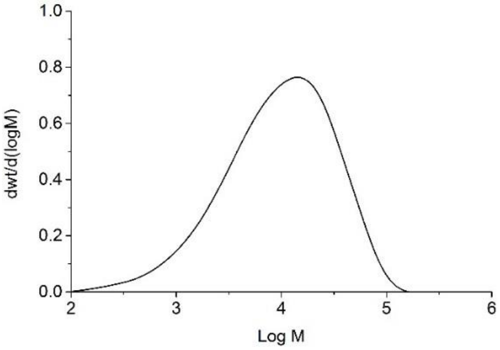


Figure 3-3: *GPC trace obtained for the polymerisation of styrene in bulk.*

The MALDI-ToF analysis of the polymer (**Figure 3-4**) suggested that all the chains were initiated by a proton and terminated by a double bond. This structure is in agreement with a cationic polymerisation mechanism with the unsaturated group arising from β-hydrogen elimination, which is usually the main chain termination mechanism in cationic polymerisation. This confirms the cationic pathway of the polymerisation of styrene in bulk using BMI·Fe_2Cl_7 ionic liquid as a catalyst.

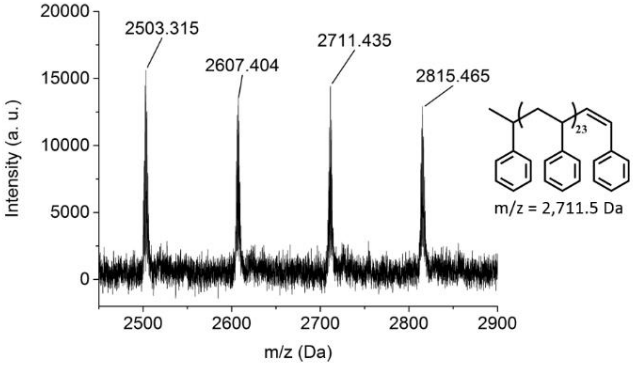


Figure 3-4: *MALDI-ToF spectrum of the polystyrene obtained in bulk with an IL:St molar ratio of 1:5,000 (Run 3-2).*

The polymerisation was then performed in toluene (Run 3-3), as previously attempted by Rodrigues *et al.*.[5] The reaction reached full conversion and the polymer had a M_n of 1,200 $g.mol^{-1}$ and a dispersity of 5.4 (**Figure 3-5**). **Figure 3-6** represents the MALDI spectra of the final polymer. In this case, two different species can be observed. The main one corresponds to chain initiated by a proton and terminated by a double bond, resulting from β-hydrogen elimination (m/z = 1,253 Da), similar to the polymer obtained in bulk system. The second species detected corresponds to chains initiated by a proton and terminated by toluene due to transfer reactions to solvent (m/z = 1,242 Da). The significantly lower molar mass in these solution polymerisation experiments compared to in bulk is likely due to the increased rate of transfer to solvent as well as the reduced extent of intermolecular chain transfer to polymer due to the lower polymer concentration. These structures confirm the cationic process for the polymerisation of styrene in toluene.

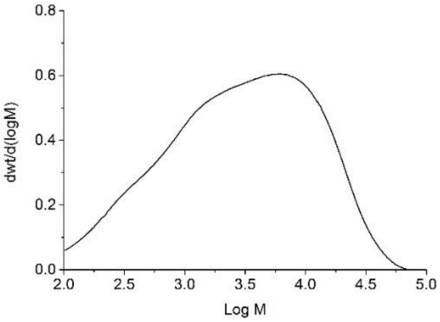


Figure 3-5: *GPC trace of the polystyrene obtained in toluene.*

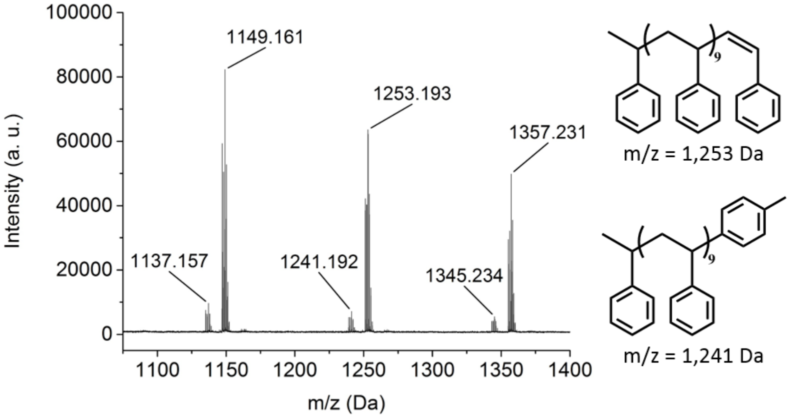


Figure 3-6: *MALDI-ToF spectrum of the polystyrene obtained in toluene.*

The above results demonstrate that BMI·Fe_2Cl_7 initiates the cationic polymerisation of styrene in bulk and in solution. To see if this is also true in the presence of water, the polymerisation of styrene was also performed in miniemulsion using a 1:1,000 molar ratio of BMI·Fe_2Cl_7:St. At 90 °C, an inhibition period of 4h was observed before the polymerisation began, the final conversion was 50.5% after 24h (**Figure 3-7**) with M_n = 423,200 g.mol^{-1} and a dispersity (Đ) of 3.55 (M_v = 1,320 kg.mol^{-1}) (Run 3-4). The final molecular weight is in reasonable agreement with the one observed by Alves *et al.*,[6] who obtained polymers of M_v = 2,231 kg.mol^{-1} with a final conversion of 88%. These very high molecular weights are remarkable because although such high molecular weights have previously been reported for cationic polymerisations in water using Lewis acid-surfactant complex catalysts,[10,11] as explained in **Chapter 2** those reactions in fact proceed *via* a radical polymerisation instead of a cationic pathway.

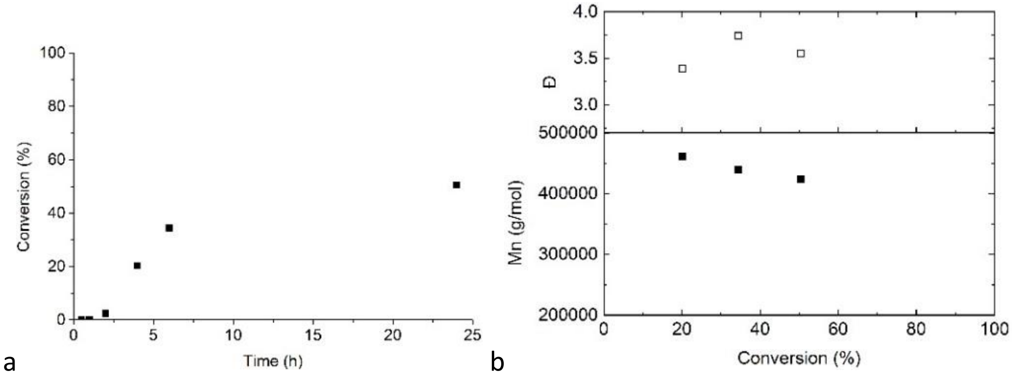


Figure 3-7: *(a) Evolution of the conversion with time and (b) evolution of the molecular weight (full symbols) and dispersity (empty symbols) with conversion for the polymerisation of styrene in miniemulsion at 90 °C.*

In order to probe the polymerisation pathway of this reaction, a series of polymerisations were carried out. First, an experiment without ionic liquids was performed in miniemulsion, to check the efficiency of the IL to initiate the polymerisation (Run 3-5). As can be seen in **Figure 3-8**, there was no difference in the kinetics and molecular weights with and without the presence of ILs in the system, which means that the IL does not play the role of catalyst here.

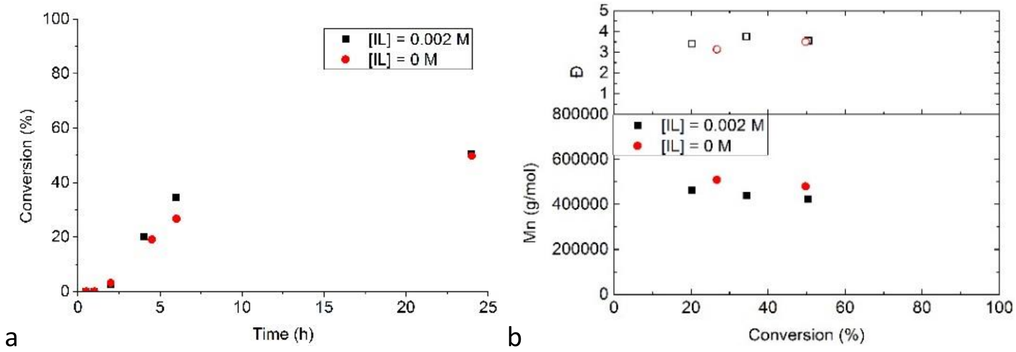


Figure 3-8: *(a) Evolution of the conversion with time and (b) evolution of the molecular weights (full symbols) and dispersities (empty symbols) with conversion for the polymerisations of styrene in miniemulsion with (black squares) and without (red circles) ionic liquids.*

Then, 20 wt-% of methyl methacrylate (MMA) compared to the total amount of monomer was added to the formulation (Run 3-6). MMA is a monomer that can only polymerise through radical polymerisation. An inhibition period of 3h was also present and the polymerisation proceeded to a limited extent (37.4% conversion in 24h) but high molecular weights were obtained (M_n = 219,000 g.mol^{-1}, Đ = 2.82). The ^{1}H NMR spectra (**Figure 3-9**) showed the presence of the different signals from the polystyrene but also those characteristic of poly(MMA), which means that radicals were present in the system. In order to verify whether only radical polymerisation or a combination of cationic and radical polymerisation occurred, β-pinene, a monomer capable of undergoing only cationic polymerisation was used instead of styrene (Run 3-7). In this case, no polymerisation was observed after 24h, refuting the hypothesis of a cationic polymerisation process.

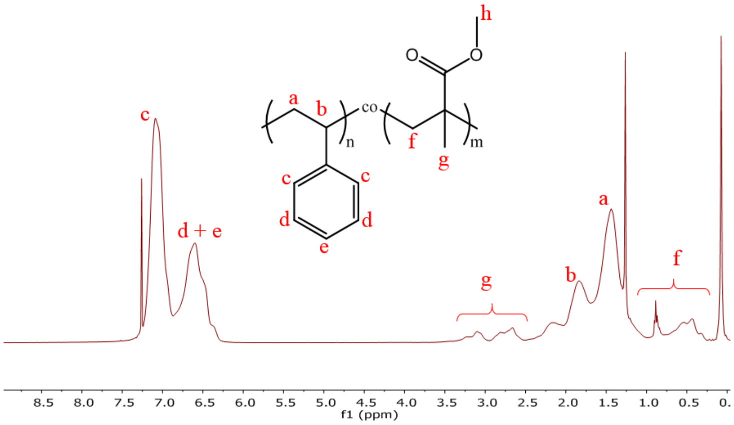
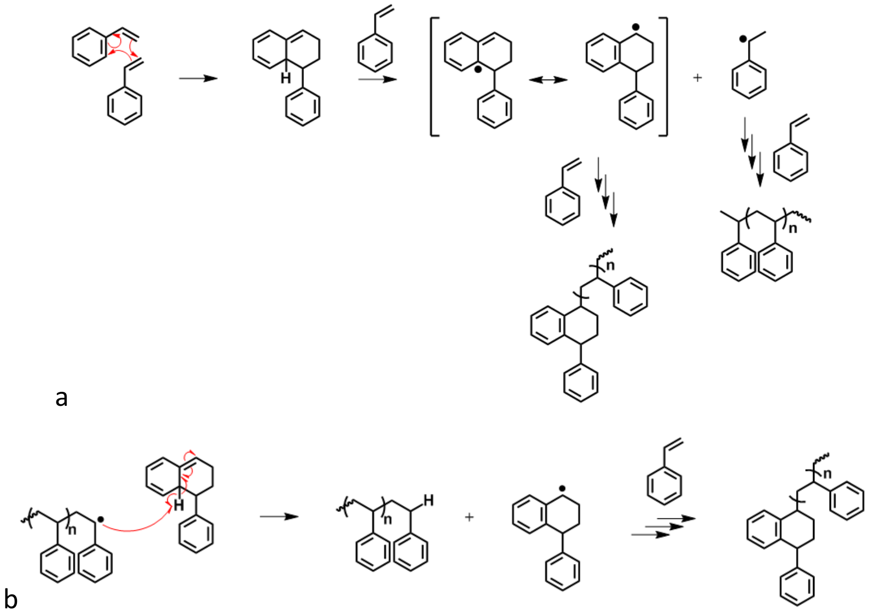


Figure 3-9: *^{1}H NMR spectrum of the polymer obtained from the polymerisation of styrene with 20 wt-% MMA.*

Styrene is known to self-initiate, creating radicals at high temperature.[12,13] Here we performed the polymerisations at 90 °C, which could be high enough for styrene to create radicals. In order to verify this theory, the polymerisation of MMA alone was attempted, but no polymerisation occurred in 24h (Run 3-8). This suggests that the radicals were not generated by the components of the miniemulsion, as it was the case for the Lewis acid-surfactant combined catalyst systems reported in **Chapter 2**, but instead would come from the self-initiation of styrene. In order to further probe this idea, the polymerisation of St (Run 3-9) and St with 20 wt-% MMA compared to the total amount of monomers (Run 3-10) were performed at 60 °C. At this temperature, St does not generate significant numbers of radicals by self-initiation. As expected, no polymerisation occurred in both cases, even after 24h. These results are in agreement with Alves *et al.*, who did not observe any polymerisation at temperatures below 70 °C. The polymerisation of St was also performed in the presence of 2,6-di-tert-butyl-4-methylphenol (BHT), a radical inhibitor, in order to prove the presence of radicals (Run 3-11). Here again, no polymerisation occurred in 24h, which is in agreement with the radical pathway of these reactions.

Further proof for the radical polymerisation was given by the MALDI-ToF spectra of the polystyrene obtained in Run 3-4. **Figure 3-10** represents the MALDI-ToF spectra at low molecular weight range of the polystyrene synthesised in miniemulsion compared to a polystyrene made by radical polymerisation and both polymers present the same species. It is worth noting that due to technical limitations, only the low molecular weight ranges were analysed and therefore might not be fully representative of the whole sample. The same species are present in both Run 3-4 and a polystyrene made *via* radical polymerisation in emulsion. One species corresponds to the bimolecular termination by recombination product of two chains initiated by a fragment which may be formed either through thermal initiation of styrene or by chain transfer to the Diels-Alder dimer (m/z = 1,147 Da), the mechanisms for which are shown in **Scheme 3-2**. The other two peaks were assigned to chains initiated by the same moiety with either an unsaturated group (m/z = 1,161 Da) or a benzyl group (m/z = 1,135 Da) at the ω chain end. Both of these species can arise from intra- or intermolecular radical chain transfer to polymer followed by β-scission.[14] It should be noticed that typical chain ends associated to termination events from cationic polymerisation were absent, such as transfer to water reactions[15] (m/z = 1,167 Da) or transfer to polymer reactions (m/z = 1,149 Da). This result highlights the fact that the polystyrene synthesised in miniemulsion using BMI·Fe_2Cl_7 ionic liquid as a catalyst did not undergo cationic polymerisation.



Scheme 3-2: *(a) Thermal initiation of styrene and (b) transfer to the Diels-Alder dimer.*

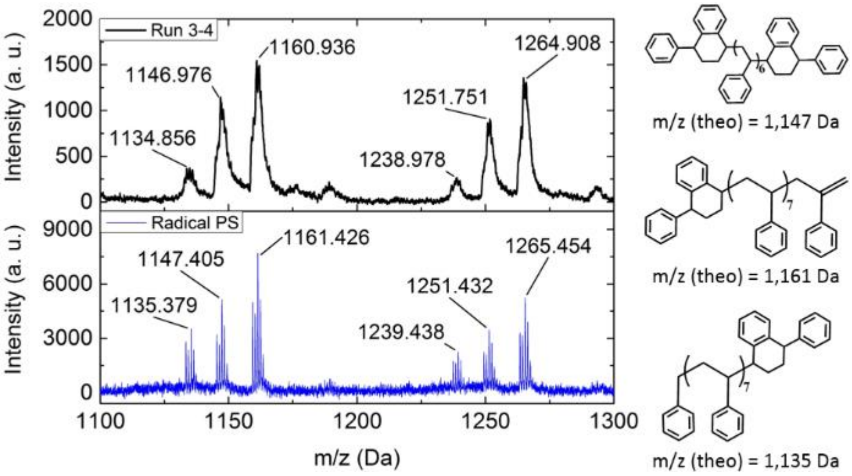


Figure 3-10: *MALDI-ToF spectra of the polystyrene synthesised (a) in Run 3-4 and (b)* via *radical polymerisation in emulsion.*

The difference in reaction mechanism between bulk/solution and miniemulsion is likely a result of the partioning of the ionic liquid catalyst into the aqueous phase where it is not possible to efficiently catalyse the reaction. Alves *et al.* proposed that cations would first be generated in the aqueous phase and by further propagation of the styrene, the growing chains undergo entry into the miniemulsion droplets where the majority of the polymerisation would occur (**Scheme 3-1**). This idea is similar to the Maxwell-Morrison model for radical entry in radical emulsion polymerisation.[16]

However, in a cationic polymerisation this kind of mechanism does not seem feasible. As highlighted in the introduction chapter, carbocations readily undergo transfer/termination reactions with water. The frequency of termination is then determined by the concentration of water ($[H_2O] \approx 55$ mol.L^{-1}) and the rate coefficient for transfer reaction to water, $k_{tr,w}$. This rate coefficient for styrene at 25 °C has been found to be $k_{tr,w}/k_p = 0.32$.[17] At elevated temperatures this ratio is likely to be higher. Taking $k_p = 2 \times 10^5$ L.mol^{-1}.s^{-1},[18] the transfer to water constant equals $k_{tr,w} = 64{,}000$ L.mol^{-1}.s^{-1}. This gives a frequency of termination reaction of 3.5×10^6 s^{-1}. The propagation reaction can be estimated $k_p[St]_{aq} = 600$ s^{-1}, considering $[St]_{aq} = 3 \times 10^{-3}$ mol.L^{-1}. This suggests that the termination of the carbenium ions by transfer to water is significantly higher than the propagation reaction in the aqueous phase, such that it is unlikely that chain growth will occur to any significant extent. As a result, the hydrophilic ionic liquid catalyst used in this work is not capable of catalysing the polymerisation in the presence of water and polymerisation occurs simply through a thermally induced free radical emulsion polymerisation process.

3.4. Conclusions

In conclusion, in this chapter we have demonstrated that although the polymerisation of styrene in bulk and solution using ionic liquid as a catalyst undergoes cationic polymerisation, the miniemulsion system exhibits a radical pathway, probably initiated by thermal initiation of styrene due to the high temperature at which the experiments need to be performed in order to polymerise. This was proven by the ability of methyl methacrylate to copolymerise with styrene but unable to polymerise alone in the same conditions, the influence of radical scavengers, the high molecular mass obtained in miniemulsion compared to bulk or solution systems and the detection of radical transfer reaction products by mass spectroscopy.

3.5. References

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Chapter 4: Limitations of Cationic Polymerisation in the Aqueous Dispersed Media

4.1. Introduction

With the results from **Chapter 2** and **Chapter 3** in mind, it is worth re-evaluating the feasibility of synthesising high molecular weight polymers by cationic polymerisation in aqueous media from a fundamental point of view. Looking back at **Table 1-1** shown in the introduction, it is clear that the results can be broadly separated into those achieving molecular weights of < 10,000 g.mol^{-1} and those for which much higher molecular weights were obtained. For the systems in which lower molecular weight polymers were obtained, an often-cited cause of the low degree of polymerisation (DP) is the idea of a so-called “critical DP” above which the chains are transferred from the interface to the interior of the polymerising system where further polymerisation cannot occur. This theory originated from the work of Ganachaud and co-workers,[1] in which they observed a systematic maximum molecular weight of around 800 g.mol^{-1} for the cationic polymerisation of *p*-methoxystyrene (pMOS) in miniemulsion using surface active sulfonic acids as both initiator and surfactant.

Based on the idea that interfacial polymerisation limits the molecular weight, a lot of focus on the synthesis of higher molecular weight polymers has been placed on the use of initiator/catalyst systems that promote polymerisation within the polymer particles.[2–5] However, regardless of the interfacial nature of the polymerisation, when targeting molecular weights in excess of 10^4 g.mol^{-1} there remains the question as to what extent chain transfer events can be avoided. In order to emphasise the importance of this point, **Figure 4-1** displays literature values of M_n for a number of cationic polymerisations of styrene conducted in dry solution and in aqueous dispersed media. Looking at the solution polymerisation data there is a clear tendency towards lower M_n polymers at higher temperatures; this is understandable due to the increased rate of chain transfer relative to propagation as temperature is increased. In direct contrast to this, for the purported cationic polymerisations in aqueous media, temperature does not appear to limit the degree of polymerisation in any distinguishable way.

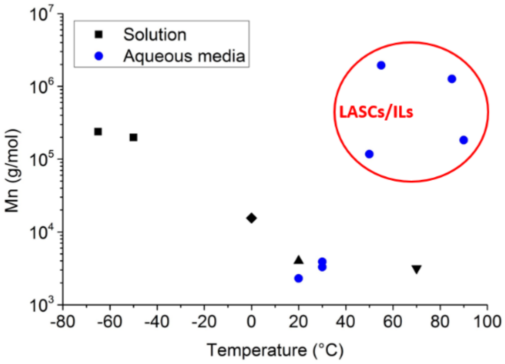


Figure 4-1: *Evolution of the molecular weight of polystyrenes reported in the literature with temperature synthesised in solution (black) and aqueous media (blue spheres). The values in aqueous media are reported from the references in Table 1-1 and the values in solution are taken from ref [6] (squares), ref [7] (diamond), ref [8] (triangle) and ref [9] (reverse triangle).*

In this chapter, we look to explore the influence of unavoidable transfer and termination reactions that put an intrinsic limit on the molecular weight of polymers that can be synthesised by cationic polymerisation in aqueous media. First, we consider the molecular weight limits that are imposed as a result of transfer reactions at temperatures at which reactions in aqueous media are generally conducted. Then, using experimental data, we highlight that this value is necessarily reduced due to transfer to water reactions that occur within the water saturated monomer phase in reactions conducted in dispersed aqueous media. Finally, we briefly explore the differences between suspension polymerisation systems, for which particle sizes are in the range of micrometres, and similar polymerisations carried out in miniemulsion where the particle size is on the order of 100 nanometres.

4.2. Experimental Part

4.2.1. Materials

Styrene (Quimidroga, technical grade) was distilled under reduced pressure prior to use and stored at -22 °C. *p*-Methoxystyrene (pMOS, TCI, > 98.0% purity), (1S)-(-)-β-pinene (β-pinene, 99% purity, Alfa Aesar) was stored at 4 °C until use. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, 97% purity, Alfa Aesar) was stored at -22 °C until use. Dichloromethane (DCM, > 99.5% purity, Sigma Aldrich), 1-(4-methoxyphenyl) ethanol (**1**, 95% purity, Alfa Aesar), lithium chloride (LiCl, > 99%

purity, Acros Organics), sodium chloride (NaCl, Fischer), Mowiol 4-88 (polyvinyl alcohol, 88% hydrolysed, $M_n \approx 31{,}000$ g.mol^{-1}) were used as received.

4.2.2. Methods

Dynamic light scattering (DLS) measurements were performed with a Zetasizer Nano – ZS. For each samples, three runs were carried out at 25 °C, with an equilibrium time of 60 s prior to the first measurement.

Gel permeation chromatography (GPC) was conducted using three columns in series (Styragel HR2, HR4 and HR6) with a refractive index (RI) detector (Waters 2410) and UV detector (Waters 2487). The flow rate at which THF was eluted was 1 mL.min^{-1}. For the sample preparation, solutions of 2 mg of polymer per millilitre of THF were prepared and filtered with a 45 µm pores nylon filter. The molecular weight of the polymers were calculated using the RI detector and the results were based on polystyrene standards.

Proton nuclear magnetic resonance (^{1}H NMR) was recorded on a Bruker 400 MHz at 25 °C. The samples of the precipitated polymers were analysed in deuterated chloroform ($CDCl_3$) and the signals obtained were calibrated relative to the solvent peak at 7.26 ppm.

Matrix-assisted laser desorption/ionisation – time of flight mass spectroscopy (MALDI-ToF MS) was performed on a Bruker Autoflex Speed system equipped with a

355 nm NdYAG laser. The matrix was composed of *trans*-2-[3-(4-*tert*-butylhenyl)-2-methyl-2-propenylidene] malonitrile (DCTB, Sigma-Aldrich) dissolved in THF at a concentration of 10 mg.mL^{-1}; silver trifluoroacetate (AgTFA, Sigma-Aldrich) was used as cation donor (10 mg.ml^{-1} dissolved in THF). A matrix:salt:polymer mixture (10:1:1) was prepared and 0.5 µL was hand spotted on a ground steel target plate. Both linear and reflectron modes were used. An accumulation of 10,000 laser shots was made for each spectrum. A mixture of different polyethylene glycol standards (PEG, Varian) was used as external calibration of the spectra.

Karl-Fisher titration was employed to measure the amount of water in the organic phases. A Metrohm 899 Coulometer was used, filling the vessel with 100 mL of Hydranal Coulomat AG (Honeywell, Fluka) anolyte based on methanol and the electrode was filled with 5 mL of Hydranal Coulomat CG (Honeywell, Fluka) catholyte solution based on methanol. The samples at saturated conditions in water or eutectic salt mixture were stirred for a few hours and left without stirring overnight to reach the equilibrium. For most of the samples, 1 mL of the organic solvent or monomer was added to the vessel in order to determine the water quantity. Due to the higher quantity of water present, only 0.5 mL of β-pinene was tested for each measurement. Each value results from the average of three measurements.

4.2.3. Procedures

In a typical cationic polymerisation of styrene in dichloromethane (DCM), 1-(4-methoxyphenyl) ethanol (**1**) (0.0140 g, 0.02 M), styrene (0.3636 g, 0.65M) and DCM (5 mL) were stirred in a round bottom flask. The $B(C_6F_5)_3$ (0.0138 g, 0.005 M) solution in DCM (1 mL) was then added to the round bottom flask. The polymerisation was performed at 23 °C in air in an enclosed flask. After predetermined times, the polymer was precipitated in an excess of methanol. Monomer conversions were determined by ^{1}H NMR analysis in deuterated acetone (deuterated chloroform for β-pinene).

In a typical cationic polymerisation of styrene in a 1:1 (v/v) mixture of DCM/water, a $B(C_6F_5)_3$ (0.0138 g) solution in DCM (1 mL) was prepared in a vial. The organic phase composed of (**1**) (0.0140 g, 0.02 M), styrene (0.3636 g, 0.65M) and DCM (4 mL) were stirred in a beaker and added to the water phase (5 mL) containing 1 wt-% of poly(vinyl alcohol) as surfactant in a round bottom flask. The catalyst solution was then added and the polymerisation was performed at 23 °C in air in an enclosed flask. After predetermined times, the polymer was precipitated in an excess of methanol. Conversions were determined by ^{1}H NMR analysis in deuterated acetone (deuterated chloroform for β-pinene).

In a typical cationic polymerisation of styrene in suspension, a $B(C_6F_5)_3$ (0.0138 g) solution in DCM (0.1 mL) was prepared in a vial. The organic phase composed of (**1**) (0.0140 g) and styrene (0.3636 g) were stirred in a vial and added to the water phase (5 mL) containing 1 wt-% of poly(vinyl alcohol) as surfactant in a round bottom flask. The catalyst solution was then added and the polymerisation was performed at 23 °C in air in an enclosed flask. After predetermined times, the polymer was precipitated in an excess of methanol. Conversions were determined by gravimetry.

For a typical cationic polymerisation of styrene in miniemulsion, a $B(C_6F_5)_3$ (0.0138 g) solution in DCM (0.1 mL) was prepared in a vial. The organic phase composed of (**1**) (0.0140 g), hexadecane (0.0182 g) and styrene (0.3636 g) were stirred in a vial and added to the water phase (5 mL) containing 1 wt-% of poly(vinyl alcohol) as surfactant in a round bottom flask. The system was sonicated in an ice bath during 10 min at 100% amplitude, full cycle duty. The catalyst solution was then added and the miniemulsion was sonicated for an additional 30 sec. The polymerisation was performed at 23 °C in air in an enclosed flask. After predetermined times, the polymer was precipitated in an excess of methanol and conversions were determined by gravimetry.

Table 4-1: *Summary of the experiments performed for this chapter.*

Run	Monomer	Solvent	Time (h)
4-1	St	DCM	8
4-2		DCM/1% PVA aqueous solution	8
4-3		DCM/water	24
4-4		DCM/eutectic salt mixture	24
4-5		1% PVA aqueous solution	24
4-6		Water	24
4-7		Eutectic salt mixture	25
4-8	pMOS	DCM	0.33
4-9		DCM/1% PVA aqueous solution	0.2
4-10		DCM/water	24
4-11		DCM/eutectic salt mixture	1.5
4-12		1% PVA aqueous solution	24
4-13		Water	24
4-14		Eutectic salt mixture	1
4-15	β-pinene	DCM	2
4-16		DCM/1% PVA aqueous solution	6
4-17		DCM/water	24
4-18		DCM/eutectic salt mixture	24
4-19		1% PVA aqueous solution	48
4-20		Water	24
4-21		Eutectic salt mixture	25

4.3. Results and Discussion

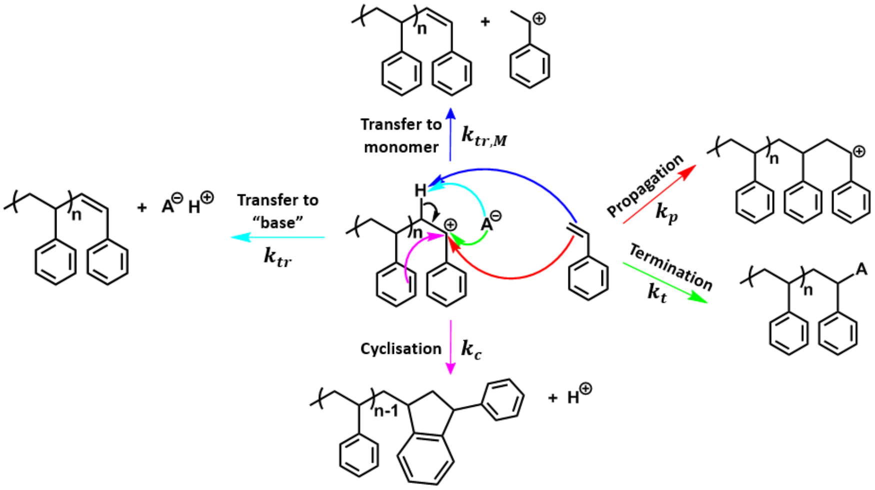
4.3.1. Transfer and Termination in Cationic Polymerisation at Elevated Temperatures

As detailed in **Chapter 1** and summarised in **Scheme 4-1**, various transfer and termination reactions compete with propagation in cationic polymerisation and place a limit on the molar mass of the polymer that can be obtained. Let us first consider an ideal polymerisation, in which the counteranion does not undergo recombination with the propagating chain or take part in any β-hydrogen elimination reactions, a solvent is used for which chain transfer to solvent does not occur (*e.g.* DCM), and there are no additional impurities that may otherwise induce termination/transfer reactions. Neglecting these potential reactions, there remain a number of intrinsic transfer reactions, such as transfer to monomer ($k_{tr,M}$) (and intramolecular transfer (cyclisation, k_c) for styrenic derived monomers), that limit the degree of polymerisation (DP) to a value that can be estimated following the equation:

$$DP = \frac{R_p}{R_t + \Sigma R_{tr}} \tag{4-1}$$

With R_p the rate of propagation, R_t the rate of termination and ΣR_{tr} the sum of the rates of transfer. Taking into account only transfer to monomer and cyclisation reactions this equation leads to:

$$\frac{1}{DP_{max}} = \frac{k_{tr,M}}{k_p} + \frac{k_c}{k_p[M]} \tag{4-2}$$



Scheme 4-1: *Mechanism of the different possible transfer and termination reactions occurring in cationic polymerisation.*

Values of maximum degree of polymerisation (DP_{max}) calculated across a range of temperatures for styrene (St), *p*-methoxystyrene (pMOS) and β-pinene are presented in **Table 4-2** using rate coefficients obtained from literature. As observed in the table, the higher activation of chain transfer reactions relative to propagation results in increased k_{tr}/k_p at higher temperatures and therefore a reduced DP. Although additives can of course lower the freezing point of water, a practical limit for conducting polymerisation in aqueous dispersed media would be on the order of 0 °C, which would place an absolute limit on the molecular weight for styrene of ≈ 15,000 $g.mol^{-1}$ and for pMOS ≈ 60,000 $g.mol^{-1}$. At the elevated temperatures that many supposed cationic polymerisations in aqueous media have been conducted, these values are drastically reduced. For example, polymerisation of styrene at 60 °C and 90

°C results in a limiting molecular weight of 2,000 g.mol^{-1} and 900 g.mol^{-1} respectively. It is important to highlight that these values neglect a multitude of additional system-specific chain transfer reactions that can occur and will further reduce this theoretical limit.

Table 4-2: *Determination of DP$_{max}$ for the polymerisation of styrene,* p*-methoxystyrene and β-pinene in ideal conditions, considering [M] = 0.65 mol.L^{-1}. ^{a}The values were calculated from the Arrhenius parameters given in ref.* [10] *and the reported values in ^{b}Ref.* [11]. *^{c}Ref.* [12].

Monomer	Temperature (°C)	$k_{tr,M}/k_p$	k_c/k_p	DP$_{max}$
Styrene^{a}	25	1.78 x10^{-2}	7.52 x10^{-6}	56
	0	6.89 x10^{-3}	1.28 x10^{-5}	145
	-60	2.86 x10^{-4}	4.00 x10^{-4}	1,109
	-90	2.67 x10^{-5}	2.97 x10^{-4}	2,068
pMOS^{b}	25	4.59 x10^{-3}		218
	0	1.89 x10^{-3}		529
	-15	2.28 x10^{-4}		4,386
β-pinene^{c}	20	1.68 x10^{-2}	-	60

4.3.2. Cationic Polymerisation in Excess of Water

Above, only transfer to monomer was taken into account but it is clear that in aqueous dispersed media chain transfer to water will be expected to contribute to further lowering the maximum theoretical molar mass. In order to explore this, in the next sections of this chapter, we report a comparison of the reaction kinetics and molar mass obtained in both solution and suspension experiments for a few typical monomer systems: styrene, *p*-methoxystyrene and β-pinene.

4.3.2.1. Case of Styrene

The cationic polymerisation of styrene using tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) as a catalyst and 1-(4-methoxyphenyl) ethanol (**1**) as initiator was first performed in dichloromethane (DCM) at 23 °C for 8h (Run 4-1, **Table 4-1**). Following an initial rapid polymerisation rate, a relatively slow polymerisation occurred with a final conversion of 72% after 8 h (**Figure 4-3a**). This rapid conversion period occurs as a result of the initial high carbocation concentration that is generated by the ionisation of the initiator molecules. A final molecular weight (M_n) of 1,900 $g.mol^{-1}$ and a dispersity (Đ) of 2.0 were obtained (**Figure 4-3b and c**).

Two comparative polymerisations were performed. First, using the same organic phase as Run 4-1, a suspension polymerisation was conducted using a 1:1 (v/v) mixture of DCM and a 1% poly(vinyl alcohol) (PVA) aqueous solution (Run 4-2, **Table 4-1**). A scheme of the experimental difference between solution and suspension experiments is presented in **Figure 4-2**. In this case, the reaction kinetics were similar to the polymerisation in solution. However, the final M_n drastically dropped to 500 $g.mol^{-1}$.

A second suspension polymerisation was conducted in the absence of DCM in the organic phase using the same $B(C_6F_5)_3$:**1**:styrene ratio (Run 4-5, **Table 4-1**). This experiment resulted in lower final molecular weight (M_n = 1,100 $g.mol^{-1}$) than the polymerisation in solution, but conversion was limited to 51%, even after 24h of reaction. Note that although PVA is a surfactant often used in suspension polymerisation, it contains alcohol groups that can lead to grafting reactions by chain transfer. For this reason, experiments in suspension removing the PVA surfactant were also performed in order to verify the influence of the surfactant on the polymerisation (Runs 4-3 and 4-6 in **Table 4-1**). In these systems, the droplets are unstable and the reactions are effectively solution (or bulk) polymerisations carried out with a water saturated organic phase. Similar results regarding the conversion and the molecular weights were obtained for the suspension experiments of DCM/water compared to the DCM/PVA aqueous solution. However, the suspension polymerisation performed in pure water resulted in higher molecular weights (M_n = 2,100 g.mol^{-1} against 1,100 g.mol^{-1} in PVA aqueous solution), which can be attributed to the absence of chain transfer reactions to the alcohol groups of PVA.

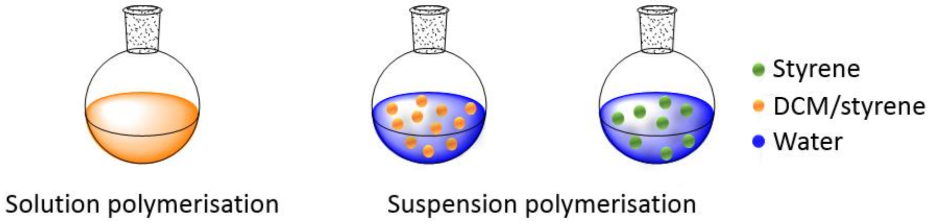


Figure 4-2: *Differences between (left) solution and (right) suspension experiments.*

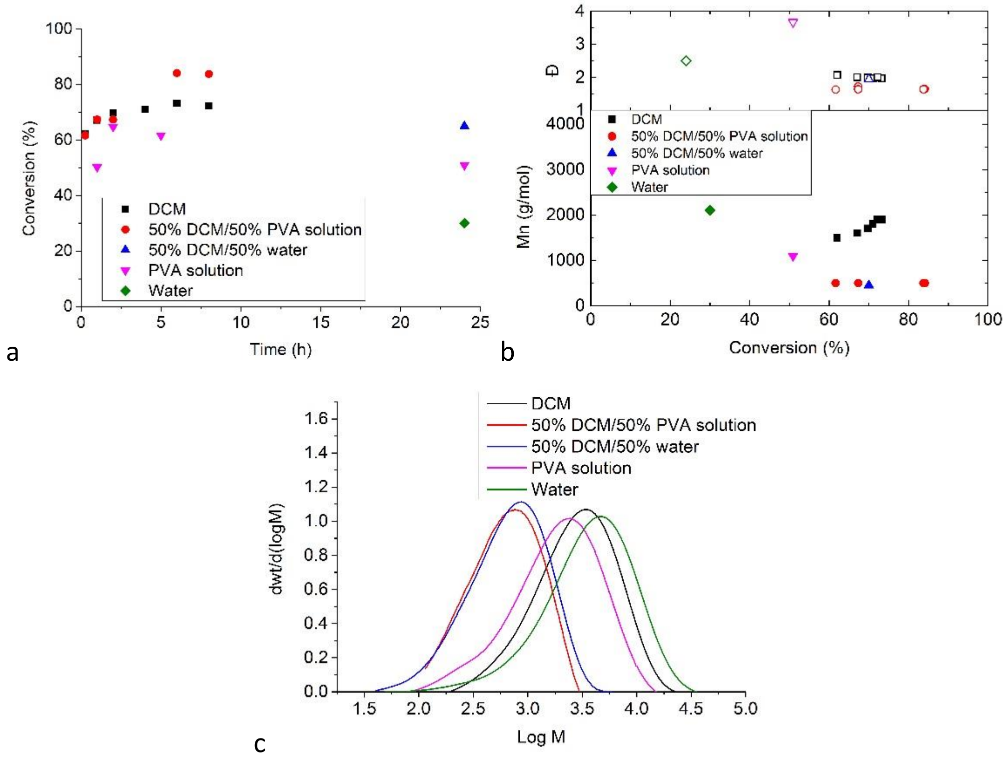


Figure 4-3: *(a) Evolution of the conversion with time, (b) evolution of the molecular weight (full symbols) and dispersity (empty symbols) with conversion and (c) molecular weight distributions for the cationic polymerisation of styrene in dichloromethane (black), a 1:1 (v/v) mixture of DCM and PVA aqueous solution (red), a 1:1 (v/v) mixture of DCM and water (blue), PVA aqueous solution (pink) and water (green).*

The results shown in **Figure 4-3** can be explained by considering the suspension polymerisations as pseudo-bulk reactions in which the polymerisation rate and molecular weight are determined by the conditions within the micron sized droplets of the organic phase. Looking first at the reaction kinetics, these polymerisations proceed *via* the $B(C_6F_5)_3$ catalysed activation of OH terminated chains and therefore the rate of polymerisation is primarily determined by the equilibrium between active and dormant chains. In the case of Run 4-1 and Run 4-2, the organic phase is similar in both cases and the local carbocation concentration would be expected to be equal, leading to similar rates of polymerisation. In contrast, as styrene is less polar than DCM, despite the higher local concentrations of monomer, catalyst and initiator, the equilibrium is shifted to the dormant state and therefore the rate of polymerisation is reduced.

Looking now to the final molecular weights obtained in these reactions, it was postulated that chain transfer to water was responsible for changes in the molecular weight distributions obtained. In order to explore this idea, Karl-Fischer titrations were performed to measure the amount of water in the organic phase. In solution, a relatively low concentration of water was present (127 ppm, 7.1 x10^{-3} M). This value is lower than the amount of initiator used in the experiments and since, in addition, in solution any water that reacts is not replenished, the extent to which water can influence the molar mass of the solution polymerisation is limited. This is in contrast to reactions in suspension for which the dispersed phase is constantly saturated with water. Indeed, in suspension, 665 ppm (3.7 x10^{-2} M) of water was measured for the styrene phase in saturated conditions, and when the organic phase contained DCM this increased to 1,604 ppm (8.9 x10^{-2} M). The higher concentration of water in the DCM/water mixture compared to the pure suspension is simply due to the higher polarity of DCM compared to styrene.

Using these concentrations of water, an estimate of the effect of chain transfer to water on the molecular weight can be made. In a controlled/living cationic polymerisation with an initial concentration of monomer and initiator of $[M]_0$ and $[I]_0$ respectively, the number average DP can be given by the amount of monomer units polymerised divided by the number of chains generated in the reaction such that:

$$DP = \frac{X[M]_0}{[C_M]+[C_W]+[I]_0} \tag{4-3}$$

Where X is the fractional conversion, $[C_W]$ is the concentration of chains generated from transfer to water, and $[C_M]$ is the concentration of chains generated by transfer to monomer. $[C_M]$ and $[C_W]$ are given by:[13]

$$[C_M] = \frac{k_{tr,M}}{k_p} X[M]_0 \tag{4-4}$$

In the case of saturated conditions with water:

$$[C_W] = -\frac{k_{tr,w}[H_2O]}{k_p} \ln(1-X) \tag{4-5}$$

Note that this equation assumes a constant concentration of water in the organic phase whereas in reality for systems carried out using a pure monomer phase, polymerisation is likely to reduce the concentration at high conversions. In the case where the organic phase is not saturated (*i.e.* a solution polymerisation carried out without solvent drying) and each transfer event lowers the water concentration:

$$[C_W] = [H_2O]_0 - \frac{[H_2O]_0}{e^{-{k_{tr,w}}/{k_p} \ln(1-X)}} \tag{4-6}$$

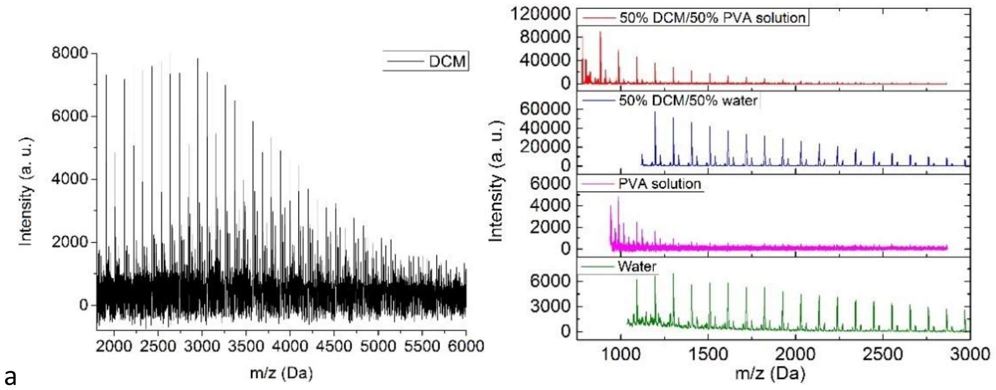
Incorporating these effects of transfer leads a characteristic maximum in the evolution of M_n with conversion and ultimately limits the degree of polymerisation that is possible for a given system. **Table 4-3** presents the different DP_{max} (and corresponding maximum molecular weight ($M_{n,max}$)) obtained using equation (4-3) and the data obtained experimentally. Taking $k_{tr,w}/k_p$ = 0.3, a value previously reported in the $SnCl_4$ mediated polymerisation of styrene in solution,[14] a fairly good agreement between the experimental and theoretical molar mass is obtained with the exception of the reaction in suspension using PVA where, as highlighted above, transfer reactions to PVA can result in lower molar mass. In the case of aqueous dispersed polymerisation in which the organic phase contained DCM, the high water concentration leads to substantial amount of chain transfer to water and therefore a reduction in the molar mass. Interestingly, for reactions conducted in suspension in aqueous media without DCM the predicted molar mass is *higher* than an equivalent reaction conducted in solution, a result that was also observed experimentally. This occurs because despite the water concentration in the organic phase being much higher in the suspension case, the higher concentration of initiator compensates and results in relatively less chain transfer. As a result, chain transfer to water has only a limited influence on the molecular weight for the suspension polymerisation carried out using styrene.

Table 4-3: *Maximum degree of polymerisation (DP_{max}) and molecular weight ($M_{n,max}$) as well as experimental molecular weight ($M_{n,exp}$) for the cationic polymerisation of St in the different systems. The calculation of DP_{max} was based on equation (4-3) taking into account $k_{tr,w}/k_p = 0.3$ and [St] = 0.65 mol.L^{-1}.*

Reaction	$[H_2O]$ (mol/L)	DP_{max}	$M_{n,max}$ (g/mol)	$M_{n,exp}$ (g/mol)	Đ
DCM – solution	7.0 x10^{-3}	18	1,800	1,900	2.0
DCM/1% PVA aqueous solution – suspension	8.9 x10^{-2}	7	770	500	1.6
DCM/water – suspension	8.9 x10^{-2}	7	770	500	1.9
1% PVA aqueous solution – suspension	3.7 x10^{-2}	19	1,950	1,100	2.3
Water – suspension	3.7 x10^{-2}	19	1,950	2,100	2.5

To confirm these effects of water on the molecular weight distribution, MALDI-ToF measurements were performed for determination of the terminal groups of the polymer chains for each system (**Figure 4-4**). In the case of the polymerisation in solution, most of the chains are initiated by an initiator molecule and terminated by an unsaturated group (**Figure 4-4b**). The unsaturated group may arise from β-hydrogen elimination but no hydrogen-initiated chains were observed, which suggests an alternative cause. One explanation could be that the terminal double bond arises from the elimination of the terminal group during the MALDI analysis. This has previously been reported in MALDI analysis for similar –OMe terminated systems that result from the use of methanol to quench the reaction.[15,16] Chains initiated by the initiator and terminated by a hydroxyl group, which result either from the recombination of the OH from the counterion or from chain transfer to water were also present. Additional peaks arising from chain transfer to polymer reactions were also seen as evidenced by the two other peaks present in the MALDI-ToF spectra (m/z = 1,938.992 Da and 1,956.991 Da). As for styrene the chain transfer constant for alkoxy substituted aromatic compounds is orders of magnitude higher than alkyl substituted ones (*e.g.* $C_s = 1.6$ for anisole but 1×10^{-2} for *p*-xylene),[17] it is likely that this structure occurs due to electrophilic aromatic substitution of the *p*-methoxy substituted initiating moiety.

For reactions conducted in suspension (both with and without added DCM), the dominant chain end was not the unsaturated but instead the majority of chains were terminated by a hydroxyl group (**Figure 4-4b**). Additional structures that can be related to chain transfer to polymer reactions, either by electrophilic aromatic substitution reactions or by chain transfer to the OH terminated polymers leading to an ether bridge, were also observed in the MALDI spectra. This is particularly obvious in the reaction conducted in the absence of DCM due to the higher concentration of the OH terminated polymers relative to water.



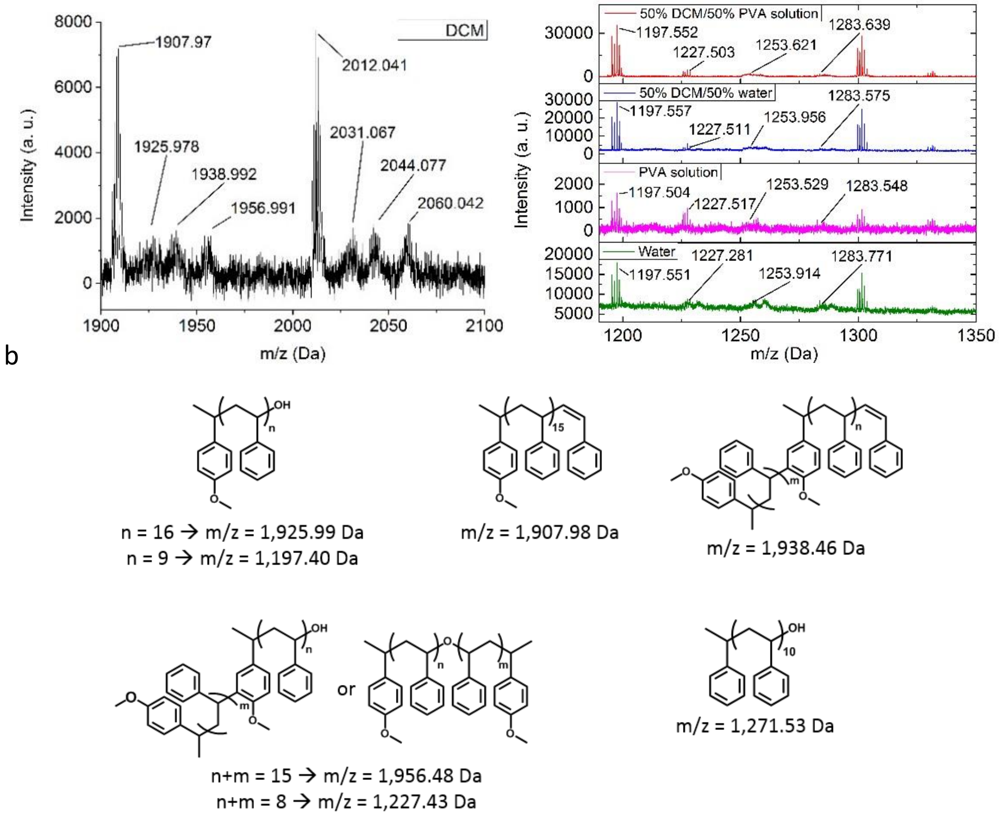
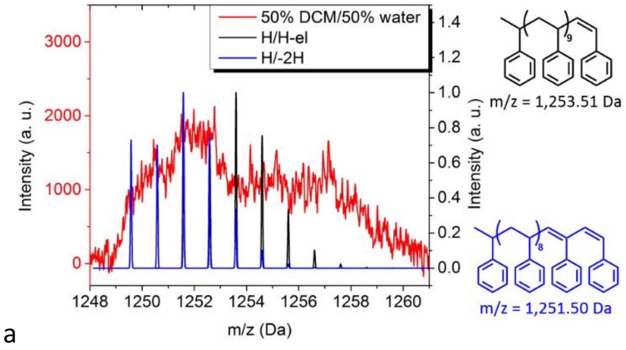


Figure 4-4: *MALDI-ToF (a) full and (b) zoomed spectra of the polystryrenes obtained from the cationic polymerisation in dichloromethane (black), a 1:1 (v/v) mixture of DCM and PVA aqueous solution (red), 1:1 (v/v) mixture of DCM and water (blue), PVA aqueous solution (pink) and water (green).The structures correspond to the peaks in the MALDI spectra.*

Two other peaks can be observed in the MALDI spectra of polystyrenes synthesised in all the suspension polymerisations that are in fact composed of multiple species. The first peak at 1,253 Da (**Figure 4-5a**) corresponds to proton initiated chains terminated by β-hydrogen elimination reaction (theoretical m/z = 1,253.51 Da), as well as chains arising from hydride abstraction (theoretical m/z = 1,251.50 Da) due to the easily abstractable hydrogen close to the terminal double bond (see **Scheme 4-2**).[18] In agreement with the lower molar masses reported in **Table 4-3**, these signals were of higher intensity in suspension reactions conducted in the presence of DCM where the extent of chain transfer was higher. Finally, regarding the signal around 1,283 Da (**Figure 4-5b**), one of the species can be ascribed to chains initiated by an initiator molecule and terminated either by β-hydrogen elimination reaction or by the indanyl end-group resulting from intramolecular cyclisation (theoretical m/z = 1,283.54). A second species can be observed that results from chains initiated by the initiator and terminated by hydride abstraction, which is consistent with the hydride elimination-terminated chains observed (theoretical m/z = 1,285.55 Da).



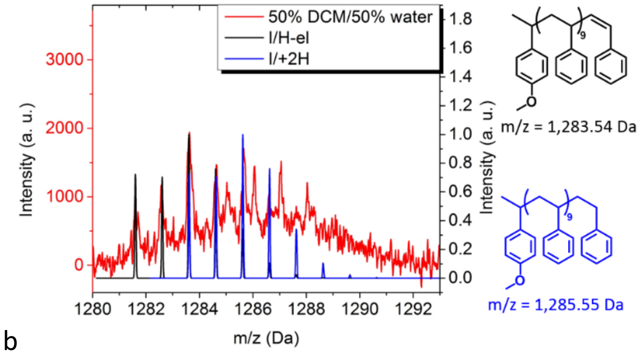
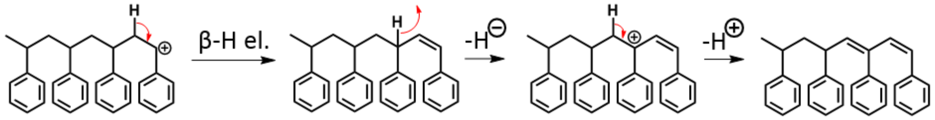
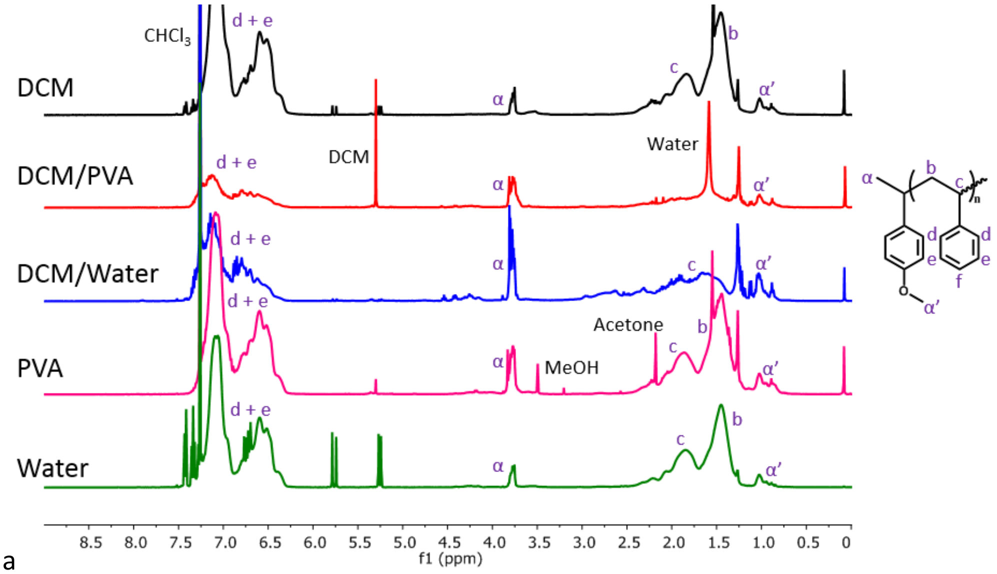


Figure 4-5: *Zoomed spectra of polystyrene synthesised in a 1:1 (v/v) mixture of DCM and PVA aqueous solution (red) and the theoretical isotopic patterns corresponding to (a) chains initiated by a proton and terminated by β-H elimination (black) or elimination of hydride (blue) and (b) chains initiated by an initiator molecule and terminated by β-H elimination (black) or hydride abstraction (blue).*



Scheme 4-2: *Mechanism of the hydride elimination.*

The structures of the chains were further backed up by the ^{1}H NMR spectra (**Figure 4-6**). Indeed, the end groups corresponding to the initiation by an initiator molecule (labelled α and α’ in **Figure 4-6**) are clearly visible in the spectra of the all systems. The degree of polymerisation obtained from the ratio between the α signal and the hydrogens from the aromatic ring of styrene between 6.5 and 7.5 ppm are in good agreement with the degree of polymerisation obtained by GPC in all the systems. Moreover, for the DCM system, a signal of relatively high intensity at 3.6 ppm (labelled ω_3’ in **Figure 4-6b**) corresponding to $–OCH_3$ group resulting from the combination of the propagating cation with the methanol (MeOH) added to quench the reaction is present. This is consistent with the major peak in MALDI that corresponds to chains terminated by an unsaturation that would be due to the elimination of the MeOH group during the analysis.[15,16] Regarding the suspension polymerisations, whether with or without DCM, the NMR spectra present a signal around 4.25 ppm (labelled ω_2 and ω_3 in **Figure 4-6b**) that corresponds to the –C*H*-O from the recombination of the propagating chain with the counterion, MeOH or from the ether bridge. This is consistent with the two main species observed in the MALDI spectra of these systems. Furthermore, in the NMR spectrum of the DCM/PVA mixture, a small signal at 6.0 ppm (labelled ω_1 in **Figure 4-6b**) is detectable, that arises from the hydrogen at the terminated double bond, that can also be observed in the MALDI.



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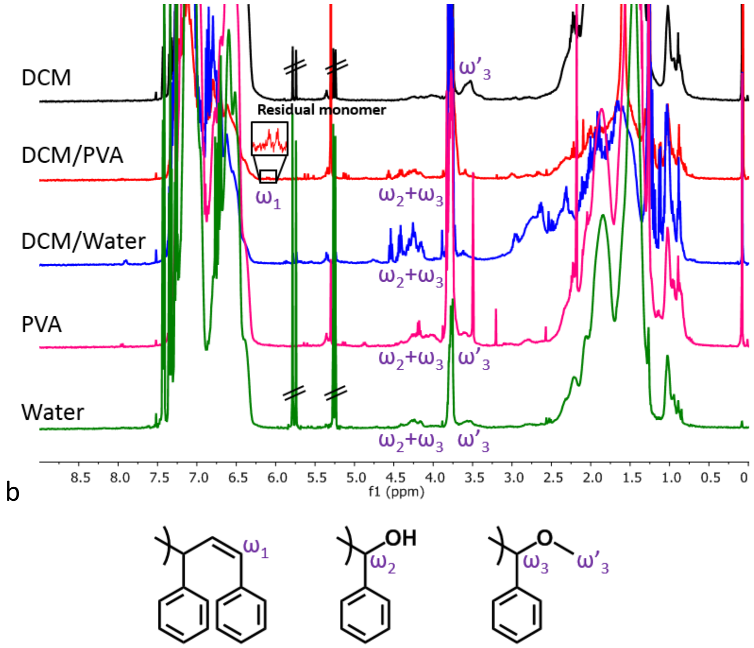

Figure 4-6: *(a) ^{1}H NMR spectra and (b) the amplified spectra of polystyrenes synthesised in dichloromethane (black), a 1:1 mixture of DCM and 1% PVA aqueous solution (red), a 1:1 mixture of DCM and water (blue), a 1% PVA aqueous solution (pink), water (green) and the structures corresponding to the chain ends of the chains.*

4.3.2.2. Case of p-Methoxystyrene

To explore the generality of the results described in Section 4.3.2.1, a similar series of reactions was conducted with *p*-methoxystyrene. Thus, the cationic polymerisation of *p*-methoxystyrene (pMOS) was performed at 23 °C in air in dichloromethane (DCM), in a 1% PVA aqueous solution, in pure water as well as in a 1:1 (v/v) mixture of DCM and PVA aqueous solution and a mixture of DCM and water.

The polymerisations in solution and in the DCM/PVA aqueous solution mixture (Runs 4-8 and 4-9, **Table 4-1**, respectively) were effectively instantaneous and no difference in polymerisation rate could be distinguished between them. In contrast, the polymerisation in PVA aqueous solution (Run 4-12, **Table 4-1**) led to 76% conversion only after 24h (**Figure 4-7**). Similar to the case of styrene, this can be related to the shift in equilibrium to the active carbocation when the reaction occurs in the more polar DCM solution. The molecular weight (M_n) decreased from 8,000 g.mol^{-1} in solution to 5,100 g.mol^{-1} in the DCM/PVA aqueous solution mixture and 3,600 g.mol^{-1} in PVA aqueous solution. This reduction may be the result of increased rates of transfer to water for reactions conducted in suspension as water concentration increased in the organic phase from 150 ppm (8.3 x10^{-3} M) in DCM to 1,517 ppm (8.4 x10^{-2} M) for pMOS in water and 1,604 ppm (8.9 x10^{-2} M) in the pMOS/DCM in water system. However, in all cases the value of M_n was substantially above the predicted value based on the [pMOS]:[initiator] ratio assuming efficient initiation.

As for styrene, suspension polymerisations of pMOS in the absence of PVA were performed, both reaching full conversion after 24h. Poly(pMOS) obtained for the suspension of the DCM/water mixture (Run 4-10 in **Table 4-1**) had a molecular weight (M_n) of 3,800 g.mol^{-1} and a dispersity (Đ) of 1.9 whereas in water only (Run 4-13 in **Table 4-1**), M_n = 2,400 g.mol^{-1} and Đ = 3.4. The lower molecular weights observed in the absence of PVA could be explained by the interaction of $B(C_6F_5)_3$ with the surfactant, which decreases the rate of initiation and in turn results to a fewer chains being generated from the initiator.

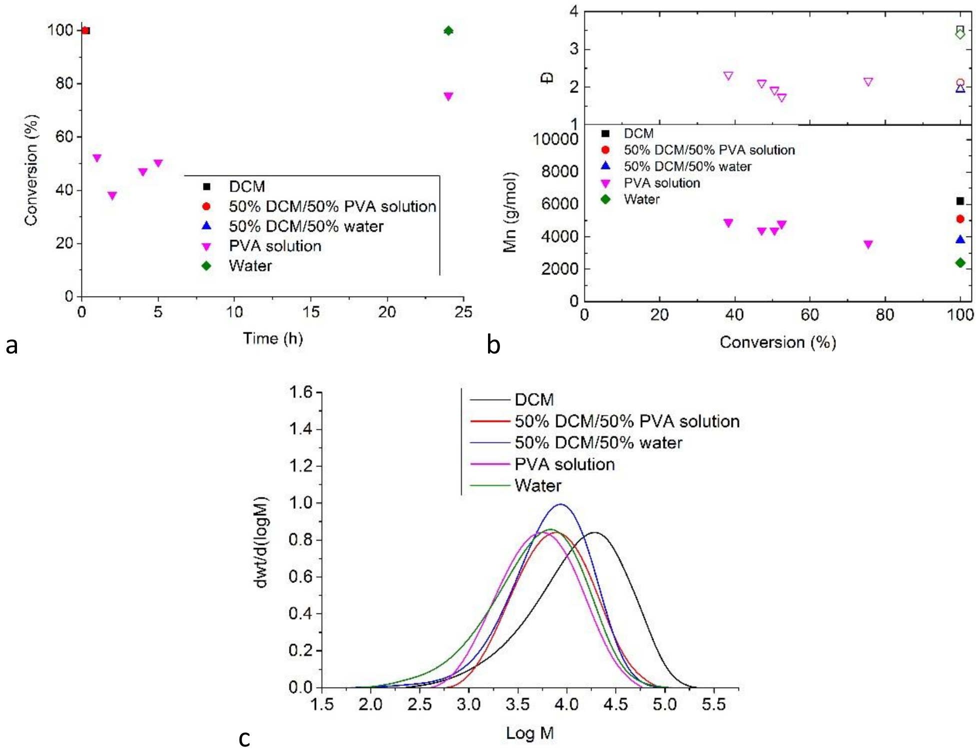

Figure 4-7: *(a) Evolution of the conversion with time, (b) evolution of the molecular weight (full symbols) and dispersity (empty symbols) with conversion and (c) molecular weight distributions for the cationic polymerisation of pMOS in dichloromethane (black), a 1:1 (v/v) mixture of DCM and PVA aqueous solution (red), a 1:1 (v/v) mixture of DCM and water (blue), PVA aqueous solution (pink) and water (green).*

The data shown for *p*-methoxystyrene suggest that transfer to water limits the molecular weight in aqueous dispersed systems but due to the very high rate of polymerisation, the control is not sufficient to point to transfer reactions as a definitive cause of the lower molar mass obtained. However, pMOS has been used extensively in pseudo-living cationic polymerisations in aqueous media where a common observation has been a limiting molar mass. In **Figure 4-8** the M_n-conversion curves of a series of cationic polymerisations using pMOS with a variety of catalysts ($Yb(OTf)_3$, $Zn(BF_4)$, $Zn(OTf)_2$) and different initiating systems (pMOS-HCl adduct or pMOS-methane sulfonic acid adduct) but identical [pMOS]/[I] ratios from the group of Sawamoto are shown. For comparison, a reaction carried out under anhydrous conditions in toluene is also shown. It can clearly be observed that reactions conducted in water have a limiting molar mass. Using the saturated water concentration of the water phase reported here, fitting of the data using Eq (4-3) gives a value of $k_{tr,w}/k_p = 0.75$, which is close to the reported value for styrene ($k_{tr,w}/k_p = 0.3$).[14]

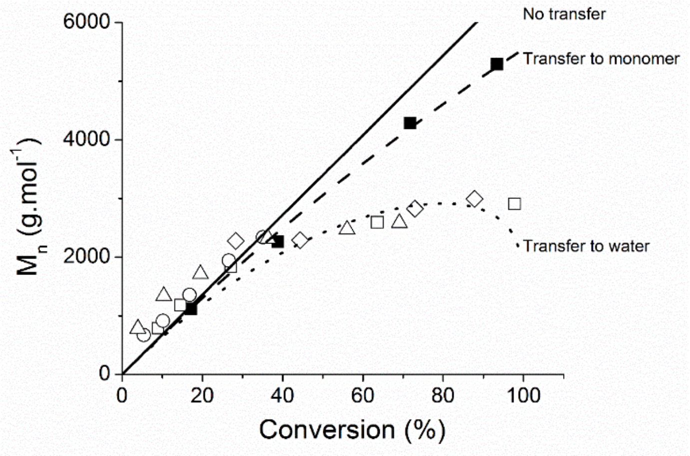

Figure 4-8: *Evolution of the molecular weight with conversion for a series of cationic polymerisations of pMOS conducted in aqueous dispersed media at 30 °C with [pMOS]/[I] = 50. Open symbols for reactions conducted in dispersed media,*[19–21] *closed symbols for a reaction conducted in toluene in solution.*[21] *The three lines show the theoretical evolution of M_n using equation 4-3 with* $k_{tr,w}/k_p = k_{tr,M}/k_p = 0$ *(Full line),* $k_{tr,w}/k_p = 0$ *and* $k_{tr,M}/k_p = 0.0045$ *(dashed line) or* $k_{tr,w}/k_p = 0.75$ *and* $k_{tr,M}/k_p = 0.0045$ *(dotted line).*

The NMR spectra of the polymers obtained for each system are very similar (**Figure 4-9**). Note that unlike the case of styrene, proton and initiator derived chains cannot be distinguished due to the nature of the initiator used. In any case, the peaks around 1 ppm (labelled α in **Figure 4-9**) corresponding to the initiator (or proton initiated chains) are clearly visible. The ratio between the integrals of the α peak with the signals 6 and 7.2 ppm corresponding to the aromatic ring are in good agreement with the degree of polymerisation found by GPC.

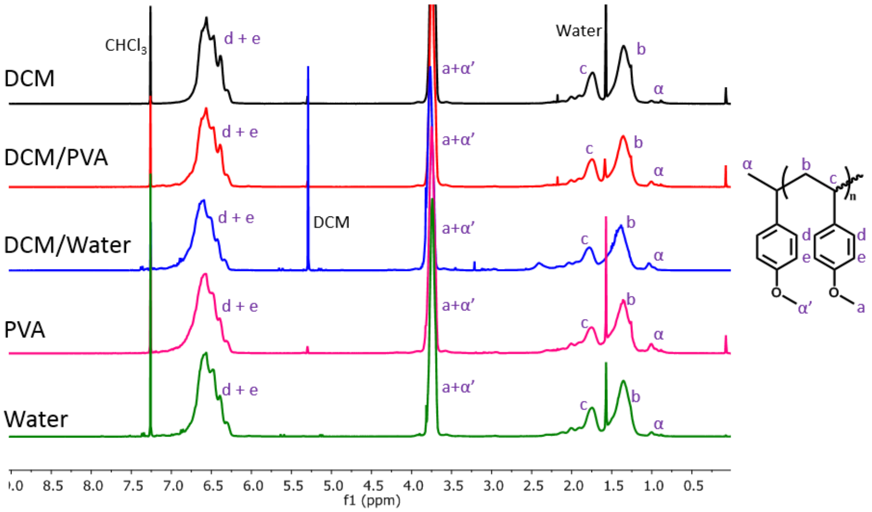

Figure 4-9: *^{1}H NMR spectra of poly(*p*-methoxystyrene)s synthesised in dichloromethane (black), a 1:1 mixture of DCM and 1% PVA aqueous solution (red), a 1:1 mixture of DCM and water (blue), a 1% PVA aqueous solution (pink), water (green).*

4.3.2.3. Case of β-Pinene

Finally, the cationic polymerisation of β-pinene was also conducted using (**1**)/B(C_6F_5)$_3$ catalytic system at 23 °C in solution and suspension. The polymerisations in DCM (Run 4-15, **Table 4-1**) and DCM/1% PVA aqueous solution (Run 4-16, **Table 4-1**) were fast, achieving full conversion in 2 to 4h (**Figure 4-10a**). The polymerisation performed in the 1:1 (v/v) mixture of DCM and water led to 94% conversion after 24h. However, the same polymerisation performed without DCM in the PVA aqueous solution or pure water led to limited conversions of 33% and 7%, respectively, after 24h. The final molecular weight (M_n) in solution in DCM was substantially lower than in the case of St and pMOS, only 1,000 g.mol^{-1} (**Figure 4-10b**). This is likely related to the higher water concentration in the presence of β-pinene and the higher rate of transfer to water, for which values of $k_{tr,w}/k_p$ as high as 10 have previously been reported.[12] In the case of the cationic polymerisations carried out in aqueous dispersion (DCM/water mixture and water, with and without PVA), the final molecular weights were low and out of the GPC calibration range. This drop in M_n is probably caused by chain transfer to water and is consistent with the much higher quantities of water in the organic phases, 1,604 ppm (8.9 x10^{-2} M) in the DCM/β-pinene in water system and 1,901 ppm (1.1 x10^{-1} M) for β-pinene in water.

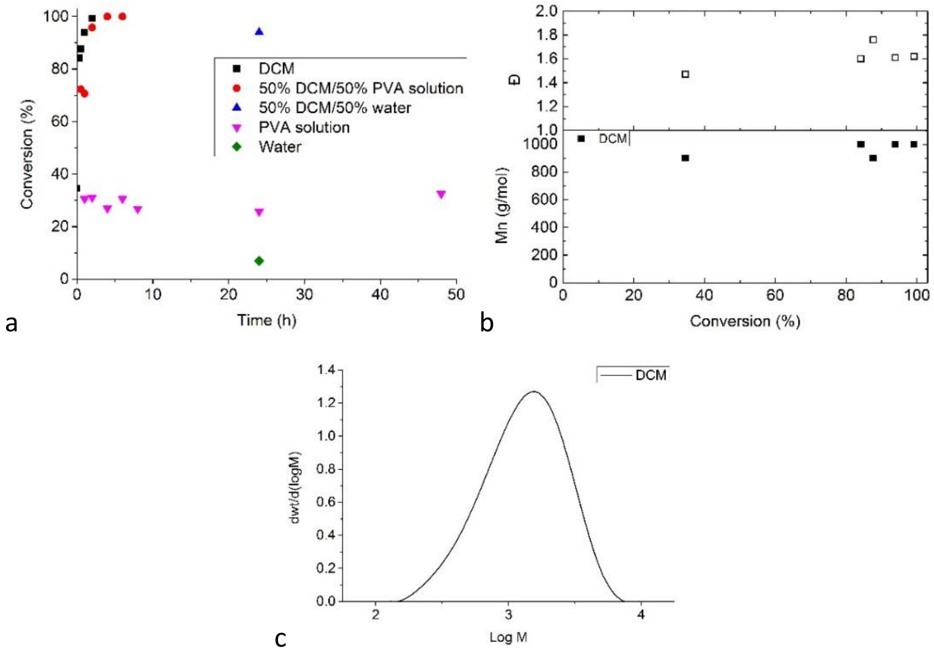

Figure 4-10: *(a) Evolution of the conversion with time for the cationic polymerisation of β-pinene in dichloromethane (black squares), a 1:1 (v/v) mixture of DCM and PVA aqueous solution (red circles), a 1:1 (v/v) mixture of DCM and water (blue triangles), PVA aqueous solution (pink reverse triangles) and water (green diamonds). (b) Evolution of the molecular weight (full symbols) and dispersity (empty symbols) with conversion and (c) molecular weight distributions for the cationic polymerisation of β-pinene in dichloromethane.*

The ^{1}H NMR spectra shown in **Figure 4-11** confirm these results, with the presence of multiple sharp peak from the monomer and the high intensity of the aromatic protons from the initiator compared to the signal from the unsaturated group confirm that the polymerisation is limited to the production of oligomers.

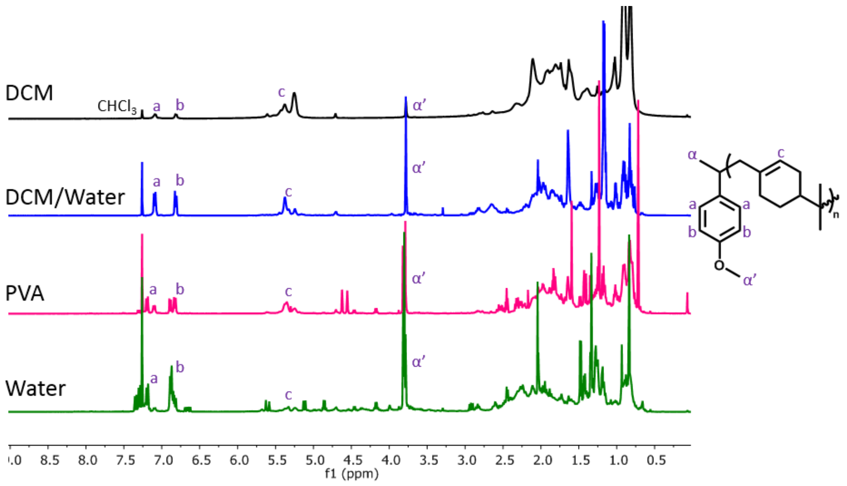

Figure 4-11: *^{1}H NMR spectra for the polymerisation of β-pinene in DCM (black), 1:1 mixture of DCM and water (blue), PVA aqueous solution (pink) and water (green).*

4.3.2.4. Eutectic Salt Mixtures as Continuous Phase

The results above suggest that in suspension the reaction can effectively be understood to proceed as a pseudo-bulk reaction in which the reactions kinetics are largely determined by the polarity of the organic phase and the molecular weight is limited by both chain transfer to polymer and chain transfer to water. The latter becomes particularly important for systems in which the saturated water concentration in the organic phase is high. In order to reduce the amount of water present in the organic phase for the cationic polymerisation of styrene and isobutene in suspension, Mathers and Lewis[22] proposed to replace the pure water by an eutectic salt mixture composed of 23.0 wt-% of lithium chloride (LiCl), 1.20 wt-% of sodium chloride (NaCl) and 75.8 wt-% of water. Using tris(pentafluorophenyl)gallium ($Ga(C_6F_5)_3$) as a catalyst, they observed substantially higher conversion when using the eutectic salt mixture as continuous phase and M_w of 25.1 kg.mol^{-1} for St at 26 °C. It was supposed that the presence of salts in the aqueous phase allowed for the reduction of water content in the organic phase, thus decreasing the transfer and termination reactions with water.

Following this work, in order to confirm the decrease of the amount of water in the organic phase in the presence of salts, Karl-Fischer titrations were made on the organic phase following stirring in the aqueous salt mixture for a few hours. **Table 4-4** presents the results obtained for the different organic phases (monomers for suspension experiments and DCM for the 1:1 mixture). These analyses corroborate the decrease of water concentration in the organic phases when using the eutectic salt mixture for all the systems.

Table 4-4: *Amounts of water in the organic phases saturated with water or eutectic salt mixture for styrene,* p*-methoxystyrene (pMOS), β-pinene and dichloromethane (DCM).*

Organic phase	Aqueous phase	Water quantity (ppm)	Water quantity (mmol.L^{-1})
Styrene	Water	664.7	36.9
	Eutectic salt mixture	376.5	20.9
pMOS	Water	1,516.5	84.3
	Eutectic salt mixture	897.4	49.9
β-pinene	Water	1,901.1	105.6
	Eutectic salt mixture	1,519.7	84.4
DCM	Water	1,603.8	89.1
	Eutectic salt mixture	941.8	52.3

The previous cationic polymerisations of St, pMOS and β-pinene in the DCM/water mixture and in suspension were attempted, replacing water by the eutectic salt mixture. The presence of salt in the aqueous phase led to a decrease of the conversion in most of the systems, likely due to combination of propagating cations with chloride anions (**Table 4-5**). In addition, for St and β-pinene the eutectic salt mixture did not have any influence on the final molecular weight. In the case of styrene, this is not surprising since the calculations performed in section 4.3.2.1 suggest that chain transfer to water does not impact critically on the molar mass in these reactions. For β-pinene chain transfer to water does impact on the molar mass, but the use of the eutectic salt mixture does not reduce the water content to a sufficient extent to substantially reduce chain transfer to water. Thus, while the use of salt to reduce the water concentration in the organic phase may result in a small improvement in the molar mass, in most cases it reduces the conversion to such an extent that it does not appear to be a practical solution to the issue of chain transfer to water.

Table 4-5: *Summary of the characteristics of the different polymers obtained for the cationic polymerisations of styrene,* p-*methoxystyrene and β-pinene in excess of water.*

Monomer	Media	Conversion (%)	M_n (g/mol)	Đ
Styrene	50% DCM/ 50% PVA solution	83.8	500	1.6
	50% DCM/ 50% eutectic salt	17.3	600	2.0
	PVA solution	30.5	2,100	1.6
	Eutectic salt	9.3	1,800	1.6
pMOS	50% DCM/ 50% PVA solution	99.7	5,100	2.1
	50% DCM/ 50% eutectic salt	63.6	9,700	1.9
	PVA solution	75.5	3,600	2.2
	Eutectic salt	68.2	5,100	2.0
β-pinene	50% DCM/ 50% PVA solution	> 99.0	400	1.5
	50% DCM/ 50% eutectic salt		400	1.5
	PVA solution	32.5	n. d.[a]	n. d.[a]
	Eutectic salt	99.0	n. d.[a]	n. d.[a]

[a] Molecular weight out of the GPC calibration range.

4.3.3. Compartmentalisation Effects in Cationic Polymerisation in Aqueous Media

From the results obtained so far, it seems that the cationic polymerisation in aqueous media only allows for the production of low molecular weight polymers and the reaction can be understood to proceed in pseudo-bulk conditions. In that case, it would be assumed that the colloidal nature of the reaction can be effectively ignored. This is in contrast to radical polymerisations where compartmentalisation effects allow for a reduction in the rate of bimolecular termination and result in substantially different kinetics and molecular weight distributions for reactions where the primary reaction loci are colloidal particles. In order to test this idea, comparative experiments in suspension and miniemulsion polymerisation were performed for St and pMOS. The aqueous and organic phases in both cases were identical with the exception that in the miniemulsion systems, hexadecane was added as a hydrophobe and the system was sonicated for 10 min prior to the addition of the catalyst to give stable miniemulsion. For both monomers, the molecular weights and dispersities achieved in suspension and miniemulsion were similar (**Table 4-6**) but substantially lower conversions were obtained in miniemulsion.

Table 4-6: *Final characteristics of polystyrene (St) and poly(*p*-methoxystyrene) (pMOS) obtained in suspension and miniemulsion polymerisations.*

Monomer	System	Time (h)	Conversion (%)	d_p (nm)	M_n (g/mol)	Đ
St	Suspension	24	50.9	-	1,100	2.3
	Miniemulsion	22.5	26.5	205	1,200	1.9
pMOS	Suspension	20	84	-	3,500	2.0
	Miniemulsion	20	49	185	3,400	1.9

Given that bimolecular reactions between carbocationic centres are not considered to be substantial, one possible explanation for these results lies in the potential fate of carbocations generated by chain transfer in the organic phase. In the event of generation of small molecule carbocations, either by ionisation of the initiator or by chain transfer to monomer, the initial monomeric carbocation can either undergo propagation or it can diffuse to the surface where it can desorb into the aqueous phase. Taking the saturated concentration of monomer in the particle [M] = 5 M and $k_p = 2 \times 10^5$ $M^{-1}s^{-1}$,[23] the frequency of propagation in the polymer particle is given by $k_p[M] = 1 \times 10^6$ s^{-1}. The rate coefficient for desorption, k_0, from a particle of diameter d_p is given by:[24]

$$k_0 = 60 \frac{D_p}{{d_p}^2} \tag{4-7}$$

In **Figure 4-12** the value of $k_0 / k_p[M] + k_0$ is plotted as a function of particle size. This gives a measure of the probability of desorption of monomeric carbocations into the aqueous phase relative to propagation. From this plot, it can clearly be seen that for the large particle sizes present in a suspension type system ($d_p \approx 1 \times 10^{-5}$ m) exit is unlikely. In contrast, in a miniemulsion type system ($d_p \approx 1 \times 10^{-7}$ m), it becomes increasingly more favourable for the monomeric cation to exit. As highlighted in the previous chapter, the most likely fate of carbocations that are desorbed into the aqueous phase is a chain termination reaction with water. As such, for cationic polymerisation conducted in aqueous media with small particle sizes, ionisation of the initiator species and chain transfer in the organic phase will often lead to desorption and termination, thus reducing the rate of polymerisation in agreement with the data shown in **Table 4-6**.

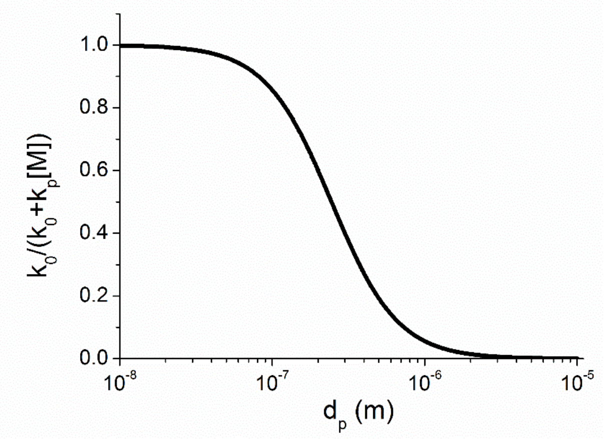

Figure 4-12: *Graph of exit probability* vs *radius for cationic polymerisation of styrene.*

4.4. Conclusions

In conclusion, the cationic polymerisation of vinylic monomers in aqueous dispersed media proceeds under pseudo-bulk conditions in which the rate of polymerisation and molar mass obtained is dependent on the nature of the water saturated organic phase. The practical limitations on reaction temperatures in polymerisations conducted in water restricts reaction conditions to those in which the extent of chain transfer to monomer is substantial. For monomers such as styrene that have relatively high transfer to monomer constants, this limits the degree of polymerisation to around 50 units at room temperature. Coupled to this, chain transfer to water can also further reduce the maximum degree of polymerisation that is practically achievable. This is particularly important when the organic phase has a high saturation concentration of water or where the transfer to water constant is high, as has been shown here to be the case for β-pinene. For monomers that have relatively low saturated water concentrations, such as styrene, chain transfer to water can be largely ignored as chain transfer to monomer will be more significant under most conditions but in any case, molar mass in excess of 10,000 g.mol^{-1} seems unrealistic for most practical situations. For reactions carried out using particles of colloidal dimensions, chain transfer to monomer/water can also result in an irreversible desorption of the propagating species into the aqueous phase, thus reducing the rate of polymerisation. This study suggests that any cationic polymerisation system performed in aqueous dispersed media will generate only low molar mass polymers and for the multiple systems in which extremely high molecular weight have been claimed in the literature, a careful analysis of the mechanism should be made.

4.5. References

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Chapter 5: Cationic Polymerisation of β-Pinene Using $B(C_6F_5)_3$ as a Lewis Acid for the Synthesis of Tackifiers in Pressure Sensitive Adhesives

5.1. Introduction

The first part of this thesis aimed at understanding the possibilities of cationic polymerisation performed in excess of water. Based on the results in the preceding chapters. it is clear that cationic polymerisation carried out under mild conditions, typically at room temperature and without dry conditions, leads to the synthesis of only low molecular weight polymers. However, such low molecular weight polymers can be of great use. In fact, many commercial cationic polymerisation processes specifically target low molecular weight polymers.[1] This is particularly the case for tackifying resins, which tend to be low molecular weight systems that can be produced from C5/C9 feedstocks derived from naptha cracking, as well as from bio-sourced terpenes. This latter category is of particular interest from the viewpoint of sustainability, with a whole range of terpenes being produced from turpentine.[2–4] Among the terpene monomers, β-pinene, with a current US market production volume of 20 ×10^6 kg/year,[5] is one of the most commonly used and is known to homopolymerise *via* cationic polymerisation without the need of further chemical modification.[6,7]

The cationic polymerisation of β-pinene occurs through an addition-isomerisation mechanism that leads to a polymer containing alternating isobutyl and cyclohexenyl units.[8] The polymerisation is typically conducted using Lewis acid catalysts, such as $AlCl_3$ and $EtAlCl_2$, and adventitious water to initiate the polymerisation.[6,7,9] At relatively low temperatures (*ca.* -80 °C) high molecular weights can be achieved in such systems (up to 40,000 $g.mol^{-1}$). More recently, Kukhta *et al.* have demonstrated that $AlCl_3$ etherates can yield relatively high molecular weight polymers without performing the reaction at excessively low temperatures.[10] For example, the use of $AlCl_3OPh_2$ as a catalyst gave molecular weights in excess of 10,000 $g.mol^{-1}$ at room temperature. Living cationic polymerisation of β-pinene has also been successfully demonstrated by the Lewis acid mediated activation of alkyl chloride initiators such as cumyl chloride at low temperatures (-78 °C).[11–13] It should be noted that all these polymerisations required extensive purification drying of the solvent and monomer to remove trace impurities and water.

Poly(β-pinene) is produced commercially by polymerisation at 30-50 °C using $AlCl_3$ and adventitious water as initiator.[14] This polymerisation leads to relatively low molecular weight polymers (< 5,000 $g.mol^{-1}$) that are used as tackifying resins in pressure sensitive adhesive formulations.[15] Terpene resins in particular, are notable for their good compatibility with a wide range of polymers used in adhesives, including natural rubber, as well as for their good heat resistance, tack and peel adhesion.[16,17]

One important feature in the use of terpene resins as tackifiers is their molecular weight, which determines the softening point of the resin as well as its influence on the rheological profile of the adhesive. Due to the strong influence of water in cationic polymerisations, control over the polymer molecular weight in commercially produced poly(β-pinene) is challenging.[18] In this work we seek to explore the use of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) as a catalyst for the cationic polymerisation of β-pinene. It should be noted that although the cost of $B(C_6F_5)_3$ is currently prohibitively high to implement commercially, especially when compared to the widely used $AlCl_3$, it has been demonstrated that $B(C_6F_5)_3$ can be attached to a solid support such as silica that would allow for the recycling of the catalyst.[19,20] Unlike most Lewis acid catalysts used in cationic polymerisation, $B(C_6F_5)_3$ is stable in the presence of water. As a result, $B(C_6F_5)_3$ has attracted interest for the cationic polymerisation of a wide range of monomers including styrenics,[21–25] isoprene,[26,27] cyclopentadiene[28,29] and vinyl ethers.[30] It has been shown for a number of monomer systems that when combined with alcohol initiators, the reaction proceeds by reversible activation of the C-OH chain end[31] to give a propagating carbocation, thus allowing for some living character to the reaction and good control over the molecular weight.[21,22]

In this chapter, we demonstrate the polymerisation of β-pinene at room temperature in dichloromethane using tris(pentafluorophenyl)borane as catalyst. The influence of catalyst and initiator concentrations was studied in order to determine the extent to which molecular weight and polymerisation kinetics could be controlled. The potential application of polymers synthesised using this route was demonstrated by exploring the influence of the polymers on the adhesive properties of polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) triblock copolymers.

5.2. Experimental Part

5.2.1. Materials

(1S)-(-)-β-pinene (β-pinene, 99%, Alfa Aesar) was stored at 4 °C until use. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, 97% purity, Alfa Aesar) was stored at -22 °C until use. Dichloromethane (DCM, > 99.5% purity, Sigma Aldrich), toluene (> 99.5% purity, Fischer Scientific), 1-(4-methoxyphenyl) ethanol (**1**, 95% purity, Alfa Aesar), polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS, Sigma Aldrich, 22 wt-% styrene) and Piccotac 1095N (Eastman) were used as received.

5.2.2. Methods

Gel permeation chromatography (GPC) was performed using three columns in series (Styragel HR2, HR4 and HR6) and a refractive index detector (Waters 2410). THF was eluted at a flow rate of 1 mL.min^{-1}. The samples were prepared at a concentration of 2 mg.mL^{-1} of polymer in THF and filtered using a nylon filter with pores of 45 µm. The molecular weights and dispersities calculated were based on polystyrene standards.

Proton nuclear magnetic resonance (^{1}H NMR) was recorded on a Bruker 400 MHz at 25 °C. Samples were prepared in deuterated chloroform ($CDCl_3$) and the signals obtained were calibrated relative to the solvent peak (7.26 ppm). Carbon nuclear magnetic resonance (^{13}C NMR) was recorded on a Bruker 500 MHz at 25 °C. Samples of 30 mg.mL^{-1} were prepared and the signals obtained were calibrated relative to the solvent peak (77.16 ppm).

Matrix assisted laser desorption/ionisation – time of flight mass spectrometry (MALDI-ToF MS) measurements were performed on a Bruker Autoflex Speed system equipped with a 355 nm NdYAG laser. Both positive reflectron and linear modes were used to obtain the spectra. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malonitrile (DCTB, Fluka) was used as a matrix, dissolved in THF at a concentration of 20 mg.mL^{-1} and silver trifluoroacetate (AgTFA) was added as the ionisation agent (10 mg.mL^{-1} dissolved in THF). Polymer samples were dissolved in THF at a concentration of 10 mg.mL^{-1}. The matrix, the salt and the polymer were premixed at a ratio 10:1:1. Around 0.5 µL of the mixture was hand spotted on a ground steel target plate. For each spectrum, 10,000 laser shots were accumulated. The spectra were externally calibrated with a mixture of different polyethylene glycol standards (PEG, Varian).

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 8000 equipped with an Intracooler II. Samples between 3 and 5 mg were placed in sealed aluminium pans to perform the measurements. For poly(β-pinene) samples, the samples were first cooled from 25 to -40 °C at a cooling rate of 20 °C.min^{-1}, kept for 3 min at -40 °C then heated from -40 °C to 220 °C at a heating rate of 20 °C.min^{-1} and kept at 220 °C for 3 min in order to erase the thermal history. Subsequent cooling and heating scans between 220 and -40 °C were recorded at 20 °C.min^{-1}. The glass transition temperature (T_g) of the poly(β-pinene) was calculated using the curve obtained during the second heating scan. For adhesive samples, the samples were first cooled from 25 to -80 °C at a cooling rate of 10 °C.min^{-1}, kept for 3 min at -80 °C then heated from -80 °C to 120 °C at a heating rate of 10 °C.min^{-1} and kept at 120 °C for 3 min in order to erase the thermal history. Subsequent cooling and heating scans between 120 and -80 °C were recorded at 1 °C.min^{-1}. The glass transition temperatures (T_g) were calculated using the curves obtained during the second heating scan.

Probe tack experiments were performed using a TA HD Plus texture analyser with a 1’’ stainless steel ball. Solutions of commercial SIS and synthesised poly(β-pinene) with different poly(β-pinene) amounts in toluene were prepared with a 30% solid content. Films were cast on a glass substrate and left to dry at 23 °C overnight before testing. The dry film thickness was 120 µm. The probe tack measurement was conducted by applying an initial compressive force of 1.5 MPa for 1 s after which the probe was removed from the surface at a velocity of 55 µm/s. The stress (σ) was defined as the force divided by the contact area and the strain (ε) as the displacement divided by the calculated thickness of the dry film. The work of adhesion was calculated by

$$W_{ad} = h \int_0^{\varepsilon_{max}} \sigma(\varepsilon) d\varepsilon \qquad (5\text{-}1)$$

Dynamic mechanical thermal analysis (DMTA) was performed on a Tritec 2000 DMA (Triton technology) in tension deformation mode. The films with a thickness of around 0.2 mm were heated from -110 °C to 120 °C with a constant heating rate (4 $°C.min^{-1}$) and a frequency of 1 Hz.

AFM measurements were carried out using a Multimode 8 microscope, equipped with a Nanoscope V controller (Bruker). SIS and ADF08 (40 wt-% SIS, 60 wt-% poly(β-pinene) thin films were prepared by spin coating. Pieces of casted polymer films were dissolved in toluene at a concentration of 20 $g.L^{-1}$. The polymer solutions were spin casted (3000 rpm, 2 min) onto SiOx substrates, previously washed in acetone. The polymer thin films had thicknesses of *ca.* 150 nm and 350 nm for ADF08 and SIS respectively, as determined by AFM measurements. The polymer thin films were studied using a tapping mode protocol (intermittent contact) and Tap190Al-G probes (BudgetSensors). The resonant frequency of the probes was 145 kHz, with a usual Q factor of 470, and a tip radius < 10 nm. The free amplitude (A_0) was set to 400 mV, while for imaging the amplitude setpoint (A_{sp}) was decreased to 320 mV ($A_{sp} = 0.8 \cdot A_0$). All images were analysed using the Nanoscope 1.90 software (Bruker).

5.2.3. Procedures

Polymerisations were conducted using the formulations shown in **Table 5-1**. In a typical polymerisation (Run 5-4), a solution of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (0.0276 g, 0.005 M) in dichloromethane (DCM) (2.66 g) was prepared in a vial. 1-(4-methoxyphenyl) ethanol (0.0287 g, 0.017 M), β-pinene (0.9592 g, 0.63 M) and DCM (10.64 g) were stirred in a round bottom flask. The $B(C_6F_5)_3$ solution was then added and the reaction was performed at 23 °C in air in an enclosed flask. After predetermined times, the polymerisation was precipitated adding methanol. Monomer conversions were determined by ^1H NMR analysis in $CDCl_3$.

Table 5-1: *Summary of the experiments for the polymerisation of β-pinene in dichloromethane at 23 °C.*

Run	1 (mg)	$B(C_6F_5)_3$ (mg)	DCM (g)	β-pinene (g)	Time (h)
5-1	0	280	13.3	0.959	0.25
5-2	0	111	13.3	0.959	0.25
5-3	0	28	13.3	0.959	8
5-4	29	28	13.3	0.959	2
5-5	57	28	13.3	0.959	2
5-6	1,120	554	266.9	19.2	2
5-7	0	11	13.3	0.959	24
5-8	29	11	13.3	0.959	24
5-9	57	11	13.3	0.959	8

5.3. Results and Discussion

Initially, the polymerisation of β-pinene by cationic polymerisation was explored using tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) as a catalyst and 1-(4-methoxyphenyl) ethanol (**1**) as initiator at 23 °C. Although aromatic solvents are commonly used in the commercial production of terpene resins by cationic polymerisation, here we used dichloromethane as solvent in order to avoid complications arising from chain transfer reactions through electrophilic aromatic substitution. Unlike most cationic polymerisation systems, $B(C_6F_5)_3$ is stable in the presence of moisture and therefore the polymerisations were conducted without any purification of the starting materials. Two series of experiments containing different amounts of initiator and catalyst were carried out in order to study the influence of their concentration on the kinetics of the polymerisation.

The first series of experiments was dedicated to understand the influence of the catalyst on the polymerisation. No initiator was used and the concentration of $B(C_6F_5)_3$ was varied from 0.05 to 0.002 $mol.L^{-1}$ (Runs 5-1 to 5-3 and 5-7, **Table 5-1**). In the absence of any initiator, $B(C_6F_5)_3$ would be expected to initiate chains through the presence of adventitious water that can act as a proton source as has been demonstrated for other monomer systems.[24,25]

Figure 5-1 presents the evolution of the conversion with time for the four different catalyst concentrations used: 0.05, 0.02, 0.005 and 0.002 $mol.L^{-1}$. At the higher concentrations of $B(C_6F_5)_3$ (Run 5-1 (0.05 $mol.L^{-1}$) and Run 5-2 (0.02 $mol.L^{-1}$)) the reaction was effectively instantaneous. In these reactions, a change of colour of the solution from colourless to red/orange was also noted. This coloration is unlikely to be related directly to the propagating cationic species, which would be expected to be colourless in the visible region, but may be the result of the formation of stable, delocalised carbocations, as has been known to occur in the polymerisation of styrenic monomers[32–34] and vinyl ethers.[35] These reactions also resulted in an exotherm that reached the boiling point of the solvent (boiling point DCM = 40 °C). In contrast, it took 24h to reach full conversion using 0.002 mol.L^{-1} of the catalyst (Run 5-7).

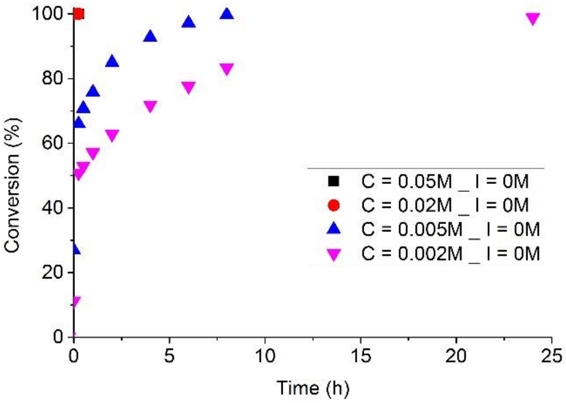


Figure 5-1: *Evolution of the conversion with time for the polymerisation of β-pinene with [**1**] = 0 mol.L^{-1} and [B(C_6F_5)$_3$] = 0.05 mol.L^{-1} (Run 5-1, black squares), 0.02 mol.L^{-1} (Run 5-2, red circles), 0.005 mol.L^{-1} (Run 5-3, blue triangles) and 0.002 mol.L^{-1} (Run 5-7, pink reverse triangles).*

Figure 5-2a presents the molecular weight distributions obtained for the precipitated polymers using different catalyst concentrations. For both the lower catalyst concentrations ([B(C_6F_5)$_3$] = 0.005 M and 0.002 M) similar molecular weights were obtained and the molecular weight distribution did not change significantly during the reaction time (see **Figure 5-2b and c**). Surprisingly, the molar masses (M_n) obtained for the polymers using high concentrations of B(C_6F_5)$_3$ were significantly higher than the ones obtained at low concentrations of catalyst, with slightly higher dispersities (Đ) (see **Table 5-2**).

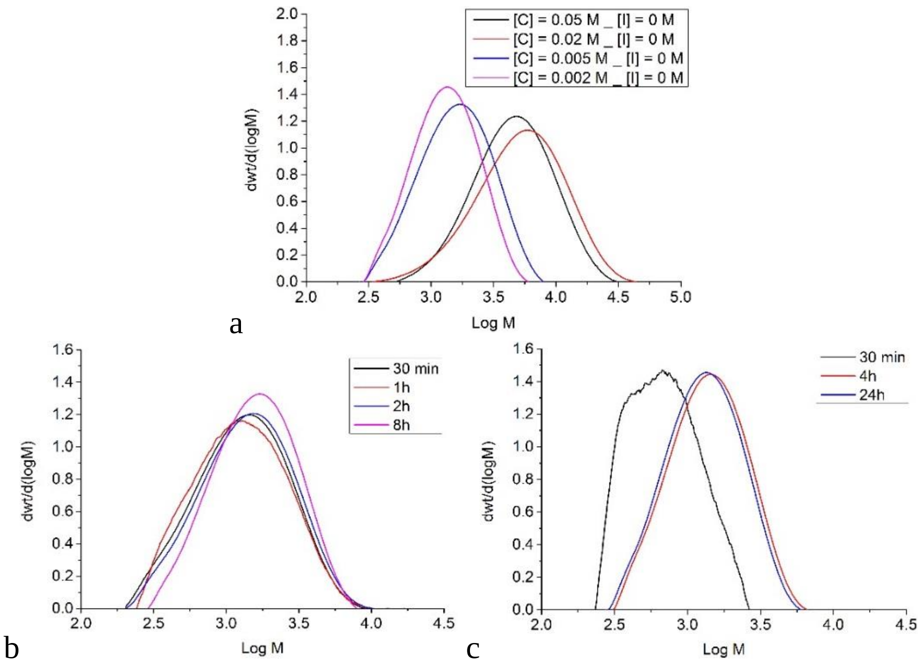


Figure 5-2: *(a) GPC traces of the precipitated polymers obtained with [**1**] = 0 mol.L^{-1} and [$B(C_6F_5)_3$] = 0.05 mol.L^{-1} (Run 5-1, black), 0.02 mol.L^{-1} (Run 5-2, red), 0.005 mol.L^{-1} (Run 5-3, blue) and 0.002 mol.L^{-1} (Run 5-7, pink). (b and c) Molecular weight distributions during the reaction time for [**1**] = 0 mol.L^{-1} and 0.005 mol.L^{-1} (Run 5-3, b) and 0.002 mol.L^{-1} (Run 5-7, c).*

Our initial thoughts were that the increased M_n may be due to copolymerisation of terminal double bonds at high conversions. However, in the polymerisation of isobutylene, for which the polymerising unit is of similar structure to that of β-pinene, only a single coupling step is generally observed,[36] which would not explain the near tripling of the molecular weights observed here. Furthermore, multiple propagation events of terminal double bonds would also be expected to lead to a broadening of the molecular weight distribution, which again is not observed experimentally.

One possible explanation for this increase in molar mass at higher catalyst concentration arises from initiation and transfer reactions that occur due to the presence of water in the system. Measurement of the water content of the reaction mixture by Karl Fischer titration gave a water concentration of 12 mM. Assuming each molecule of water generated a single chain, then based on the [β-pinene]:[H_2O] ratio M_n would be expected to be ≈ 7,100 $g.mol^{-1}$. Since the experimentally determined values of M_n are significantly below this value, it appears that transfer reactions control the molar mass. If the molecular weight is determined by transfer reactions involving water, the relative [$B(C_6F_5)_3$]:[H_2O] ratio may impact substantially on transfer rates. Previous work has shown that when [$B(C_6F_5)_3$]/[H_2O] > 1, the majority of water will be bound directly to [$B(C_6F_5)_3$], whereas for [$B(C_6F_5)_3$]/[H_2O] < 1, after formation of the initial [$(C_6F_5)_3B(OH_2)$] adduct, additional water molecules are hydrogen-bonded to the protons of B-bound water.[37] This change in the nature of the water molecules in the reaction at low [$B(C_6F_5)_3$] could lead to increased rate of β-hydrogen abstraction and therefore lower molar mass.

Table 5-2: *Final molecular weight distributions for solution polymerisation of β-pinene in the absence of initiator using different concentrations of $B(C_6F_5)_3$.*

Run	[$B(C_6F_5)_3$] (mol/L)	Conversion (%)	M_n (g/mol)	Đ
5-1	0.05	> 99.9[a]	3,500	1.8
5-2	0.02	> 99.9[a]	3,700	1.9
5-3	0.005	99.8	1,100	1.7
5-7	0.002	98.9	1,000	1.6

[a] No signal from monomer vinyl protons in NMR.

In order to determine the structure of the chain-ends of the polymers, MALDI-ToF analyses were performed. The spectra in the region 1,320-1,540 Da for reactions using $[B(C_6F_5)_3]$ = 0.05 mol.L^{-1} (Run 5-1), 0.005 mol.L^{-1} (Run 5-3) and 0.002 mol.L^{-1} (Run 5-7) are presented in **Figure 5-3**. In all cases, three main structures can be seen which are separated by a mass of 136 Da. The peak of highest intensity (labelled (a) in **Figure 5-3**) corresponds to polymer chains initiated by a proton and terminated by a double bond, arising from β-H elimination. Note that although the *exo*-olefin is drawn in Figure 5-3, the *endo*-olefin is also present as is explained further below. The second peak (labelled (b) in **Figure 5-3**), of much lower intensity, corresponds to the chains terminated with an OH group, that would be expected to form as a result of recombination of the propagating carbocation with the hydroxyl group. The final peak can be attributed to reaction between the carbocation chain ends and methanol that is added to quench the reaction. A comparison of the experimental spectra and the theoretical isotopic distribution patterns for these structures is given in **Figure 5-4** and further confirms this assignment.

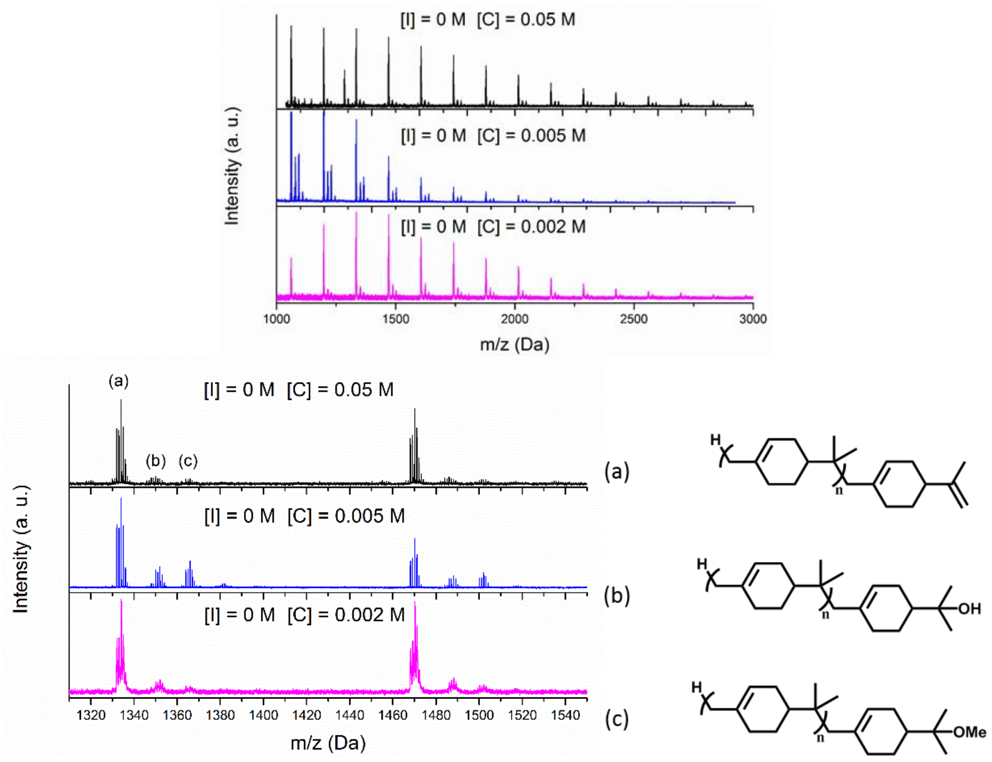


Figure 5-3: *Expanded and zoomed MALDI-ToF spectra of poly(β-pinene) synthesised with [**1**] = 0 mol.L^{-1} and [B(C$_6$F$_5$)$_3$] = 0.05 mol.L^{-1} (Run 5-1, black), 0.005 mol.L^{-1} (Run 5-3, blue) and 0.002 mol.L^{-1} (Run 5-7, pink). The structures correspond to the labelled peaks in the MALDI spectra.*

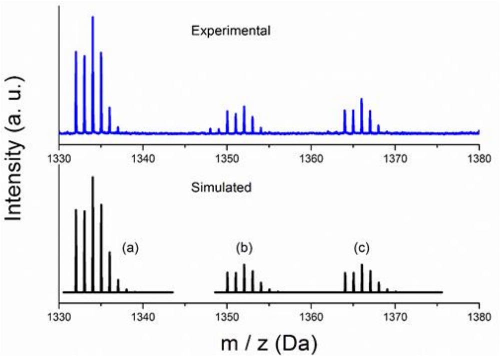


Figure 5-4: *(top) MALDI-ToF spectra of the poly(β-pinene) obtained using [B(C_6F_5)$_3$] = 0.005 M and [**1**] = 0 M (Run 5-3). The lower panel shows the simulated isotopic distribution patterns for the structures shown in Figure 5-3. The intensity of each peak has been adjusted manually to approximately match the relative intensity of the experimental data.*

The structures of the polymers were also studied using ^{1}H and ^{13}C NMR spectroscopy. **Figure 5-5** presents the ^{1}H and ^{13}C spectra of the poly(β-pinene)s obtained using 0.05, 0.005 and 0.002 mol.L^{-1} of catalyst, respectively. In the ^{1}H NMR spectra the presence of terminal vinyl protons for the *exo*-olefin structure can clearly be observed at 4.7 ppm, confirming the presence of double bond ended chains. In Runs 5-3 and 5-7, the relative intensity of this peak is significantly higher than in the case where high catalyst concentrations were employed (Run 5-1). This is in agreement with the higher observed molar mass in the case of Run 5-1.

In all cases, however, the intensity of the vinyl proton signal is significantly lower than expected given the molecular weights shown in Table 5-2. Furthermore, the expected absorptions at 109 and 150 ppm in the ^{13}C spectra for this kind of *exo*-olefin were not visible.[38] The cause of this discrepancy is likely due to the preferable formation of the *endo*-olefin group. Indeed, the characteristic signals of the *endo*-olefin end groups are visible at 129 and 125 ppm in the ^{13}C NMR,[10] indicating that this is likely the dominant end group. This may be expected as in cationic polymerisations of methyl styrenes the endo end-group has been shown to be the thermodynamic product.[32]

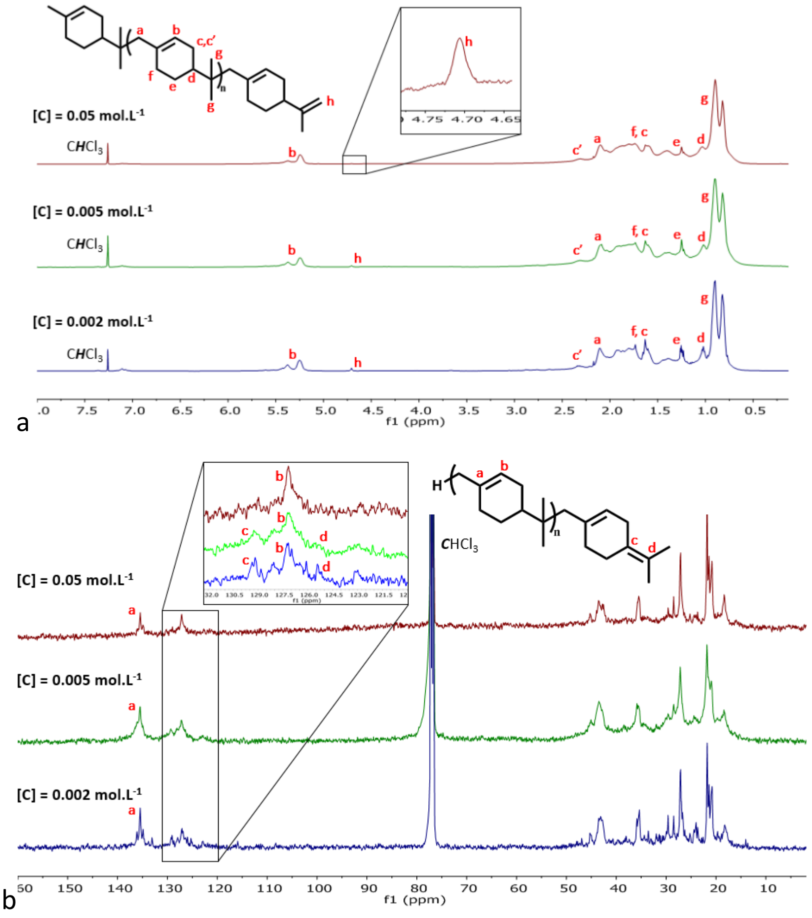


Figure 5-5: *(a) ^{1}H and (b) ^{13}C NMR spectra of the precipitated polymers obtained using 0.05 mol.L^{-1} (Run 5-1, top, red), 0.005 mol.L^{-1} (Run 5-3, middle, green) and 0.002 mol.L^{-1} (Run 5-7, bottom, blue) of catalyst without initiator.*

The second series of experiments sought to determine the influence of adding an initiator in the formulation. To do so, two sets of experiments were performed, using catalyst concentrations of 0.005 and 0.002 mol.L^{-1}. For each set, initiator concentration of 0.017 mol.L^{-1} and 0.033 mol.L^{-1} were used (Runs 5-4, 5-5, 5-8 and 5-9 **Table 5-1**). **Figure 5-6** presents the evolution of the conversion with time for the sets of experiments using [$B(C_6F_5)_3$] = 0.005 and 0.002 mol.L^{-1}, respectively. Faster polymerisations were obtained when using (**1**) as an initiator. However, no major differences in the reaction time were observed with further increase of the initiator amount. This indicates that the concentration of $B(C_6F_5)_3$ is limiting the rate of polymerisation in that case since the concentration of initiator is substantially higher than the catalyst concentration.

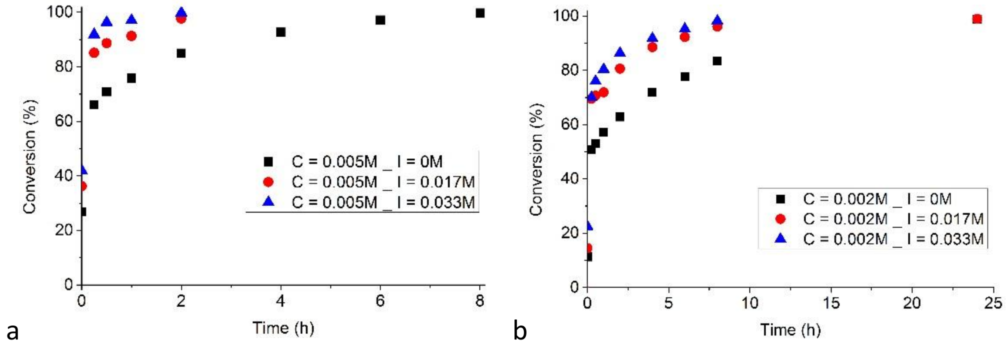
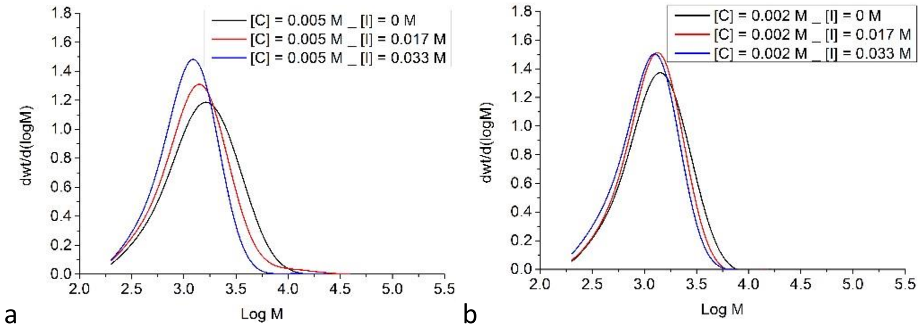


Figure 5-6: *Evolution of the conversion with time for the polymerisation of β-pinene with (a) [$B(C_6F_5)_3$] = 0.005 mol.L^{-1}, (b) [$B(C_6F_5)_3$] = 0.002 mol.L^{-1} and [**1**] = 0 mol.L^{-1} (black squares), 0.017 mol.L^{-1} (red circles) and 0.033 mol.L^{-1} (blue triangles).*

The increase of initiator concentration led to a decrease in the molecular weights (M_n) as well as the dispersities (Đ) (see **Figures 5-7a and b** and **Table 5-3**) which is indicative of a certain degree of living character of the polymerisation. The decrease of molecular weight with the increase of initiator used in the formulation was expected as when increasing the initiator concentration a higher number of chains are generated. However, the experimental molecular weights are lower than the theoretical ones based on the idea that chains are only generated by the initiator molecules (from the [β-pinene]:[1] ratio $M_{n,theo}$ = 5,040 g.mol^{-1} and 2,520 g.mol^{-1} for [**1**] = 0.017 mol.L^{-1} and 0.033 mol.L^{-1} respectively). This indicates the substantial occurrence of chain transfer reactions, as already highlighted from the MALDI spectra, which show the unsaturated group as the major chain end. Despite this, the partially living nature of reactions can be seen in the evolution of molecular weights as shown in **Figures 5-7 c to f**. In most cases, the reaction proceeds rapidly such that all samples are taken in a period of time where conversion is almost constant and therefore there is only limited expected evolution of molecular weight.



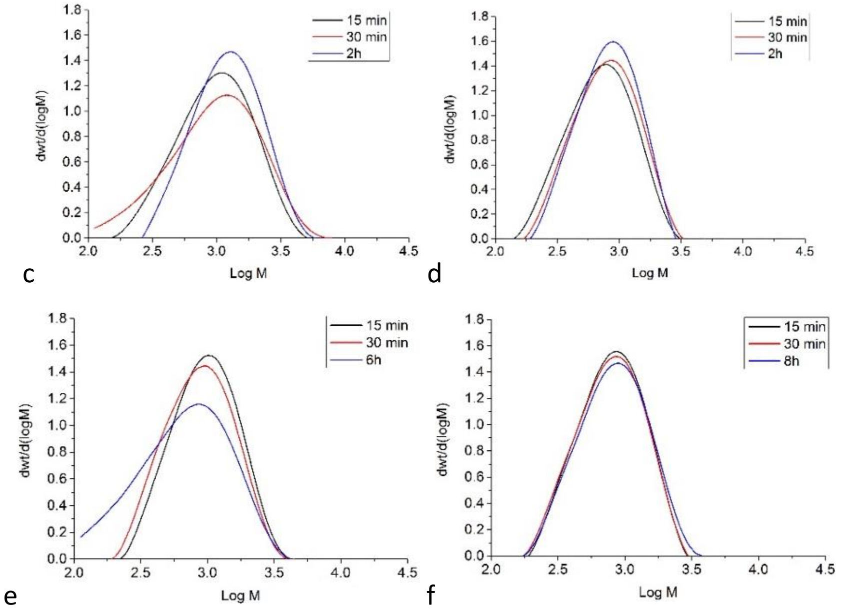


Figure 5-7: *(a and b) GPC traces of the precipitated polymers obtained with (a) [B(C_6F_5)$_3$] = 0.005 mol.L^{-1}, (b) [B(C_6F_5)$_3$] = 0.002 mol.L^{-1} and [**1**] = 0 mol.L^{-1} (black), 0.017 mol.L^{-1} (red) and 0.033 mol.L^{-1} (blue). (c to f) Molecular weight distributions during the reaction time for (c) Run 5-4, (d) Run 5-5, (e) Run 5-8 and (f) Run 5-9.*

Table 5-3: *Final molecular weight distributions for solution polymerisation of β-pinene using different concentrations of initiator at low concentrations of B(C_6F_5)$_3$.*

Run	[1] (mol/L)	[B(C_6F_5)$_3$] (mol/L)	Conversion (%)	M_n (g/mol)	Đ
5-3	0	0.005	> 99.9[a]	1,100	1.7
5-4	0.017	0.005	> 99.9[a]	1,000	1.4
5-5	0.033	0.005	> 99.9[a]	700	1.3
5-7	0	0.002	> 99.9[a]	1,000	1.6
5-8	0.017	0.002	> 99.9[a]	800	1.4
5-9	0.033	0.002	99.7	700	1.4

[a] No signal from monomer vinyl protons in NMR.

The determination of the chain ends was studied using MALDI-ToF analysis and ^1H NMR. The MALDI spectra in the range 1,320-1,380 Da obtained for the formulation $[B(C_6F_5)_3]$ = 0.005 mol.L^{-1} and 0.002 mol.L^{-1} with [**1**] = 0 mol.L^{-1} (Runs 5-3 and 5-7), 0.0017 mol.L^{-1} (Runs 5-4 and 5-8) and 0.033 mol.L^{-1} (Runs 5-5 and 5-9) are shown in **Figure 5-8** and ^1H NMR in **Figure 5-9**. Results using both catalyst concentrations are qualitatively similar so only the results obtained for $[B(C_6F_5)_3]$ = 0.005 mol.L^{-1} are discussed in detail. The presence of the initiator in the NMR spectra is clearly visible through the characteristic peak of the methoxy protons at 3.8 ppm and the aromatic protons in the region 6.7-7.2 ppm. From the integral of the peak at 3.8 ppm relative to the 15 protons in the aliphatic region (0.5-2.5 ppm) (labelled (b) in **Figure 5-8**) a M_n of 4,500 g.mol^{-1} and 2,600 g.mol^{-1} is estimated. This is in good agreement with theoretical values of M_n calculated based on the [β-pinene]:[**1**] ratio ($M_{n,theo}$ = 5,040 g.mol^{-1} and 2,520 g.mol^{-1} for [**1**] = 0.017 mol.L^{-1} and 0.033 mol.L^{-1} respectively) and suggests good initiation efficiency. The significant discrepancy between these values and those obtained by GPC is likely due to the presence of β-H elimination reactions that lead to additional chains being generated.

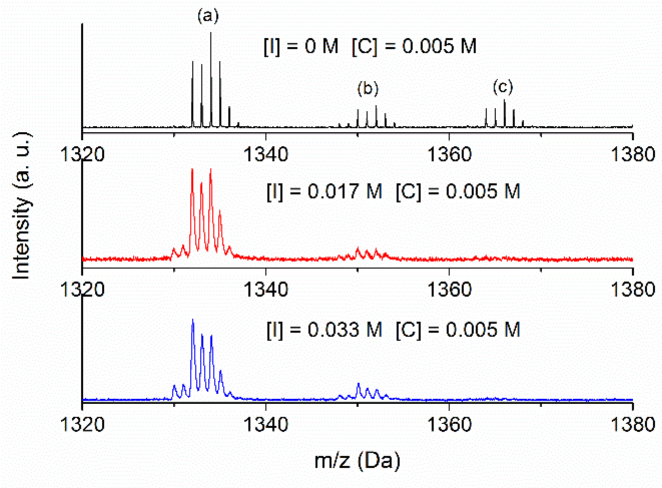


Figure 5-8: *MALDI-ToF spectra of poly(β-pinene) obtained using a catalyst concentration of 0.005 mol.L^{-1} and an initiator concentration of 0 mol.L^{-1} (Run 5-3, black), 0.017 mol.L^{-1} (Run 5-4, red) and 0.033 mol.L^{-1} (Run 5-5, blue). The labelled peaks correspond to the same structures as shown in Figure 5-3 although each peak also has a contribution from initiator derived chains as shown in Figure 5-10.*

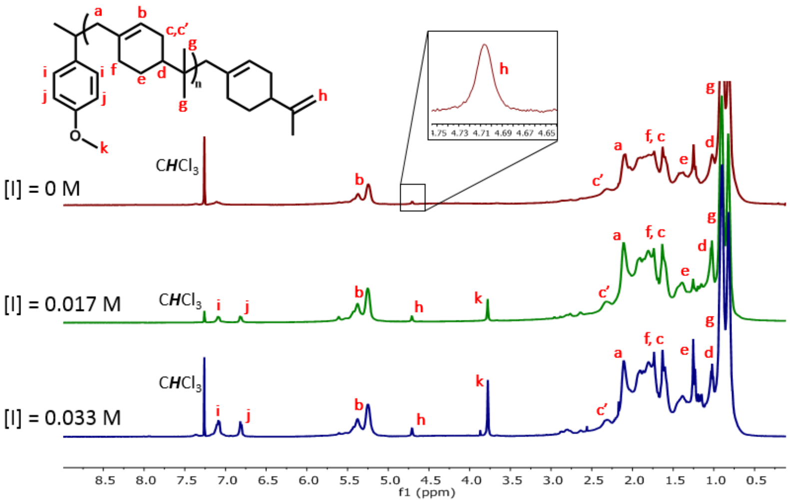


Figure 5-9: *^{1}H NMR spectra of the precipitated polymers obtained using a catalyst concentration of 0.005 mol.L^{-1} and an initiator concentration of 0 mol.L^{-1} (Run 5-3, black), 0.017 mol.L^{-1} (Run 5-4, green) and 0.033 mol.L^{-1} (Run 5-5, blue).*

Evidence for the combination of both initiator and chains arising from β-H elimination reactions can be seen in the MALDI spectra. At first glance, the MALDI spectra in the presence and absence of initiator look similar and the two main peaks can again be attributed to chains terminated by an unsaturated group (major chain end) and chains terminated by recombination with OH. However, the nature of the isotopic distribution patterns of the spectra changes when the reactions are conducted in the presence of initiator. To highlight this, in **Figure 5-10** the isotopic pattern of the highest intensity peak is presented for the highest initiator concentration (Run 5-5). The difference in isotopic distribution pattern can be attributed to a mixture of initiator and non-initiator derived chains which overlap in the MALDI spectra. This can be seen by comparison with the theoretical isotopic distribution patterns for a 1:1 mixture of initiator and proton initiated chains shown in the lower panel of **Figure 5-10**. This difference also explains the change in the shape of the isotopic distribution pattern of the major product (a) in **Figure 5-8** when increasing the initiator concentration. The peak originating from H initiated chains with maximum at 1,334 Da decreases in intensity relative to the peak at 1,332 Da which corresponds to the maximum for initiator derived chains.

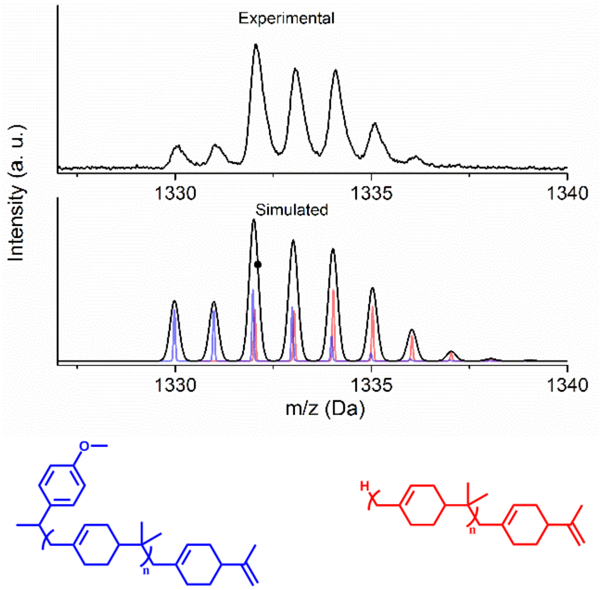


Figure 5-10: *MALDI-ToF spectra of poly(β-pinene) obtained using a catalyst concentration of 0.005 mol.L^{-1} and an initiator concentration of 0.033 mol.L^{-1} (Run 5-5). The lower panel shows the simulated isotopic distribution pattern for a 1:1 mixture of proton initiated chains (red lines) and initiator derived chains (blue lines) with structures shown below.*

The results shown so far demonstrate that the cationic polymerisation of β-pinene can be conducted under relatively mild conditions, with control of molecular weight arising from the use of an initiator. In order to demonstrate the potential utility of this technique, a scale-up experiment was performed in a 250 mL reactor using [$B(C_6F_5)_3$] = 0.005 mol.L^{-1} and [**1**] = 0.033 mol.L^{-1} (Run 5-6, **Table 5-1**). The final molecular weight obtained was 1,000 g.mol^{-1} with a dispersity of 1.3. Differential scanning calorimetry (DSC) determined that the glass transition temperature (T_g) of the poly(β-pinene) obtained was 31 °C (**Figure 5-11**).

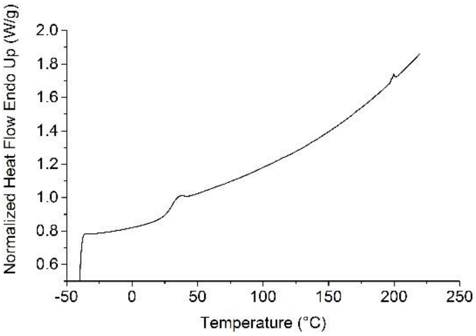


Figure 5-11: *DSC of the poly(β-pinene) obtained using [B(C_6F_5)$_3$] = 0.005 mol.L^{-1} and [**1**] = 0.033 mol.L^{-1} (Run 5-6).*

This polymer was used to demonstrate the ability of these low molecular weight poly(β-pinene)s to be used as tackifiers in a typical pressure sensitive adhesive formulation. Polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) is a phase separated triblock copolymer system that is often used in the formulation of pressure-sensitive adhesives with the addition of tackifiers.[39,40] AFM phase images of the pure triblock copolymer shown in **Figure 5-12** demonstrate that it consists of a soft network of polyisoprene with domains of harder polystyrene. Similarly, AFM images of the triblock copolymer with added poly(β-pinene) (40:60 wt/wt) again show a film structure containing a continuous soft phase with dispersed hard domains. Although the morphology was less well defined in the case of the tackfied block copolymer, these results suggest reasonable miscibility between the poly(β-pinene) and the triblock copolymer and are in good agreement with morphological changes seen using closely related triblock copolymer systems using commercial tackifiers.[41]

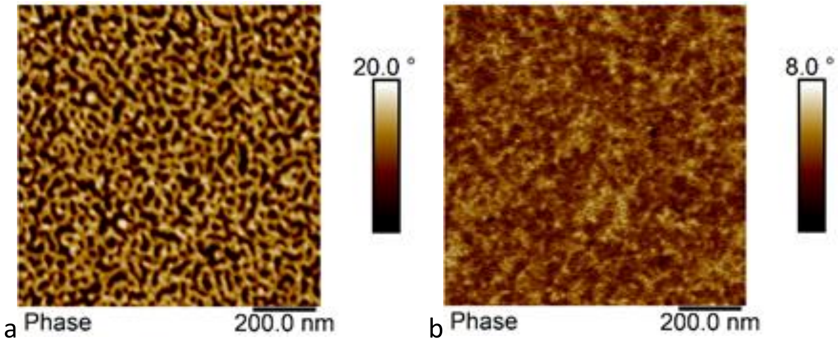


Figure 5-12: *Phase images for (a) pure SIS triblock copolymer and for (b) blends of SIS triblock copolymer (40 wt%) and of poly(β-pinene) (60 wt-%).*

Films of commercial SIS and poly(β-pinene) with different poly(β-pinene) contents (from 0 to 60 wt-%) were cast and probe tack experiments were performed. For comparison, a commercial tackifier designed for use in adhesives, Piccotac 1095 N, was also analysed. Piccotac 1095 N is a hydrocarbon resin (M_n = 1,100 g.mol^{-1}, Đ = 1.8) synthesised by polymerisation of a C5 piperylene feedstock derived from cracking of naphtha. As seen in **Figure 5-13**, the film of pure triblock copolymer SIS presented no tackiness and had poor adhesive properties. The clear influence of the addition of poly(β-pinene) can be seen in the shape of the probe tack curves. In the absence of poly(β-pinene) there is essentially no adhesion. At low amounts of poly(β-pinene) (SIS/pinene 80/20), the curve follows the typical pattern of adhesives that undergo brittle failure, with a sharp increase and rapid decrease in stress at low strain.[42,43] At higher amounts of poly(β-pinene), the peak stress increases and is followed by a plateau region which is indicative of the more desired adhesive debonding. With the addition of poly(β-pinene), the work of adhesion represented by the area under the stress-strain curve therefore increased substantially (see **Table 5-4**), the highest adhesion being for the SIS:poly(β-pinene) ratio 40:60 wt-%. It can be seen that at similar weight fractions the poly(β-pinene) tackifier had similar performance to the commercial, petroleum derived tackifier Piccotac 1095 N. Although the peak stress was lower in the case of the poly(β-pinene), the work of adhesion was slightly higher.

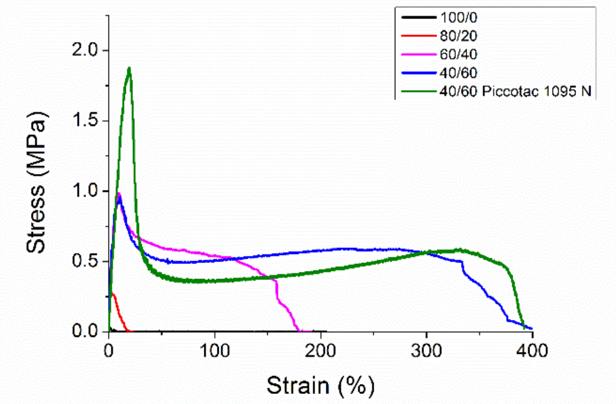


Figure 5-13: *Probe tack experiments of the films blending SIS and poly(β-pinene) produced from run 5-6 with 0 wt-% (black), 20 wt-% (red), 40 wt-% (pink) and 60 wt-% (blue) of poly(β-pinene). The reference made using 60 wt-% Piccotac 1095 N as tackifier is shown in green.*

Table 5-4: *Maximum stress and work of adhesion of the probe tack experiments from the films blending SIS and poly(β-pinene) with different SIS/pinene ratios.*

SIS/pinene ratio (wt-%)	Maximum stress (MPa)	Work of adhesion (J/m^2)
100/0	0.04 ± 0.01	0.3 ± 0.2
80/20	0.19 ± 0.05	1.9 ± 0.8
60/40	0.95 ± 0.03	92.0 ± 13.7
40/60	0.88 ± 0.05	324.8 ± 9.7
40/60 Ref[a]	1.51 ± 0.39	307.2 ± 17.2

[a] In the reference sample Piccotac 1095 N was used as tackifier.

The results of the probe tack experiment can be understood in terms of the influence of the addition of poly(β-pinene) on the rheological properties of the SIS elastomer. **Figure 5-14a** presents the evolution of the shear modulus (E’) and loss tangent (tan δ) with temperature for a pure SIS film and a blend of 40 wt-% SIS and 60 wt-% poly(β-pinene) as measured by dynamic mechanical thermal analysis (DMTA). Regarding the pure SIS film, from the tan (δ) peaks two T_gs can be observed, one at -46.6 °C, corresponding to the polyisoprene matrix phase and one at 100.2 °C, corresponding to the polystyrene domains. With the addition of 60 wt-% of poly(β-pinene) in the formulation there is a clear shift in the tan (δ) peak at lower temperatures, which increases up to -2 °C, an increase in tan (δ) above the soft phase T_g, and a decrease in the plateau modulus. This change is consistent with the influence of addition of the low molecular weight poly(β-pinene) tackifier that is expected to be miscible with the poly(isoprene) matrix.[15] Note that similar results are also observed in the DSC where the pure SIS film exhibited a sharp transition at -59 °C, corresponding to the T_g of the poly(isoprene) phase. With the addition of 60 wt-% of poly(β-pinene) in the formulation there is a clear shift of this transition to higher temperatures and a significant broadening (see **Figure 5-14b)**. In both the DMTA and DSC results, no transition was detected in the range of the T_g of the pure poly(β-pinene) which confirms the miscibility between the two polymers.

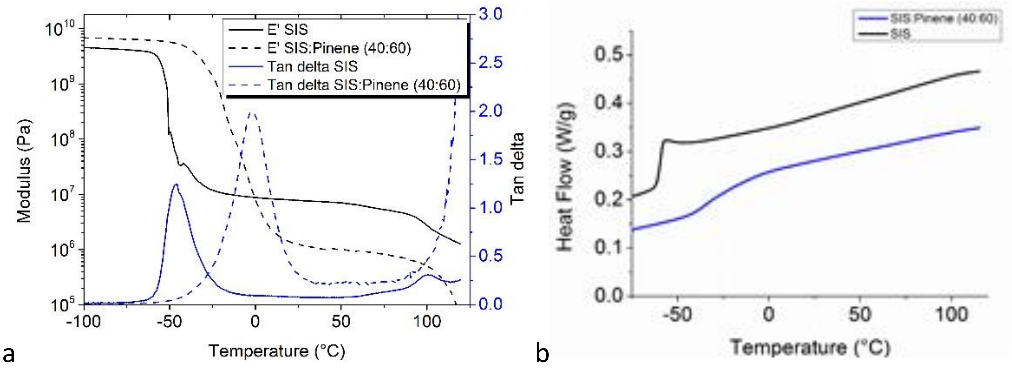


Figure 5-14: *(a) Evolution of the modulus (black) and tan delta (blue) with temperature obtained for the SIS (full lines) and SIS/poly(β-pinene) (40:60 wt-%) (dash lines) films and (b) DSC of the SIS (black) and SIS/poly(β-pinene) (40:60 wt-%) (blue) films.*

The effect of the poly(β-pinene) on the SIS triblock copolymer adhesive can thus be attributed to its influence on the rheological properties seen in **Figure 5-14a**. In the absence of any tackifier, the SIS has a relatively high elastic modulus and is substantially above the so called Dahlquist criterion, which stipulates that materials with high modulus cannot ensure sufficient interfacial contact between the adhesive and the substrate. When tackifier is present, the lowering of the plateau modulus ensures good contact between the adhesive and the substrate. In addition to this, the increase in tan (δ) ascribed to the presence of tackifier results in increased dissipation which contributes to a higher work of adhesion.

5. 4. Conclusions

In conclusion, low molecular weight poly(β-pinene)s were obtained by cationic polymerisation at 23 °C without any drying of the reactants using tris(pentafluorophenyl)borane as catalyst. The kinetics of the reaction are largely controlled by the $B(C_6F_5)_3$ concentration while the molecular weights can be controlled by the addition of an initiator. The obtained poly(β-pinene)s were demonstrated to be useful as tackifiers when blended with commercial SIS to obtain films with good adhesive properties that were comparable to commercial, petrochemical-derived tackifying agents.

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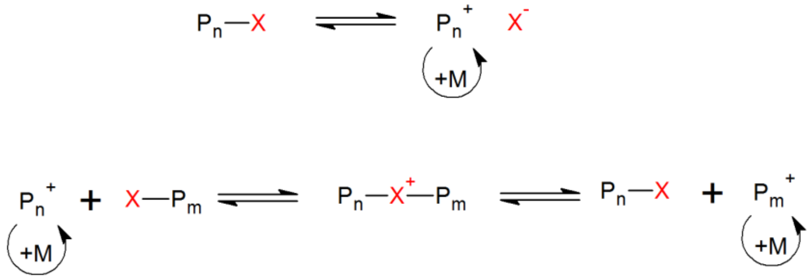
Chapter 6: A Dual Control Mechanism in the $B(C_6F_5)_3$ Catalysed Cationic Polymerisation of Styrene Mediated by RAFT Agents

6.1. Introduction

In **Chapter 5** it was shown that although controlling the initiation process can allow for some degree of control in cationic polymerisation systems targeting low molecular weights, relatively broad molecular weight distributions (MWDs) may still be observed. The ability to reduce this dispersity in order to gain homogeneity in the length and structure of the chains becomes increasingly important for low molecular weight polymers, as the dispersity can directly influence the rheological properties.[1] Since on the basis of the results presented in **Chapter 2-4** these lower molecular weight systems are the most readily accessible in cationic polymerisations conducted in the presence of water, it would therefore be desirable to improve the extent of control possible. Unfortunately, cationic polymerisations of vinyl monomers have in general proven to be challenging to control due to the high rates of chain transfer and the high rates of propagation relative to initiation.[2]

Most controlled/living carbocationic polymerisation systems that have been reported to date proceed through a Lewis acid mediated reversible termination of the propagating carbocation (see **Scheme 6-1**).[3,4] This reversible deactivation is essential in order to ensure that the rate of chain initiation is faster than that of chain growth, which is particularly challenging in cationic polymerisations due to the high propagation rate coefficient. Typically, these cationic systems have utilised either alkyl halides,[5–7] alkyl esters[8,9] or alcohols[10–12] as initiating species in combination with a suitable Lewis acid capable of activating the dormant chain end. More recently, Kumagai *et al.* showed that trithiocarbonate terminated polymers can be activated in the presence of a Lewis acid to induce the living cationic polymerisation of vinyl ethers.[13] This is interesting as it allows for a mechanistic transformation between a controlled cationic polymerisation mediated by reversible termination and controlled radical polymerisations based on the reversible addition-fragmentation chain transfer (RAFT) mechanism that is possible for polymers terminated in trithiocarbonates.

Building on this work, a fundamentally different type of control mechanism has been introduced for the controlled cationic polymerisation of vinyl ethers and *p*-methoxystyrene (pMOS) based on degenerative chain transfer[14] (see **Scheme 6-1**). The use of a degenerative transfer type mechanism is especially attractive in cationic polymerisations because the lack of bimolecular termination of the active cationic centres and the high rates of propagation mean that in principle very high polymerisation rates can be achieved without loss of control. It has been shown that a wide range of transfer agents[15] including thiocarbonylthio compounds,[16–24] thioethers,[16,25] thioacetals,[26] alcohols[27,28] and phosphates/phosponates[29] can be used to ensure a regulated chain growth across all the chains in the system. It is important to note that many of these compounds have previously been used as additives to improve control in conventional controlled cationic polymerisation systems that proceed *via* reversible termination of the chain end. The addition of an excess of ethers[30,31] or thioethers,[32,33] for example, has been shown to lead to an improved control of the Lewis acid mediated polymerisation of vinyl ethers, which has been attributed by some to the formation of a dormant, non-polymerising onium intermediate.[34–38]



Scheme 6-1: *Differences between a reversible termination type reaction (top) and a degenerative transfer mechanism that proceeds through an intermediate species that is not active in the polymerisation (bottom).*

Despite these advances in degenerative transfer based cationic polymerisations, the range of monomers that has been reported is limited largely to vinyl ethers and *p*-methoxystyrene. Furthermore, in the case of *p*-methoxystyrene, a significant retardation in the rate of polymerisation has often been observed. For example, while butyl(1-isobutoxyethyl)thioether was able to efficiently mediate the triflic acid initiated polymerisation of vinyl ethers, it resulted in the complete inhibition of the polymerisation of pMOS.[25] Only by using bulkier thioethers or aromatic thioethers could a polymerisation rate approaching that of the thioether-free reaction be obtained. These differences between vinyl ethers and *p*-methoxystyrene were attributed to the enhanced stability of the sulfonium intermediate relative to the propagating carbocation in the case of *p*-methoxystyrene.

In this chapter, we seek to explore the potential use of RAFT agents to control molecular weight and molecular weight distributions in the cationic polymerisation of styrene. In comparison to *p*-methoxystyrene, the propagating cationic centre is less stabilised and historically has proven more challenging to polymerise in a controlled/living fashion.[4] We first explore the use of a pair of widely used RAFT agents, cumyl dithiobenzoate and S,S-dibenzyl trithiocarbonate, in the $B(C_6F_5)_3$ mediated polymerisation of styrene. Kinetic measurements and structural analysis of the resulting polymers suggests that in addition to a RAFT polymerisation mechanism, there is a reversible addition mechanism established with a cationic intermediate that leads to improved control of the molecular weight distribution, even in the absence of degenerative chain transfer occurring. Finally, these results for styrene are contrasted with polymerisations using *p*-methoxystyrene.

6.2. Experimental Part

6.2.1. Materials

Styrene (Quimidroga, technical grade) was distilled under reduced pressure and stored at -22 °C until use. Dichloromethane (DCM, Sigma Aldrich), 1-(4-methoxyphenyl) ethanol (**1**, 95% purity, Alfa Aesar), tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, 97% purity, Alfa Aesar), S,S-dibenzyl trithiocarbonate (DBTTC, Arkema), cumyl dithiobenzoate (CDTB, 99% purity, Sigma Aldrich), 2-cyano-2-propyl benzodithioate (CPBDT, 97% purity, Sigma Aldrich), benzyl 1H-pyrrole-1-carbodithioate (BPCDT, 97% purity, Sigma Aldrich), and benzyl benzodithioate (BDTB, 96% purity, Sigma Aldrich) were used as received.

6.2.2. Methods

Gel permeation chromatography (GPC) was performed using three columns in series (Styragel HR2, HR4 and HR6) and a refractive index (RI) detector (Waters 2410). THF was eluted at a flow rate of 1 $mL.min^{-1}$. The samples were prepared at a concentration of 2 $mg.mL^{-1}$ of polymer in THF and filtered using a nylon filter with pores of 45 µm. The molecular weights and dispersities were calculated using the RI detector, based on polystyrene standards.

Proton nuclear magnetic resonance (^{1}H NMR) was recorded on a Bruker 400 MHz at 25 °C. Samples were prepared in deuterated acetone (for measuring conversion during the reaction) or deuterated chloroform ($CDCl_3$, for structural analysis). The UV–visible absorption measurements were performed using a Shimadzu spectrophotometer (model UV2550 230 V).

Matrix-assisted laser desorption/ionisation – time of flight mass spectroscopy (MALDI-ToF MS) was performed on a Bruker Autoflex Speed system equipped with a 355 nm NdYAG laser. The matrix was composed of *trans*-2-[3-(4-*tert*-butylhenyl)-2-methyl-2-propenylidene] malonitrile (DCTB, Sigma-Aldrich) dissolved in THF at a concentration of 10 mg.mL^{-1}. Silver trifluoroacetate (AgTFA) (Sigma-Aldrich) was used as cation donor (10 mg.ml^{-1} dissolved in THF). A matrix:salt:polymer mixture (10:1:1) was prepared and 0.5 µL was hand spotted on a ground steel target plate. An accumulation of 10,000 laser shots was made for each spectrum. A mixture of different polyethylene glycol standards (PEG, Varian) was used as external calibration of the spectra.

6.2.3. Procedures

The experimental conditions of the experiments performed in this chapter are summarised in **Table 6-1**. In a typical polymerisation reaction (Run 6-5), a solution of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (0.0444 g) in 1 mL of dichloromethane (DCM) was prepared in a vial. 1-(4-methoxyphenyl) ethanol (**1**) (0.0150 g), the RAFT agent

(0.0380 g), styrene (0.3636 g, 0.65 M) and DCM (4 mL) were stirred in another vial. The catalyst solution was then added to the vial and the reaction was performed at 23 °C, under an air atmosphere. After predetermined times, the polymerisation was quenched using methanol. The conversions were determined by ^{1}H NMR in acetone-d_6. The final polymer was precipitated in an excess of chilled methanol and dried for 24h at room temperature.

Table 6-1: *Summary of the experimental conditions for the different polymerisations performed.*

Run	Monomer	RAFT agent	[RAFT] (mol/L)	[M] (mol/L)	[Initiator] (mol/L)	[B(C_6F_5)$_3$] (mol/L)	Time
6-1	St	None	-	0.65	0	0.02	24 h
6-2	St	None	-	0.65	0.02	0.02	24 h
6-3	St	CDTB[a]	0.03	0.65	0	0.02	25 h
6-4	St	CDTB[a]	0.03	0.65	0.02	0.02	96 h
6-5	St	CDTB[a]	0.01	0.65	0.02	0.02	24 h
6-6	St	DBTTC[b]	0.03	0.65	0.02	0.02	48 h
6-7	St	DBTTC[b]	0.03	0.65	0.02	0.05	48 h
6-8	St	DBTTC[b]	0.02	0.65	0.02	0.05	24 h
6-9	St	DBTTC[b]	0.01	0.65	0.02	0.05	24 h
6-10	St	CPBDT[c]	0.03	0.65	0.02	0.02	24 h
6-11	St	BPCDT[d]	0.03	0.65	0.02	0.02	24 h
6-12	St	BDTB[e]	0.03	0.65	0.02	0.02	30 h
6-13	pMOS	None	-	0.65	0.02	0.005	20 sec
6-14	pMOS	CDTB[a]	0.03	0.65	0.02	0.005	20 sec
6-15	pMOS	DBTTC[b]	0.03	0.65	0.02	0.005	20 sec
6-16	pMOS	BDTB[e]	0.03	0.65	0.02	0.005	20 sec
6-17	pMOS	BPCDT[d]	0.03	0.65	0.02	0.005	0.5 h

[a]Cumyl dithiobenzoate. [b]S,S-dibenzyl trithiocarbonate. [c]2-cyano-2-propyl benzodithioate. [d]Benzyl 1H-pyrrole-1-carbodithioate. [e]Benzyl benzodithioate.

6.3. Results and Discussion

The cationic polymerisation of styrene in dichloromethane (DCM) was first performed using tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) as catalyst in the absence of initiator at 23 °C (Run 6-1, **Table 6-1**). In this case, the initiation process takes place due to adventitious water that is present in the reaction mixture.[39] Note that unlike the majority of catalysts used in cationic polymerisation, $B(C_6F_5)_3$ is stable in the presence of water[40,41] and no attempt was made here to dry the solvents and the reaction was run in air. The same experiment was repeated in the presence of cumyl dithiobenzoate (CDTB), where a lower rate of polymerisation was observed (Run 6-3, **Table 6-1**) (see **Figure 6-1**). This was coupled with a substantially lower molar mass of the polymer (see **Table 6-2**).

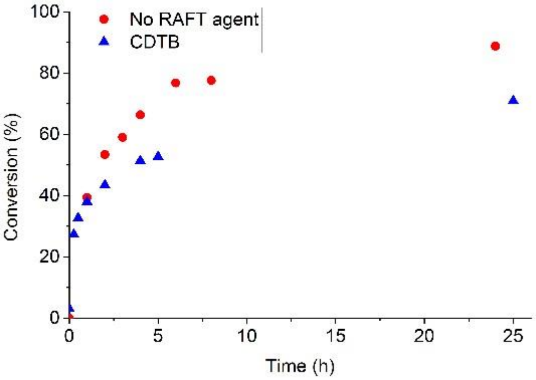


Figure 6-1: *Evolution of the conversion with time for the polymerization of styrene performed without initiator and without RAFT agent (Run 6-1, red spheres) or using CDTB as RAFT agent (Run 6-3, blue triangles).*

Table 6-2: *Final molecular weight and dispersity for reactions conducted in the absence of initiator without the addition of CDTB (Run 6-1) and with addition of CDTB (Run 6-3).*

Run	Time (h)	Conversion (%)	M_n (g/mol)	Đ
6-1	24	89	3,100	3.3
6-3	25	71	900	2.0

In an attempt to increase the rate of polymerisation and improve the control, the reactions were repeated in the presence of an initiator, 1-(4-methoxyphenyl) ethanol (Run 6-2, **Table 6-1**), similar to the work from Kostjuk *et al.*.[12] Under these conditions, the reaction has previously been shown to proceed with limited control resulting from $B(C_6F_5)_3$ mediated reversible deactivation of the alcohol terminated chains. In the absence of CDTB, final molecular weights (M_n) of 3,200 g.mol^{-1} and a dispersity (Đ) of 1.7 (**Figure 6-2**) were obtained. Similar to the case where no initiator was used, in the presence of CDTB (Run 6-4, **Table 6-1**) the polymerisation proceeded relatively quickly in the first stages before slowing substantially (**Figure 6-2**). When using CDTB, analysis of the evolution of the molecular weight showed that it was linear with respect to conversion, although the molecular weight distribution was relatively broad.

In order to gain an insight into the cause of the significant retardation in the rate of polymerisation, additional experiments were conducted using the same initiator/catalyst ratios but using S,S-dibenzyl trithiocarbonate (DBTTC) (Run 6-6 in **Table 6-1**) as RAFT agent (see **Figure 6-3** for chemical structure). Unlike cumyl dithiobenzoate, in DBTTC the R groups are poor leaving groups due to the low stability of the resulting carbocations and were therefore not expected to influence the polymerisation significantly. However, it is clear from **Figure 6-2** that the presence of DBTTC led to a similar retardation in the rate as well as a linear increase in the molar mass, although molecular weights were higher than the theoretical M_n assuming a RAFT type mechanism. The molecular weight distributions of the precipitated polymers are shown in **Figure 6-2c**.

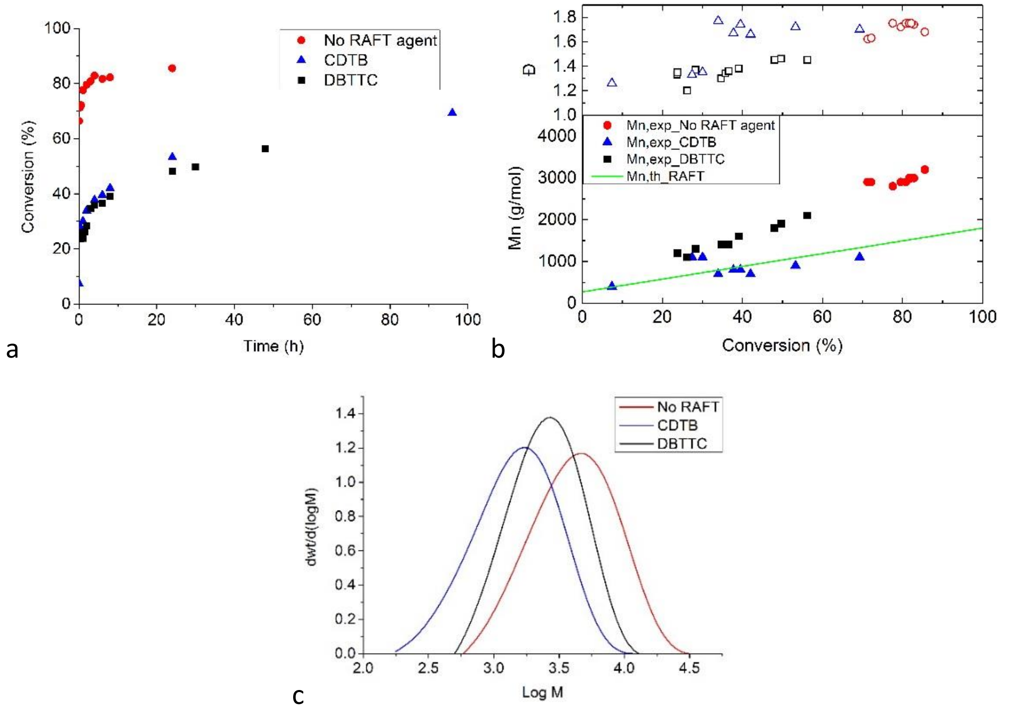


Figure 6-2: *(a) Evolution of the conversion with time, (b) evolution of the molar mass (full symbols) and dispersity (empty symbols) with conversion for the cationic polymerisation of styrene without RAFT agent (Run 6-2, red), using CDTB (Run 6-4, blue) and DBTTC (Run 6-6, black) as RAFT agents. The theoretical*

molecular weights were calculated for the following values: [RAFT] = 0.03 M, [I] = 0.02 M, [$B(C_6F_5)_3$] = 0.02 M, using the equation $M_{n,theo} = M_{RAFT} + \frac{M_{St}[St]_0}{[RAFT]_0+[I]_0}p$, with M_A the molar weight of the species A, [A] the concentration of A and p the conversion. For clarity, only one value of $M_{n,theo}$ is shown using M_{RAFT} = 272.43 g.mol^{-1}. (c) Final molecular weight distributions of the polymers obtained in Run 6-2 (red), Run 6-4 (blue) and Run 6-6 (black).

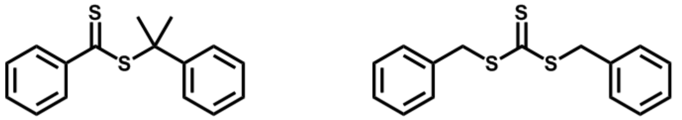

Cumyl dithiobenzoate (CDTB)
S,S-dibenzyl trithiocarbonate (DBTTC)

Figure 6-3: *Structures of the two RAFT agents employed.*

Analysis of the polymer end groups of the precipitated polymer using MALDI-ToF demonstrated that the polymer obtained using cumyl dithiobenzoate as RAFT agent (**Figure 6-4**) showed the presence of chains initiated by an initiator molecule (m/z = 1,491.5 Da) as well as chains initiated by the R group of the RAFT agent (m/z = 1,475.5 Da), that are terminated by a double bond. The structures can be further confirmed by the good agreement between the theoretical isotopic distribution and the experimental one. The terminal double bond could be the result of the removal of the RAFT moiety or by elimination of OH and OMe terminated chains during the analysis,[42] but can also arise from β-hydrogen elimination. However, the absence of any structures arising from new chains that form as the result of transfer reactions suggests that the terminal groups are eliminated during the MALDI process. This is further confirmed below, where ^{1}H NMR suggests that the contribution of these transfer reactions is negligible. In addition to these major peaks, a smaller signal at m/z = 1,505.5 Da and at 1,521.4 Da can be observed that may be attributed to intermolecular electrophilic aromatic substitution reactions, yielding chains with both an R and an initiator group terminated by an unsaturated group (m/z = 1,505.5 Da) or two initiator groups terminated by an unsaturated group (m/z = 1,521.4 Da). This transfer is likely to occur on the aromatic group of the initiator molecule, as for styrene the chain transfer coefficient for alkoxy substituted aromatic compounds is substantially higher than alkyl substituted ones (*e.g.* C_s =1.6 for anisole but 1×10^{-2} for *p*-xylene).[43] These chain transfer to polymer reactions may explain the continuous increase in dispersity observed in **Figure 6-2**.

Analysis of the polymer end groups using MALDI-ToF showed that the polymer obtained using DBTTC had similar structures but did not contain any polymers initiated with the R group from the RAFT agent (**Figure 6-4**). As commented above, this is expected due to the instability of the benzyl cation that would result from fragmentation. In the case of DBTTC as RAFT agent, a small peak at m/z = 1,509.4 Da was also observed that can be related to OH terminated chains that are not eliminated during the ionisation process. In the case of the reaction conducted in the absence of RAFT agent, the results from MALDI-ToF (**Figure 6-4**) indicate that in addition to the initiator derived chains observed in the RAFT reactions, a substantial fraction of chains with styrene at the α chain end were observed (m/z = 1,462.1 Da). These chains can arise from β-hydrogen elimination reactions that occur as the system proceeds rapidly to high conversion.

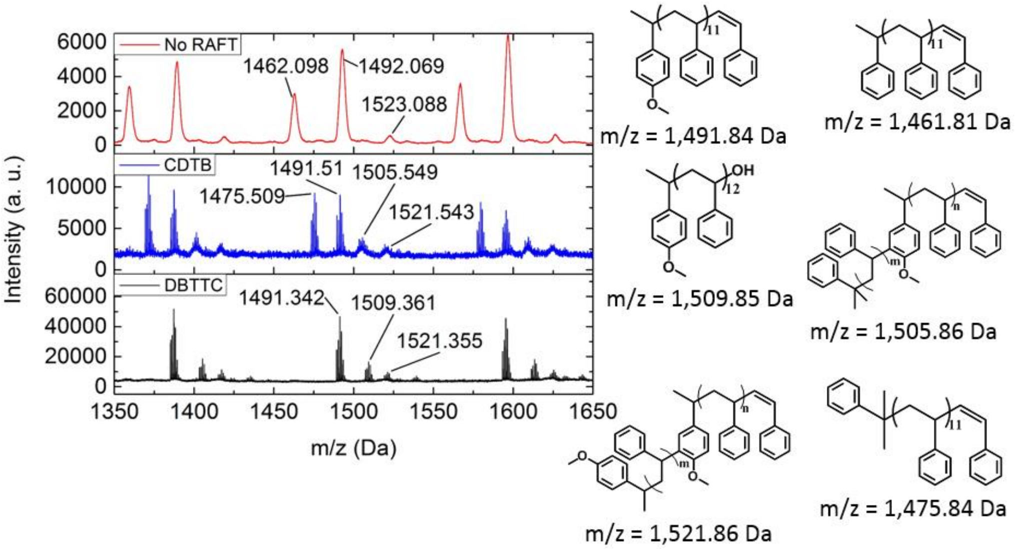


Figure 6-4: *MALDI-ToF spectra analysed with silver cations of the polystyrenes obtained without RAFT agent (top, red), using CDTB (middle, blue) and DBTTC (bottom, black) as RAFT agents and the structures corresponding to the different peaks.*

These conclusions from the MALDI results are also supported by ^{1}H NMR. In the case of the polymer synthesised in the absence of RAFT agent, the MALDI results above and previous work[12,44] suggest that the predominant structure should be formed of initiator derived chains terminated in OH (or OMe resulting from the quenching of the reaction). In the ^{1}H NMR this structure is indeed observed, with a broad proton signal arising from the terminal styrene unit next to OH and O-CH_3 in the region of 4 ppm (labelled ω_1 in **Figure 6-5**), and the methoxy O-CH_3 protons from the initiator at 3.8 ppm (labelled α_2 in **Figure 6-5**). At 3.6 ppm there is a broad peak that may be related to the O-CH_3 arising from quenching with methanol that has also been observed in previous work using the same initiator/catalyst system.[12,44] The CH_3 group from the initiator can also be observed at 1 ppm (labelled α_1 in **Figure 6-5**). Note that chains initiated by a proton also have a peak in this region as a result of the protons labelled α_1'' in **Figure 6-5**. This can be seen for example in the NMR spectra of the polymer synthesised in the absence of RAFT agent and initiator where initiation occurs by activation of adventitious water as shown in **Figure 6-6**. Although the relative integrals of the α_2 and ω_1 peaks are approximately 1:3 as would be expected for assuming good initiator efficiency, the degree of polymerisation calculated by comparison of the integral of these peaks to the signal arising from the proton in the polymer backbone (1.25-2.5 ppm) is significantly higher than calculated by GPC. This is in agreement with the MALDI, which clearly shows the presence of chain transfer reactions which would lead to proton initiated chains, but would not influence the $\alpha_2:\omega_1$ ratio.

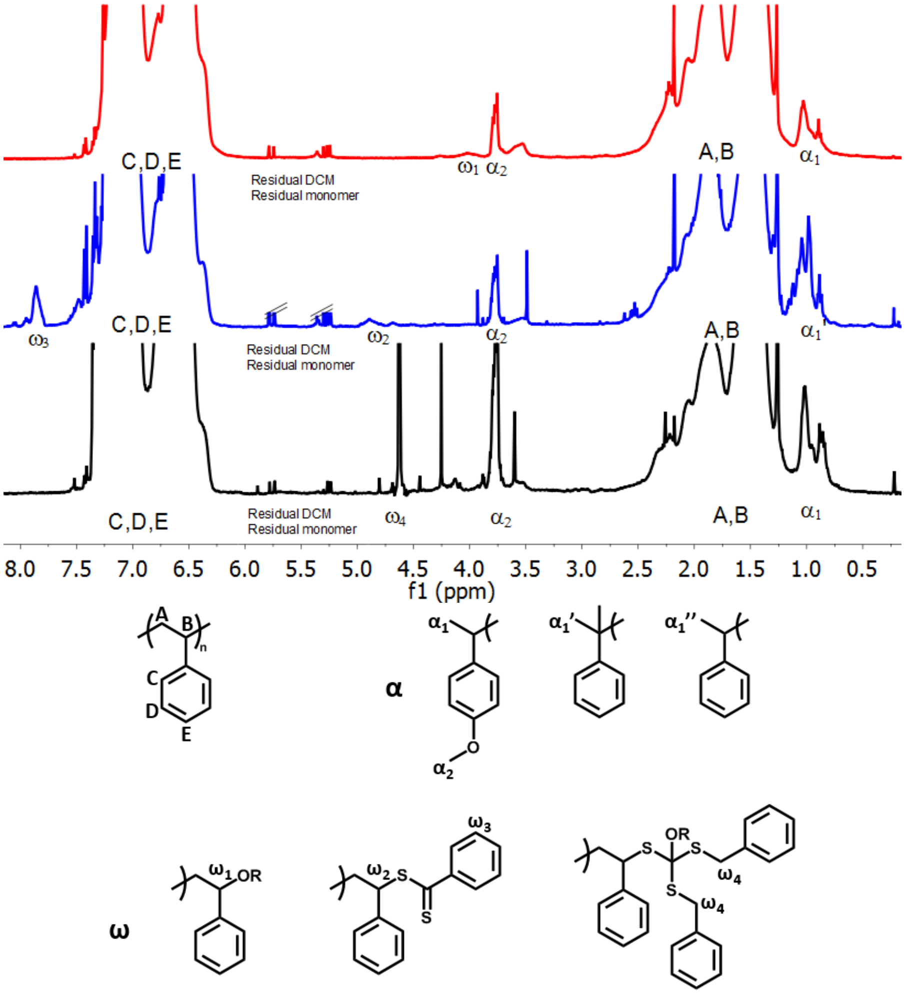


Figure 6-5: *^{1}H NMR spectra of polymers synthesised in the absence of RAFT agent (Run 6-2, red) and in the presence of CDTB (Run 6-4, blue) and DBTTC (Run 6-6, black).*

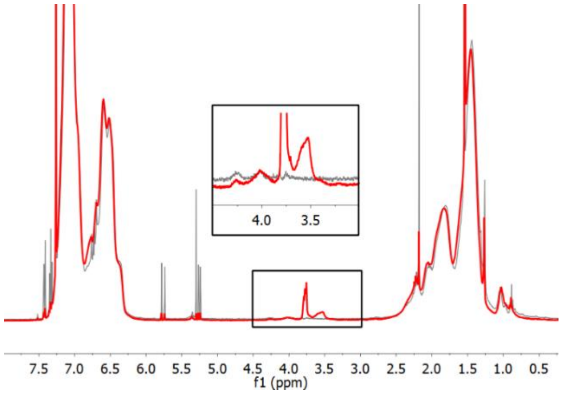


Figure 6-6: *^{1}H NMR spectra of polymers synthesised in the absence of RAFT agent with (Run 6-2, red) and without initiator (Run 6-1, grey). The insert shows an enlargement of the region 3-4.5 ppm where the peaks arising from O-CH_3 groups of the initiator moiety appear. Note that at 1 ppm the protons arising from both initiator and proton initiated chains can be observed.*

In the case of the polymerisation conducted using CDTB, additional proton signals can be observed in the region of 4.7-4.9 ppm that can be attributed to a proton in the terminal position next to the RAFT end group (labelled ω_2 in **Figure 6-5**). The additional CH_3 signals arising from initiation of the cumyl group of the RAFT agent can also be observed in the region of 1 ppm (labelled α_1' in **Figure 6-5**). Furthermore, a signal at 7.9 ppm arising from the aromatic protons in the *meta* position of the RAFT agent can also be observed (labelled ω_3 in **Figure 6-5**). Based on the integral of the proton signal arising from ω_2 to the proton signals from the backbone, a degree of polymerisation of 23 is estimated. This is significantly higher than the degree of polymerisation determined by GPC (≈ 11) as the initiator:RAFT ratio in these experiments is fairly high, which limits the number of RAFT terminated chains.

In the case of polymerisations mediated by DBTTC, the protons arising from the -CH_2-Ph in the RAFT group can clearly be observed at 4.6 ppm (labelled ω_4 in **Figure 6-5**). A broad signal in the range 4-4.5 ppm is also present that may be due to the proton of the styrene next to the RAFT group, but the intensity is low and this is difficult to confirm. By comparison of the ω_4 signal with those arising from the backbone, a degree of polymerisation of 17 is estimated, which is in excellent agreement with that derived from GPC (≈ 16) and suggests that the final polymer contains a single RAFT group per chain. The relative integral of ω_4 and α_2 was 4:3.1, which is in good agreement with a polymer structure consisting of an initiator and terminating in the RAFT moiety. The presence of the RAFT moiety in the final polymer is surprising since looking at the results from the MALDI it is clear that there is no initiation from the benzyl R group. This suggests that the intermediate RAFT species acts as a dormant species that is capped either by a hydroxyl group during the polymerisation or reacts with methanol upon reaction quenching. It may be noted structurally this system resembles the end-capping of cationic polymerisations with non-homopolymerisable monomers such as diphenylethylene, as has been extensively reported by Faust and co-workers.[45–48]

These results show that the presence of RAFT agents significantly slowed down the rate of reaction, but only in the case where the R group is a good leaving group is the R group incorporated into the final polymer. The significant decrease in the rate of polymerisation can be understood in terms of the impact of the RAFT agent on the propagating carbocation concentration. In the absence of the RAFT agent, the carbocation concentration is given by the equilibrium between dormant –OH terminated chains and active chains. The initial rapid rate of polymerisation is the result of the significantly higher rate of activation of the initiator than –OH terminated polystyrene. This effect, which has previously been noted in other Lewis acid mediated cationic polymerisations of styrene,[49–51] can be observed visually as the initially colourless solution immediately changes colour upon addition of the catalyst before decaying to a near constant value within a few seconds (see **Figure 6-7**).

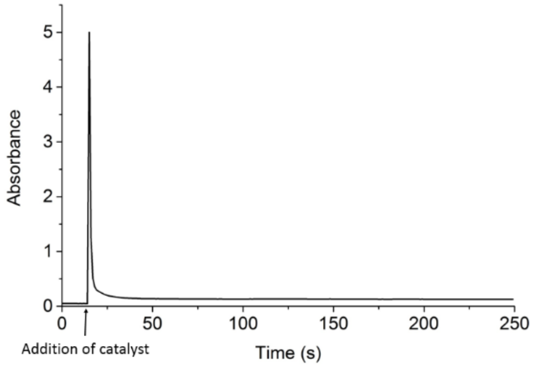


Figure 6-7: *Evolution of the absorbance at 340 nm with time following the addition of $B(C_6F_5)_3$ using [St]=0.65 M, [I] = 0.02 M, $[B(C_6F_5)_3]$ = 0.02 M.*

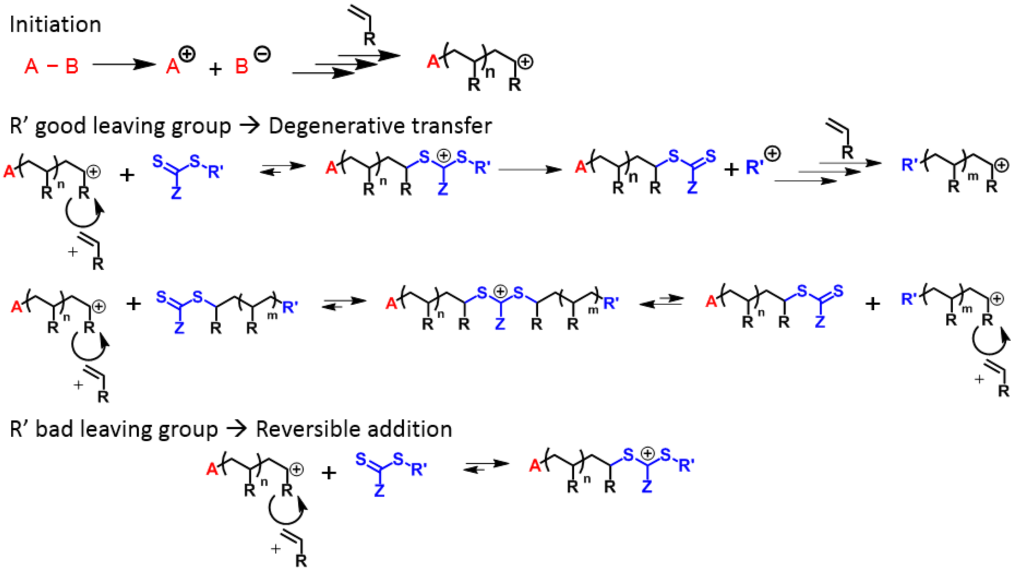
In the presence of RAFT agent, the carbocation concentration can be reduced if the addition to the RAFT agent occurs but fragmentation is slow, resulting in a build-up of the RAFT cationic intermediate. This situation is similar to that proposed for certain radical RAFT polymerisations, particularly those involving dithiobenzoates, for which retardation of the rate of polymerisation has been proposed to be the result of slow fragmentation of the RAFT agent during the main equilibrium.[52,53] This is also similar to radical polymerisation in the presence of thioketones where the intermediate radical reduces the rate of polymerisation.[54–57] However, unlike radical polymerisations, the absence of bimolecular termination means that the intermediate cation does not inherently result in a decrease of the control of the reaction. In the present case, while the slow fragmentation rate has a negative effect on the rate of polymerisation, it significantly improves the control of polymerisation. This can particularly be seen in the case of DBTTC and occurs because an equilibrium is established between active and dormant chains early in the reaction, such that initiation is relatively fast compared to the whole polymerisation time and chain growth proceeds evenly across all chains. Thus, in systems with controlled initiation, the high rate of addition to RAFT agent relative to propagation,[29] coupled with the high stability of the RAFT cationic intermediate can lead to low dispersity polymers.

The results shown in so far can therefore be understood by a traditional RAFT process occurring in tandem with a reversible addition process that establishes an equilibrium between the active carbocation and a “dormant” cationic RAFT intermediate. With regards to the molar mass of the polymer, two cases can be established based on the nature of the RAFT agent used as shown in **Scheme 6-2**. In the case of the use of a RAFT agent with an R group that forms a stable cation (*i.e.* CDTB), fragmentation can occur to give the R group and thus the number of chains would be expected to be equal to the number of initiator molecules plus the number of molecules of RAFT agent, such that

$$M_{n,theo} = M_{CTA} + \frac{M_M[M]_0}{[CTA]_0+[I]_0}X \qquad (6\text{-}1)$$

With $M_{n,theo}$ the theoretical molecular weight; M_{CTA} and M_M the molar masses of the RAFT agent and the monomer, respectively; $[M]_0$, $[CTA]_0$ and $[I]_0$ the initial concentrations of the monomer, RAFT agent and initiator, respectively; X the fractional conversion of the polymerisation. In the case of a RAFT agent with an R group that does not form a stable cation (*i.e.* DBTTC), fragmentation will not occur and the number of chains generated will be given only by the amount of initiator used, such that

$$M_{n,theo} = M_I + \frac{M_M[M]_0}{[I]_0}X \tag{6-2}$$



Scheme 6-2: *Difference in mechanism between degenerative transfer and reversible addition depending on the leaving capacity of the R' group from the RAFT agent.*

Figure 6-8 represents the evolution of the molecular weights with conversion for both RAFT agents and the theoretical molecular weights taking into account classical RAFT and reversible addition processes. Coupled with the MALDI results, this demonstrates that the polymerisations of styrene using DBTTC occurs through a reversible addition mechanism in which the intermediate RAFT cation acts as a dormant species, whereas the polymerisation of styrene using cumyl dithiobenzoate follows a dual mechanism for which both the conventional RAFT mechanism and the dormant RAFT intermediate play a role in the evolution of conversion and molecular weight.

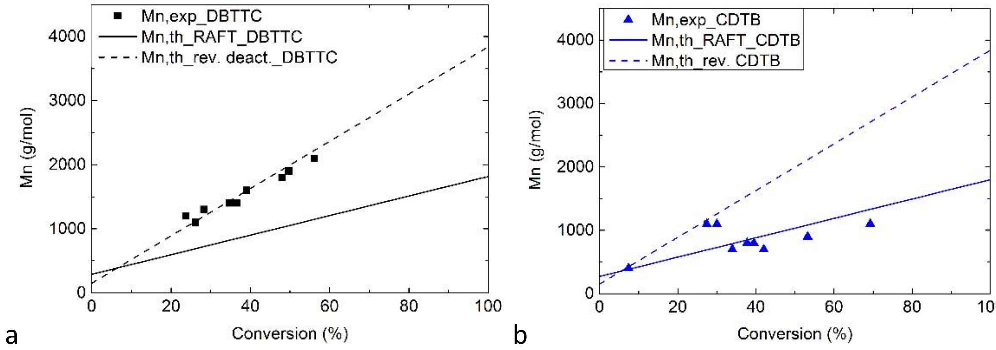


Figure 6-8: *Evolutions of the experimental (symbols) and theoretical molar mass considering classical RAFT (solid line) and reversible addition (dashed line) polymerisations with conversion using (a) DBTTC or (b) CDTB as RAFT agents.*

The dual control mechanism is further reinforced by experiments conducted at different [RAFT] for the CDTB and DBTTC as shown in **Figure 6-9**. Note that in the case of DBTTC, a slightly higher catalyst concentration was used in these experiments to try and push the system to higher conversion. As shown in **Figure 6-9**, when the amount of RAFT agent was reduced (Runs 6-4 and 6-5 for CDTB and Runs 6-7 to 6-9 for DBTTC, see **Table 6-1**), the rate of polymerisation increased and tended towards the RAFT-free case. In the case of the CDTB, there was a small increase in M_n at lower RAFT agent concentration, although this was not particularly large since a large number of chains are generated directly by the initiator in addition to undesired initiation by adventitious water. In contrast, in the case of DBTTC the reduction in RAFT agent did not change the evolution of M_n, which, as discussed above, is because the absence of fragmentation means that DBTTC does not generate any additional chains. Note that in all cases for DBTTC, the evolution of M_n is lower than the theoretical value which is likely a result of an increased rate of protic initiation by adventitious water due to the higher $B(C_6F_5)_3$ concentrations used in these runs. In both DBTTC and CDTB there is a decrease in dispersity at higher [RAFT], which is related to the enhanced rate of deactivation of the chain end relative to propagation. This is particularly notable in the case of DBTTC and reinforces the point that while the RAFT agent decreases the rate of polymerisation in these systems, it also regulates the addition of monomer, particularly in the early stages and ensures even chain growth to minimise the dispersity. The final molecular weight distributions obtained for these experiments are also shown in **Figure 6-9.**

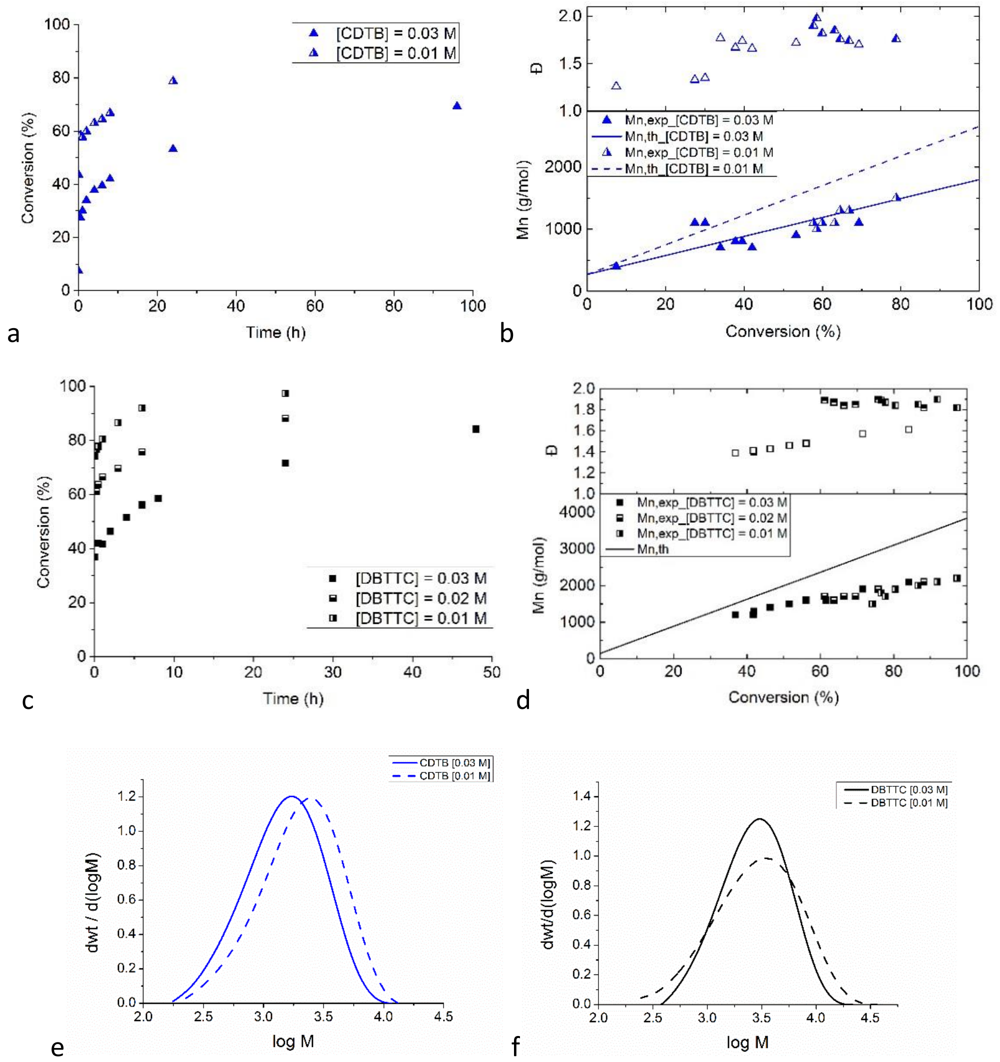


***Figure 6-9**: (a and c) Evolution of the conversion with time for [CDTB] = 0.03 mol.L^{-1} (a, filled blue triangles) and 0.01 mol.L^{-1} (a, half-filled blue triangles) and [DBTTC] = 0.03 mol.L^{-1} (c, filled black squares), 0.02 and 0.01 mol.L^{-1} (c, half-filled black squares). (b and d) Evolution of the molar mass and dispersity at different RAFT agent concentrations. (e and f) Final molecular weight distributions synthesised using (e) CDTB (0.03 M ,Run 6-4, full line) and CDTB (0.01 M, Run 6-5, dashed line) and (f) DBTTC (0.03 M ,Run 6-7, full line) and DBTTC (0.01 M, Run 6-9, dashed line).*

Although the effect on M_n is limited by reducing the concentration of RAFT agents, it will be expected that there is a significant decrease in the fraction of chains that have the RAFT terminal group since the [I]/[RAFT] ratio is changed. For CDTB, this can be observed in the NMR by the reduction in the signal attributed to the C*H* proton that is in the terminal position, next to the RAFT end group relative to the O-CH_3 signal of the initiator (see **Figure 6-10**). This is also the case in the reaction with DBTTC looking at the signal arising from the CH_2-Ph protons of the benzyl group in the RAFT agent. In this case, the relative integrals of the initiator went from 4:3 at [RAFT]:[**1**] of 3:2, which would indicate a system that exclusively has the RAFT group at the end of the chain, to ≈ 1:3 at [RAFT]:[**1**] of 1:2 (**Figure 6-11**), which suggests that less than 25% of chains have the RAFT group.

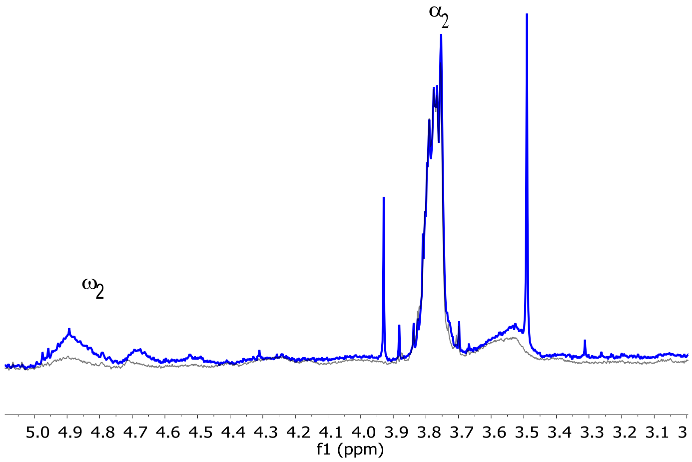


Figure 6-10: *^1H NMR spectra of polymers synthesised using 0.03 M CDTB (Run 6-4, blue) and 0.01 M CDTB (Run 6-5, grey) in the region where peaks attributed to O-CH_3 groups of the initiator moiety and terminal styrene groups next to the RAFT end group appear.*

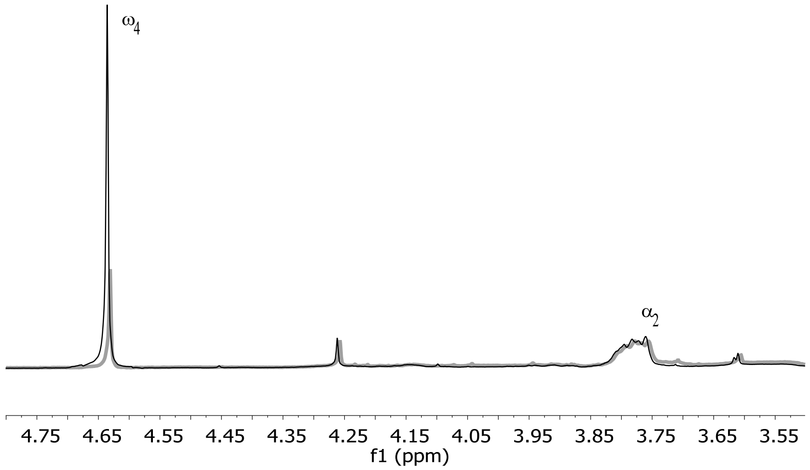


Figure 6-11: *^{1}H NMR spectra of polymers synthesised using 0.03 M DBTTC (Run 6-7, black) and 0.01 M DBTTC (Run 6-9, grey) in the region where peaks attributed to O-CH_3 groups of the initiator moiety and terminal styrene groups next to the RAFT end group appear.*

As shown above, the nature of the RAFT agent can influence both the reaction kinetics and the molecular weight distributions. In radical RAFT polymerisation, it is known that the stability of the intermediate radical can influence the reactions kinetics and therefore alternative systems were briefly explored using the non-fragmenting “RAFT” agents, benzyl benzodithioate (BDTB), 2-cyano-2-propyl benzodithioate (CPBDT) and benzyl 1H-pyrrole-1-carbodithioate (BPCDT) (structures in **Figure 6-12**). In the case of benzyl benzodithioate, which is structurally similar to CDTB with the exception that the R group does not form a stable carbocation, a similar rate of polymerisation to that of CDTB was observed. However, for BDTB the molar mass appears to tail off at higher conversion which is typical of reactions with a substantial amount of chain transfer occurring.[58,59] This is also reflected in the relatively high dispersity of the BDTB mediated polymerisation. In the presence of 2-cyano-2-propyl benzodithioate, which differs from benzyl benzodithioate only in the nature of the R group, the reaction was substantially slower and effectively stopped at 30 % conversion. In the case of benzyl 1H-pyrrole-1-carbodithioate, this retardation was even more severe and the reaction stopped at around 20% conversion after an initial rapid period (**Figure 6-12**). In the case of 2-cyano-2-propyl benzodithioate and benzyl 1H-pyrrole-1-carbodithioate, the intermediate cation appears to be so slow to fragment that the propagating carbocation concentration decreases to the point that the reaction does not progress. This is particularly obvious for the dithiocarbamate system in which the nitrogen would be expected to stabilise the intermediate to a greater extent, resulting in slower fragmentation and thus reducing the rate of polymerisation. Thus, although in this case the transfer constant would be expected to be fairly high, the equilibrium favours the cationic intermediate to an extent that the polymerisation does not proceed efficiently.

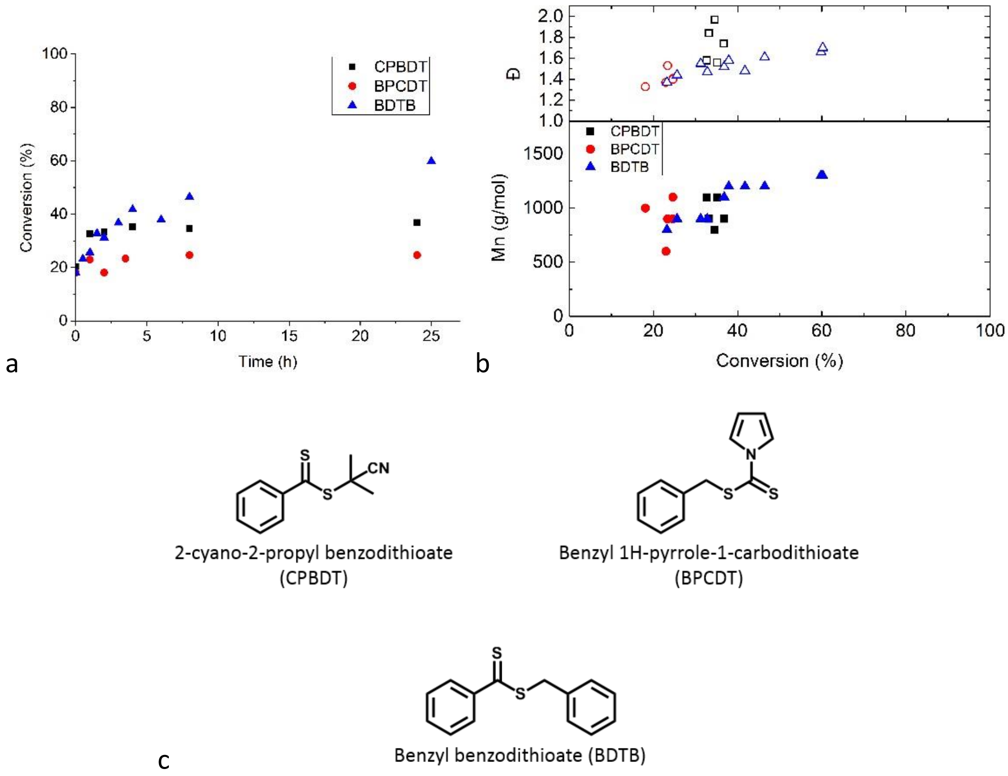


Figure 6-12*: (a) Evolution of the conversion with time and (b) evolution of the molecular weight (full symbols) and dispersities (empty symbols) with conversion for the polymerisations of styrene using 2-cyano-2-propyl benzodithioate (black squares), benzyl 1H-pyrrole-1-carbodithioate (red circles) and benzyl benzodithioate (blue triangles). (c) Structures of the different RAFT agents.*

Here it has been demonstrated that cationic RAFT polymerisation of styrene tends to proceed *via* a dual mechanism where both degenerative chain transfer and reversible addition to the RAFT agent can contribute to the control of the polymerisation and therefore it is worth considering this result in the context of other monomers that have been polymerised in RAFT cationic polymerisation systems. **Table 6-3** shows the results from a series of polymerisations of pMOS using the same RAFT agents that were applied for styrene. The molecular weight distributions of the final polymers are shown in **Figure 6-13**. In this case, in the absence of any RAFT agent the polymerisation was almost instantaneous. The molar mass of the system was also substantially above the theoretical value assuming that each initiator molecule generates one chain, which demonstrates a complete lack of control, as has previously been reported for this system in DCM.[60] Addition of DBTTC and BDTB, which were shown to significantly influence both the rate and molecular weight distribution in the case of styrene, had no effect on the polymerisation. The likely cause of this is the high stability of the pMOS cation relative to the styrene cation, which lowers the rate of addition to RAFT agents (lower transfer constant) and favours fragmentation of the cationic intermediate, thus preventing any improvement in control arising from the reversible deactivation of the pMOS carbocation. In contrast, for CDTB, which acts as a true RAFT agent in cationic polymerisation due to the stability of the R group cation, the reaction was well controlled and led to a polymer with low dispersity and a value of M_n which was in good agreement with the theoretical value. The fact that there was no measurable retardation in this experiment suggests that control is given exclusively by the RAFT mechanism. When BPCDT was used as RAFT agent, there was significant retardation of the polymerisation (see **Figure 6-13b**) although, unlike the reaction of styrene, polymerisation continued at longer reaction times, albeit at a slower rate than the initial period. In this case, despite the absence of fragmentation of the RAFT agent to benzyl cation, thus preventing the typical RAFT mechanism, the value of M_n was close to the theoretical value due to reversible addition to RAFT agent. For pMOS this is only the case for the dithiocarbamate due to the enhanced stability of the RAFT intermediate cation relative to the propagating pMOS cation.

Table 6-3: *Summary of polymerisations using pMOS in the presence of RAFT agents*

Run	Monomer	RAFT agent	Time	Conversion (%)	M_n (g/mol)	$M_{n,theo}$ (g/mol)	Đ
13	pMOS	None	20 sec	98	11,600	4,900[e]	1.9
14	pMOS	CDTB[a]	20 sec	98	2,000	2,200[e]	1.2
15	pMOS	DBTTC[b]	20 sec	97	10,100	4,900[f]	1.8
16	pMOS	BDTB[c]	20 sec	>99	12,100	5,000[f]	1.8
17	pMOS	BPCDT[d]	30 min	68	3,000	3,500[f]	1.9

[a]Cumyl dithiobenzoate. [b]S,S-dibenzyl trithiocarbonate. [c]Benzyl benzodithioate. [d]Benzyl 1H-pyrrole-1-carbodithioate. [e/f]The theoretical molecular weight values were calculated following the equation (e) $M_{n,theo} = M_{CTA} + \frac{XM_M[M]_0}{[CTA]_0+[I]_0}$ or (f) $M_{n,theo} = M_I + \frac{XM_M[M]_0}{[I]_0}$ with CTA the RAFT agent, M the monomer, I the initiator, X the fractional conversion, M_A the molar mass of the species A and $[A]_0$ the initial concentration of A.

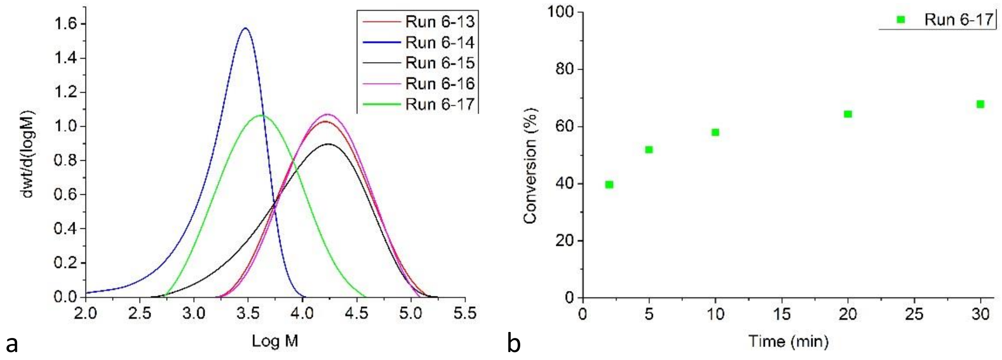
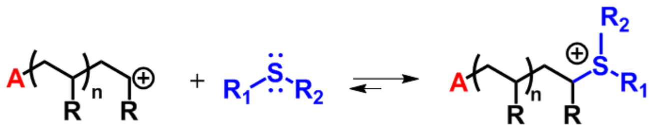


Figure 6-13: *(a) Final molecular weight distributions of poly(pMOS) synthesised without RAFT agent (Run 6-13, red) or using CDTB (Run 6-14, blue), DBTTC (Run 6-15, black), BDTB (Run 6-16, pink) or BPCDT (Run 6-17, green) as RAFT agents. (b) Evolution of the conversion with time for the polymerisation of pMOS performed in the presence of benzyl 1H-pyrrole-1-carbodithioate (Run 6-17).*

These observations can also be extended to alternative systems that have been proposed for the controlled cationic polymerisation of vinyl monomers. For example, it has been shown that when a good leaving group is used, thioethers can be used to control the polymerisation of vinyl ethers and pMOS *via* a degenerative chain transfer mechanism. However, particularly in the case that the propagating carbocation has limited stability, the intermediate cation can also act to improve control through generation of a sulfonium intermediate without the degenerative transfer step (see **Scheme 6-3**).



Scheme 6-3: *Mechanism for the formation of the sulfonium intermediate.*

This can be seen from the results in **Table 6-4**, which compares the polymerisation of styrene and pMOS in the presence of a series of thioethers that cannot generate stable carbocation species (*i.e.* they do not lead to degenerative chain transfer). In the case of styrene, the presence of diphenyl disulphide led to a significant decrease in the polymerisation rate and only 50% conversion was achieved in 24h. In this case, the low stability of the styrene carbocation drives the equilibrium in favour of the sulfonium intermediate, which reduces the polymerisation rate but results in improved control, even in the presence of low concentrations of the disulphide. In the case of pMOS, the sulphides had limited effect on conversion or molecular distribution at low concentrations, but at high concentrations led to a value of M_n that was much closer to the theoretical value determined by the [**1**]:[pMOS] ratio. The final molecular weight distributions of these polymers and the structures of the thioethers are shown in **Figure 6-14.**

Table 6-4: *Summary of polymerisations using pMOS in the presence of sulfides. T = 23 °C, 5 minutes reaction time for pMOS, 24 h for St. [**1**] = 0.02 M, [B(C_6F_5)$_3$] = 0.02 M for St and [B(C_6F_5)$_3$] = 0.005 M for pMOS.*

Run	Monomer	Sulphide	[Sulphide]	Conversion (%)	M_n (g/mol)	$M_{n,theo}$[a] (g/mol)	Đ
6-2	St	None	-	86	3,200	3,300	1.7
6-18		Phenyl disulphide	0.03	50	1,400	2,000	1.7
6-13	pMOS	None	-	98	11,600	4,800	2.0
6-19		Phenyl disulphide	0.03	>99	9,800	4,900	1.9
6-20			0.1	98	9,700	4,800	2.0
6-21			0.5	75	5,500	3,700	1.8
6-22		Diphenyl sulphide	0.03	>99	11,800	4,900	2.3
6-23			0.1	>99	11,000	4,900	2.4
6-24			0.5	>99	9,000	4,900	2.3
6-25		Dibenzyl sulphide	0.03	>99	9,700	4,900	2.1
6-26			0.1	>99	7,700	4,900	1.9
6-27			0.5	96	4,400	4,700	1.6

[a] The theoretical molecular weight values were calculated following the equation $M_{n,theo} = M_I + \frac{M_M[M]_0}{[I]_0}\frac{X}{100}$, with M the monomer, I the initiator, X the fractional conversion, M_Y the molar mass of Y and $[Y]_0$ the initial concentration of Y.

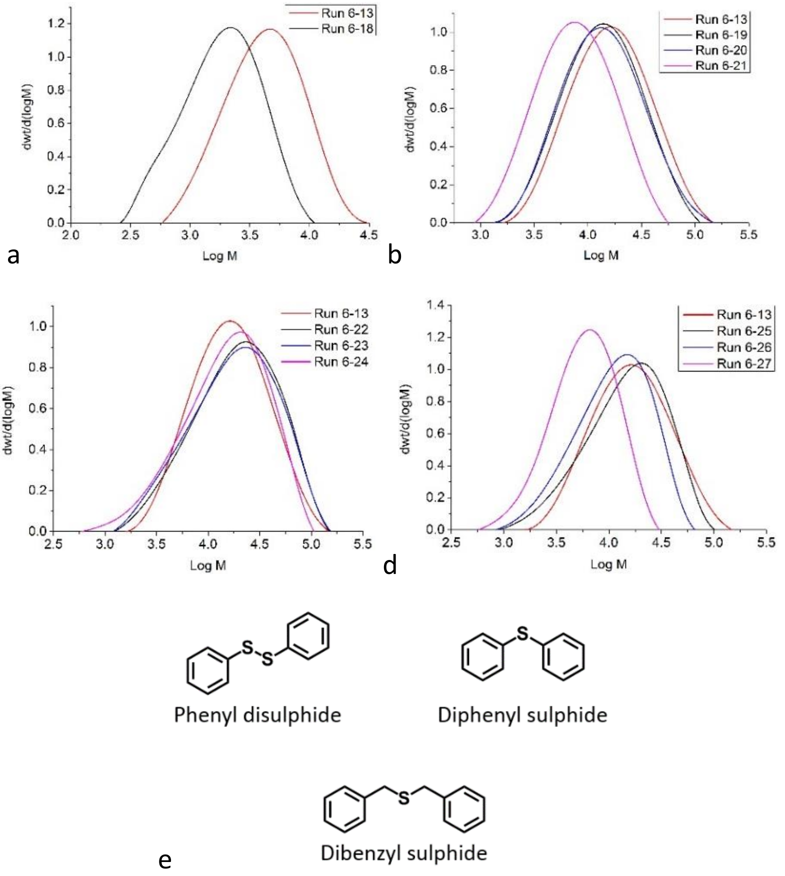


Figure 6-14: *(a to d) GPC traces of the final polymers obtained for the polymerisation of (a) styrene using phenyl disulphide and (b to d) pMOS using (b) phenyl disulphide, (c) diphenyl sulphide and (d) dibenzyl sulphide as RAFT agents with [RAFT] = 0 M (red), 0.03 M (black), 0.1 M (blue) and 0.5 M (pink). (e) Structures of the different thioethers used.*

Thus, cationic RAFT polymerisation, and in general degenerative chain transfer type polymerisations that pass through an intermediate cationic species, can lead to a dual control mechanism. On the one hand, degenerative chain transfer leads to rapid exchange of the propagating chain end which results in control through the classical RAFT-type mechanism. On the other hand, when an efficient initiating system is used, if the addition to RAFT agent is fast relative to propagation and the intermediate cation is relatively long lived, the equilibrium that is established between the active propagating carbocation and the dormant cationic intermediate can lead to a well controlled polymerisation. Using typical RAFT agents, this latter mechanism is particularly significant for carbocations with lower stability, such as styrene, and with RAFT agents that significantly stabilise the intermediate species, such as BPCDT. However, for monomers that give relatively more stable carbocations, such as pMOS and vinyl ethers, the control is largely governed by the conventional RAFT mechanism. These differences between monomer families are conceptually similar to radical RAFT polymerisation using “less activated monomers” such as vinyl acetate, in which the low stability of the vinyl acetate radical reduces fragmentation and leads to retardation or complete inhibition of the polymerisation for a number of RAFT agents.[61]

6.4. Conclusions

In conclusion, in the presence of typical RAFT agents, the cationic polymerisation of styrene proceeds with a linear evolution of the molecular weight but with a substantial decrease in the rate of polymerisation. The decreased rate of polymerisation is attributed to the reversible addition of the propagating carbocation to the RAFT agent, which leads to a dormant cationic intermediate that is slow to fragment. In the presence of a good leaving group in the RAFT agent, the presence of the RAFT group in the mass spectra clearly indicates that a degenerative chain transfer process is also occurring. However, even in the absence of a good leaving group on the RAFT agent, the reversible addition process can lead to improved control of the molecular weight distribution, with the initiator concentration controlling the molar mass. This occurs to a greater extent in styrene than other monomers that have previously been explored in cationic RAFT polymerisation due to the reduced stability of the propagating cation and opens a new mechanistic pathway for the use of RAFT agents to control cationic polymerisations.

6.5. References

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Chapter 7: Conclusions

This thesis aimed at understanding the potential and limitations of performing cationic polymerisation in the presence of water as well as in aqueous media. Due to the high water sensitivity of the most commonly used Lewis acid catalysts, coupled with the high reactivity shown by carbocations towards water, cationic polymerisations are usually performed at low temperatures and under strictly dry conditions. However, during the last decades, new Lewis acid catalysts that are tolerant to water have been reported and, as a result, the possibility to perform cationic polymerisations in the presence of water has emerged.

The synthesis of polymers in aqueous dispersed media reported so far in the literature can be divided in two groups; those that reach molecular weights below 10,000 g.mol^{-1} and, more recently, those able to obtain molecular weights well above this value (up to 1,000 kg.mol^{-1}). In this thesis, a selection of systems from the latter case, where unusually large molecular weights have been reported for cationic polymerisations, were re-evaluated. It was shown that previously reported polymerisations performed in aqueous dispersed media mediated by Lewis acid-surfactant complexes or Fe_2Cl_7 based ionic liquids that lead to very high molecular weights were in fact occurring *via* a radical process instead of a cationic one. Based on these results, a fundamental study of cationic polymerisation in aqueous media was undertaken, in which the influence of water was emphasised. This investigation showed that in addition to the intrinsic chain transfer reactions present in cationic polymerisation, reactions conducted in aqueous media are significantly affected by transfer reactions to water and therefore this polymerisation technique is inherently limited to the synthesis of low molecular weight polymers.

Although the presence of excess water was shown to limit cationic polymerisations conducted under mild conditions to lower molecular weight materials, this is not a major drawback since low molecular weight polymers make up a significant fractions of polymers produced commercially by cationic polymerisation. To explore potential of cationic polymerisations conducted in non-anhydrous conditions, the cationic polymerisation of low molecular weight poly(β-pinene) for use as tackifying agents was performed at room temperature using a water tolerant catalyst, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), without making any attempt to dry the reactants. It was observed that the amount of catalyst largely controlled the kinetics of the polymerisation. Despite the presence of a significant fraction of water, the use of an efficient initiator allowed for the control of the molecular weight. The control over the molecular weight allowed the use of the polymer in the formulation of a pressure sensitive adhesive (PSA) based on commercial triblock copolymer. It was demonstrated that the addition of 60 wt-% of the poly(β-pinene) in the adhesive led to a PSA with a performance comparable in terms of work of adhesion to the commercial petroleum-based tackifier Piccotac 1095 N.

In the low molecular region that is accessible for polymers synthesised by cationic polymerisation in the presence of water, the molecular weight and molecular weight distribution strongly influence the properties of the polymer. Therefore, in the last part of this work the use of RAFT agents to control the molecular weight of polymers produced by cationic polymerisation under mild conditions was explored. The cationic RAFT polymerisation of styrene was investigated using a $B(C_6F_5)_3$/R-OH initiator system and various RAFT agents. It was observed that the rate of polymerisation of styrene was greatly decreased in the presence of RAFT agents, which was ascribed to the addition of the propagating chain to the RAFT agent leading to the formation of stable dormant intermediates that were slow to fragment. Experiments conducted using RAFT agents that contain a poor leaving group for cationic polymerisation demonstrated that in the presence of an efficient initiator, this active/dormant equilibrium can be used to control the polymerisation, leading to linear chain growth with respect to conversion and narrow molecular weight distributions. Thus, in cationic polymerisations RAFT agents can induce control either through the conventional RAFT mechanism (*via* degenerative chain transfer) or a reversible addition process. This opens a new route to the control of cationic polymerisations.

The central aim of this work was to evaluate the potential and limitations of performing cationic polymerisation in the presence of water. Based on the initial chapters of this work it is clear that such systems are limited to the synthesis of fairly low molecular polymers but, as shown in the later chapters, such polymers can be of interest in commercial applications. Looking forward then it is worth considering what avenues are left to explore. The evidence presented in **Chapter 4** suggests that the search for catalyst systems that will produce very high molecular weight polymers in aqueous media, as has been the focus of so much work in the last 15 years, is likely to be a fruitless endeavour. In contrast, the development of efficient water-tolerant catalyst systems that target the synthesis of lower molecular weight polymers looks to have promise. A major issue with the use of the $B(C_6F_5)_3$ system that has been frequently used in this work is the cost relative to more commonly used Lewis acids such as $AlCl_3$. Future work could therefore be directed to the use of alternative Lewis acids, such as modified clays, that maintain the tolerance to water but are not prohibitively expensive for commercial use. With regards to monomer scope, one of the benefits of cationic polymerisation is that it is capable of polymerising monomers that cannot be polymerised by other means. This is the case of the β-pinene as reported in **Chapter 5** but could also be extended to the polymerisation of other bio-sourced monomers bearing electron-donor groups, such as β-methyl styrenes (i.e. anethole, isoeugenol), which would help the transition towards a greener, more sustainable polymer industry.

Finally, regarding cationic RAFT polymerisation, much of what has been done to date has tended to lead to systems that compound the negative aspects of both cationic and RAFT polymerisation. Thus, most cationic RAFT polymerisations have used relatively expensive RAFT agents and have also needed to be conducted under dry conditions and at low temperatures to minimise the influence of water and transfer reactions in general. However as shown here in **Chapter 6**, when targeting low molecular weight systems and when using water tolerant Lewis acids, water has relatively limited influence on the polymerisation. This, coupled with reports of alternative, cheaper RAFT agents for cationic polymerisation based on thioethers and phosphates suggests that there is potential to work towards taming cationic polymerisation for the synthesis of well-defined, low molecular weight polymers, which may find use in a range of applications.

List of Publications and Conference Presentations

1. List of Publications

A certain amount of this work has been published or is in preparation. In the latter case, variation in the title may occur.

Destephen, Aurélie; Lezama, Luis; Ballard Nicholas. Lewis acid-surfactant complex catalysed polymerization in aqueous dispersed media: cationic or radical polymerization? *Polymer Chemistry* **2020**, *11*, 5757-5766.

DOI: 10.1039/D0PY00363H

Destephen, Aurélie; González de San Román, Estíbaliz; Martínez-Tong, Daniel Enrique; Ballard Nicholas. Cationic Polymerization of β-Pinene Using $B(C_6F_5)_3$ as a Lewis Acid for the Synthesis of Tackifiers in Pressure Sensitive Adhesives. *Macromolecular Materials and Engineering* **2021**, *2100194*, 1-10.

DOI: 10.1002/MAME.202100194

Destephen, Aurélie; González de San Román, Estíbaliz; Ballard Nicholas. A Dual Control Mechanism in the $B(C_6F_5)_3$ Catalyzed Cationic Polymerization of Styrene Mediated by RAFT agents. *Submitted*.

Destephen, Aurélie; González de San Román, Estíbaliz; Ballard Nicholas. Limitations of Cationic Polymerization in the Aqueous Dispersed Media. *In preparation*.

2. Conference Presentations

During this PhD I had the opportunity to present some parts of this project in conferences and during the industrial liaison program (ILP) meeting.

2.1. Oral Presentation

Cationic Polymerisation in Aqueous Media Destephen, Aurélie; Ballard Nicholas. *19th Industrial Liaison Program*, UPV/EHU, Polymat, Donostia-San Sebastián, Spain, 2019.

2.2. Poster Presentations

Lewis Acid-Surfactant Complex Catalyzed Polymerization in Aqueous Dispersed Media: Cationic or Radical Polymerization? Destephen, Aurélie; Ballard, Nicholas. *European Polymer Congress*, Hersonissos Heraklion Crete, Greece, 2019.

Polymérisation cationique en milieu aqueux à l'aide de $B(C_6F_5)_3$ Destephen, Aurélie; Ballard, Nicholas. *36ème Club Emulsion*, Arkema-Colombe, France, 2019.

Resumen y Conclusiones

El desarrollo de los polímeros sintéticos al principio del siglo XX dió lugar a un cambio rápido en el diseño y la fabricación de un rango inmenso de productos, y actualmente los polímeros son parte de nuestro día a día. El impulsor de esa revolución fue el desarrollo de varias técnicas sintéticas para la producción de estructuras macromoleculares a partir de diferentes familias de monómeros, de cuales está la polimerización catiónica. La polimerización catiónica es un tipo de polimerización por crecimiento de cadena y está constituida por una etapa de iniciación, la adición rápida de los monómeros a un número pequeño de centros activos y la terminación de las cadenas por combinación de los centros activos con contraiones. Durante la polimerización también pueden ocurrir reacciones de transferencia de cadena con el monómero, polímero, agua u otras bases. Para poder estabilizar los cationes producidos durante la polimerización, es necesario que los monómeros tengan un grupo donante de electrones. Además, es necesario emplear un catalizador para activar la iniciación de la polimerización. Desde el descubrimiento de la polimerización catiónica, se han estudiado varias familias de catalizadores, de los cuales cabe destacar los ácidos de Lewis. Sin embargo, la mayoría de los catalizadores se degradan o se desactivan en presencia de agua y, por ello, las polimerizaciones catiónicas se suelen ejecutar en condiciones secas y a temperatura baja (-100 °C < T < -30 °C).

En las últimas décadas, se han descubierto nuevos catalizadores tolerantes al agua, como por ejemplo catalizadores combinados de surfactante y ácido de Lewis o líquidos iónicos, los cuales han posibilitado la polimerización catiónica en medios dispersos acuosos (suspensión, emulsión, miniemulsion) dando lugar a polímeros con pesos moleculares muy altos (hasta 1 000 kg.mol^{-1}). El objetivo de esta tesis es investigar las posibilidades de la polimerización catiónica a temperatura ambiente y en presencia de agua.

En primer lugar, utilizando trabajos previos como referencia, se estudió la polimerización catiónica del estireno y el *p*-metoxiestireno en emulsión y miniemulsion usando catalizadores combinados de surfactante y ácido de Lewis. Analizando la estructura de las cadenas de polímero y especialmente los extremos de cadena, se dedujo que las cadenas de polímero no tenían la estructura molecular típica de las cadenas sintetizadas por polimerización catiónica, sino la de polímeros sintetizados en polimerización por radicales libres. Además, utilizando esas condiciones de polimerización, no fue posible polimerizar monómeros que polimerizan exclusivamente mediante polimerización catiónica, mientras que el monómero metacrilato de metilo (MMA), que polimeriza únicamente mediante el mecanismo radicalario, sí formó polímero. Finalmente, un experimento de detección de radicales libres confirmó la presencia de radicales libres en el sistema, los cuales provenían del surfactante. De la misma manera, se investigó la polimerización de estireno en masa, en solución y en miniemulsion usando líquidos iónicos como catalizadores. Mientras que la polimerización en masa o en solución dio lugar a polímeros con pesos moleculares bajos (< 20 000 g.mol^{-1}), los polímeros producidos en miniemulsion presentaron pesos moleculares de hasta 219 000 g.mol^{-1}. La copolimerización de MMA con estireno en miniemulsion resultó en la formación de un copolímero y analizando también los extremos de cadena se concluyó que el mecanismo de polimerización de estireno en masa o en solución mediante líquidos iónicos fue catiónico, mientras que la polimerización en miniemulsion de estireno con líquidos iónicos tuvo lugar de forma radicalaria.

Teniendo en cuenta esos resultados, se examinó detalladamente la polimerización catiónica en medio acuoso, prestando especial interés en el efecto del agua. En primer lugar, se observó que al aumentar la temperatura de reacción, la relevancia de las reacciones de transferencia intrínsecas a la polimerización catiónica tales como la transferencia al monómero o al polímero aumentó, lo que limita el peso molecular final de las cadenas de polímero producidas mediante esta técnica de polimerización. Además, las reacciones en medio acuoso están significativamente afectadas por las reacciones de terminación o transferencia al agua, y por lo tanto, la polimerización catiónica está limitada a la síntesis de polímeros con bajo pesos moleculares.

Aunque el exceso de agua limita el peso molecular de los polímeros producidos por polimerización catiónica, esto no supone una limitación para su uso en productos comerciales, ya que una gran cantidad de polímeros con estas características son producidos mediante polimerización catiónica y utilizados industrialmente en diferentes aplicaciones. Para explorar el uso de los polímeros producidos por polimerización catiónica en aplicaciones industriales, se llevó a cabo la polimerización catiónica de β-pineno y se estudió la aplicación del poli(β-pineno) de bajo peso molecular producido como agente tackficante. Las síntesis se realizaron en condiciones no anhidras, a temperatura ambiente y usando un catalizador tolerante al agua, el tris(pentafluorofenil)borano ($B(C_6F_5)_3$). En primer lugar, se investigó la influencia de la concentración en iniciador y catalizador en las cinéticas de polimerización. Se concluyó que la velocidad de polimerización aumentó con la cantidad de catalizador mientras que la presencia del iniciador permitió el control del peso molecular. A continuación, se añadió el poli(β-pineno) sintetizado con un peso molecular de 1 000 $g.mol^{-1}$ a un copolímero tribloque comercial de poliestireno-*b*-poliisopreno-*b*-poliestireno para producir adhesivos sensibles a la presión. La adición de poli(β-pineno) permitió mejorar las propiedades adhesivos del film, siendo 60% en peso la concentración óptima para mejorar las propiedades. Además, las propiedades de este film fueron comparadas con las propiedades de un material análogo preparado con Piccotac 1095 N, un polímero producido a partir de petróleo empleado comúnmente como agente tackficante en la producción de adhesivos, presentando ambos films trabajos de adhesión similares.

En la región de pesos moleculares accesible por los polímeros sintetizados con polimerización catiónica en presencia de agua, el peso molecular y la distribución del peso molecular tienen un fuerte impacto sobre las propiedades del polímero. Por lo tanto, en la última parte de este trabajo se investigó el uso de agentes de adición-fragmentación reversible de transferencia de cadena (RAFT) para controlar el peso molecular de los polímeros producidos por polimerización catiónica en condiciones suaves. Se estudió la polimerización catiónica de estireno por RAFT usando un sistema iniciador de $B(C_6F_5)_3$/R-OH y varios agentes RAFT. La presencia de los agentes RAFT en la polimerización del estireno resultó en una disminución de la velocidad de propagación. Este fenómeno se puede explicar con la adición de la cadena propagadora al agente RAFT, que forma un intermedio catión inactivo más estable que el catión estireno, y se fragmenta lentamente. Los experimentos realizados con agentes RAFT con grupos “R” difíciles de fragmentar mostraron que en presencia de un iniciador eficaz, este equilibrio activo/inactivo se puede emplear para controlar la polimerización, dando lugar a un crecimiento de cadenas lineal con respeto a la conversión y una distribución de pesos moleculares estrecha. Por lo tanto, en polimerizaciones catiónicas los agentes RAFT pueden inducir un control a través del mecanismo convencional de RAFT (mediante una transferencia de cadena degenerativa) o por un proceso de adición reversible. Esto abre un nuevo camino para el control de las polimerizaciones catiónicas.