Block copolymers with polar and non-polar blocks : combination of living anionic polymerization and RAFT-mediated polymerization

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Block copolymers
with polar and non-polar blocks

Combination of living anionic polymerization and RAFT-mediated polymerization

Ellen Henrica Diana Donkers

Cover: Chinkultic disk, one of the first Maya ball court markers discovered, showing a ballplayer in a characteristic pose, kneeling to strike the ball with the heavy yoke about his waist and thighs. The Maya ballgame was played with rubber balls and confronted the Europeans with rubber for the first time in history.

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PROEFSCHRIFT

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Table of Contents

Glossary

ATRP	atom transfer radical polymerization
BuLi	butyllithium
DBU	1,8-diazobicyclo (5.4.0)undec-7-ene
DHBD	1,4-dihydro-2,3-benzodithiin
DIBTC	S-dodecyl S'-(isobutyric acid) trithiocarbonate
DRI	differential refractive index
ELSD	evaporative light scattering detector
f	initiator efficiency
GPEC	gradient polymer elution chromatography
I	initiator
k_d	dissociation rate constant
k_p	propagation rate constant
k_t	termination rate constant
k_{tr}	transfer rate constant
LC-MS	liquid chromatography-mass spectrometry
M_n	number average molecular weight
MAh	maleic anhydride
MALDI-ToF-MS	matrix assisted laser desorption-ionization time-of-flight mass spectrometry
MEK	methyl ethyl ketone
MWD	molecular weight distribution
NMP	nitroxide-mediated polymerization
NMR	nuclear magnetic resonance
P_n	number average degree of polymerization
P_w	weight average degree of polymerization
PB	polybutadiene
pBS	polybutadiene with short polystyrene block
PDI	polydispersity index
pEB	poly(ethylene-*co*-butylene)
PMDETA	N,N,N',N",N"-pentamethyldiethylenetriamine
PrLi	propyllithium

pSB	poly(styrene-*b*-butadiene)
pSEP	poly[styrene-*b*-(ethylene-*co*-propylene)]
RAFT	reversible addition-fragmentation chain transfer
SBC	styrenic block copolymer
SDS	styrene-diene-styrene
SEC	size exclusion chromatography
Sty	styrene
T_g	glass transition temperature
THF	tetrahydrofuran
TMEDA	N,N,N’,N’-tetramethylethenediamine
X	fractional conversion

1

Introduction

1.1 Rubber

Natural polymers such as cellulose, cotton and rubber have been recognized as useful materials for centuries. The first use of natural rubber can be traced back to Mesoamerican civilizations like the Aztecs and the Maya.[1] In the 16th century the Spanish Conquistadores saw them playing a ballgame with elastic balls. The Spanish were so astonished by the vigorous bouncing of the balls that they wondered if the balls were enchanted by evil spirits.

The Maya also used the rubber, which they obtained from the local rubber trees, for a sort of rubber shoes by dipping their feet into a latex mixture.

The first use of rubber when it was brought to Europe was as an eraser. In the 19th century, waterproof clothing and shoes became a success. Unfortunately, natural rubber was affected by cold weather, making it brittle, while in the sun, it tended to gum together. In 1839 Charles Goodyear succeeded in his attempts to improve on nature, by developing the vulcanization (or crosslinking) of rubber.[2] Vulcanization improves resilience and elasticity and prevents rubber from perishing. The treatment greatly improved the durability and utility.

Since applications were numerous and industry was booming at that time, the rubber industry was of great importance right from the start.

The importance of the rubber industry prompted much interest in discovering the chemical composition of rubber in order to synthesize the product.

The first commercial rubber was based on 2,3-dimethylbutadiene and produced by Bayer in 1909. The two World Wars gave an enormous impulse to the development of synthetic rubbers in order to gain independence from the natural rubber plantations.

A wide variety of synthetic rubbers has been developed since then. Their use is widespread now in a vast range of areas such as automobiles, footwear, plastics and hospital materials.

1.2 Thermoplastic elastomers[2;3]

Thermoplastic elastomers are a relatively new development in the rubber industry. In 1960, while all conventional (vulcanized) rubbers were already being sold and used in numerous applications, all thermoplastic elastomers yet had to be discovered.

In the 1950s anionic polymerization was developed,[4] which facilitated the synthesis of block copolymers. In 1961 researchers at Shell Chemical developed styrene-butadiene and styrene-isoprene block copolymers. These polymers offered a low-cost route for the production of thermoplastic elastomers. In the 1960s more systems consisting of hard polymer-elastomer block copolymers were developed, which all exhibited thermoplastic elastomeric properties. The basic requirement for a thermoplastic elastomer, a dispersed hard phase and a continuous elastomeric phase, was then established.

Thermoplastic elastomers have many of the physical properties of rubbers, *i.e.* softness, flexibility and resilience; but in contrast to conventional rubbers they are processed as thermoplastics.

Rubbers must be crosslinked to give useful properties. In the terminology of the plastics industry, vulcanization is a thermosetting process. This means it is slow and irreversible and takes place upon heating. With thermoplastic elastomers on the other hand, the transition from a processable melt to a solid rubber-like object is rapid and reversible and takes place upon cooling. Therefore thermoplastic elastomers can be processed in the melt using conventional polymer processing techniques such as injection moulding and extrusion. Moreover, since crosslinking is reversible, products and waste material are recyclable.

1.3 Styrenic block copolymers[5]

Styrenic block copolymers (SBCs) are the largest-volume category of thermoplastic elastomers with an annual production of about 1.2 million tons.

The properties of SBCs are closely related to their molecular structure. SBCs consist of (at least) three blocks: Two hard polystyrene blocks connected by a soft, elastomeric midblock. This midblock is usually polybutadiene or polyisoprene, either hydrogenated or not. The hard and soft blocks should be immiscible, so that microphase separation takes place. The polystyrene blocks form hard domains, which are dispersed in a continuous elastomeric phase formed by the soft midblocks. At room temperature these polystyrene domains are hard and act as physical crosslinks, forming a three-dimensional network. A schematic representation of the phase arrangement in SBCs is shown in Figure 1.1.

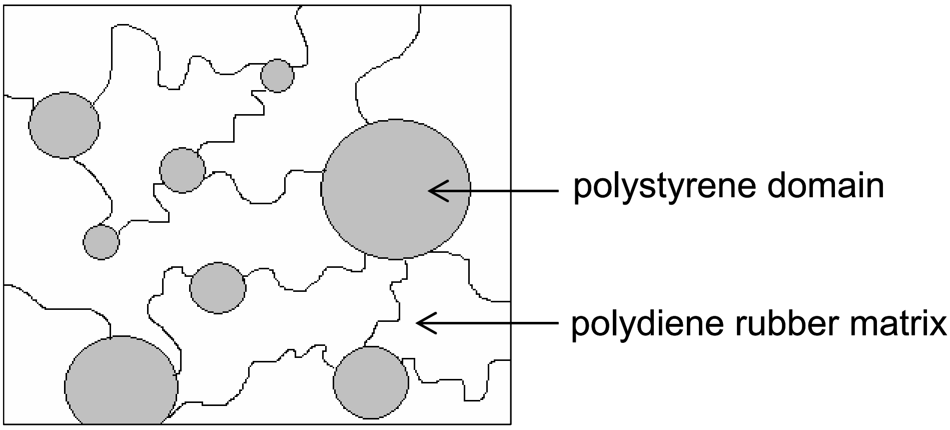


Figure 1.1. Schematic representation of the phase arrangement in styrenic block copolymers

When the temperature is raised above the glass transition temperature (T_g) of polystyrene, or when the material is dissolved, the polystyrene domains fall apart and the SBCs become processable as thermoplastics. When the material is cooled, or the solvent is evaporated, the polystyrene domains harden and the network regains its strength and elasticity.

SBCs exhibit good elastomeric properties. Tensile strength is higher than for unreinforced vulcanized rubbers. Elongation at break ranges from 500% to 1200% and resilience is comparable to that of vulcanized rubber.

Because SBCs become soft and flow when heated, the high temperature properties are inferior to those of vulcanized rubbers. Consequently, SBCs are usually not used in applications such as automobile tires. Instead, most of their applications are in areas where high temperature properties are less important.

SBCs are rarely used as pure materials, but can be readily mixed with other polymers, oil and fillers. SBCs are employed to enhance the performance of bitumen in road paving and roofing applications. Furthermore they are applied in coatings, adhesives and sealants and in footwear. Also, they can be compounded to produce materials that enhance grip, feel and appearance in, for example, toys, automotive and packaging.

1.4 Objective and outline of the thesis

Styrenic block copolymers (SBCs) are essentially non-polar materials, implying that they are miscible with other non-polar materials. Compatibility with polar materials is poor, which limits the range of applications for SBCs.

SBCs are produced via living anionic polymerization, resulting in polymers with a well-defined molecular weight and microstructure, and a narrow molecular weight distribution. The main drawback of living anionic polymerization is that the range of monomers that can be polymerized in a controlled way is limited to a small number of non-polar monomers. However, the incorporation of one or more polar blocks into SBCs is desirable to enhance compatibility with more polar materials such as nylon, ABS and cardboard, thereby increasing the application area.

The recent development of living radical polymerization techniques[6-9] has provided polymer chemists with novel tools to obtain well-defined polymer structures for a wide range of monomers, including polar ones.

The aim of the research work described in this thesis is to develop synthetic routes to obtain block copolymers containing non-polar and polar block(s) by combination of living anionic polymerization and living radical polymerization. The resulting block copolymers should exhibit the properties of thermoplastic elastomers.

We decided to combine living anionic polymerization with RAFT (reversible addition-fragmentation chain transfer) mediated polymerization, which is considered to be the most versatile living radical polymerization technique.

The approach used to synthesize the desired block copolymers consists of sequential living anionic and RAFT-mediated polymerization. A schematic representation of the different steps is shown in Figure 1.2.

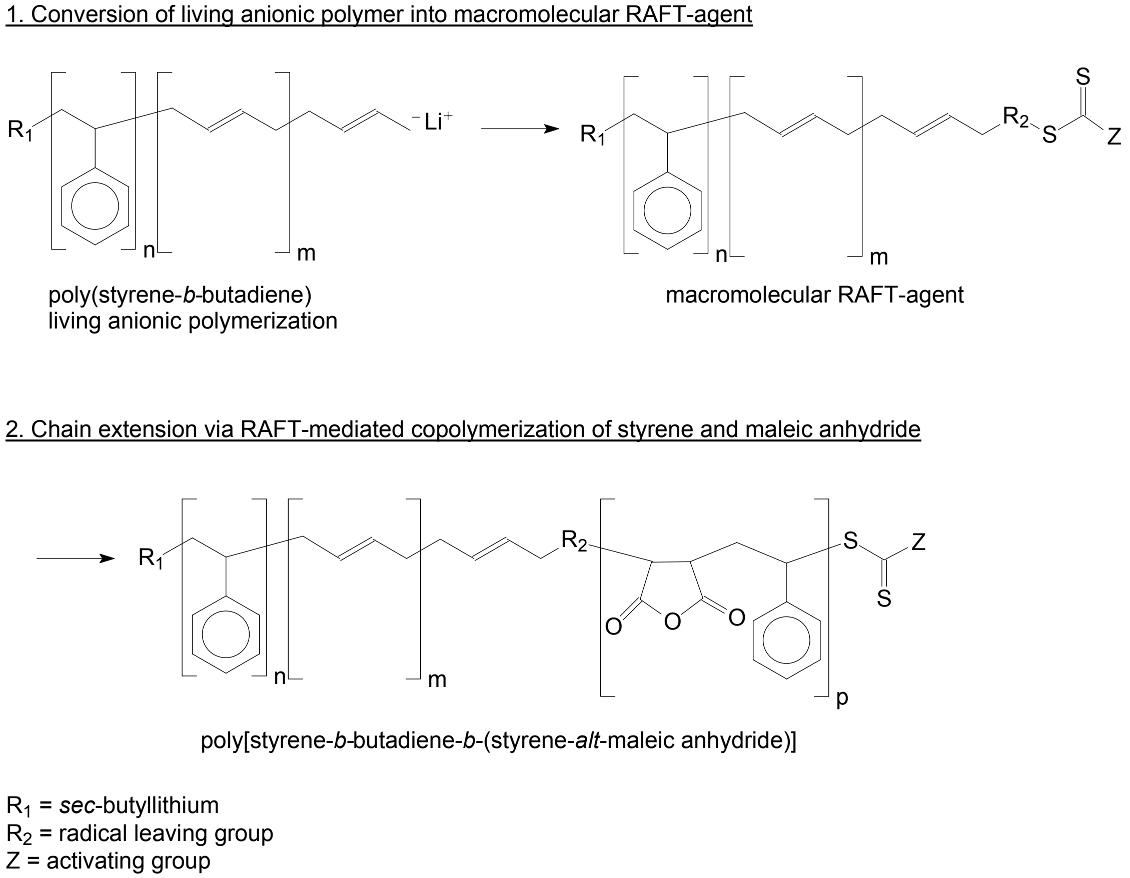


Figure 1.2. Synthesis of poly[styrene-*b*-butadiene-*b*-(styrene-*alt*-maleic anhydride)] by sequential living anionic polymerization and RAFT-mediated polymerization

First, poly(styrene-*b*-butadiene) is prepared by living anionic polymerization, as is the case for conventional SBCs. After that, instead of synthesizing another polystyrene block, the living anionic chain is converted into a macromolecular chain transfer agent. This transformation is the key step in combining living anionic polymerization and RAFT-mediated polymerization. The macromolecular chain transfer agent is designed in such a way that the poly(styrene-*b*-butadiene) acts as a polymeric radical leaving group in the subsequent polymerization step. In that polymerization step, the macromolecular chain transfer agent is employed in the RAFT-mediated copolymerization of styrene and maleic anhydride. After polymerization, a triblock copolymer is obtained with poly(styrene-*alt*-maleic anhydride) forming the polar third block.

Styrene and maleic anhydride were chosen as the monomer pair to form the polar block, because they form a hard block, which is highly polar and has a sufficiently high glass transition temperature (approximately 160 °C). Furthermore, styrene and maleic anhydride are known to readily polymerize in a controlled way via RAFT-mediated polymerization, providing alternating copolymers.[10-13] Finally, the anhydride groups are reactive towards different functional groups, providing the opportunity to tune the properties of the final material by post-polymerization reactions.

In **Chapter 2** a theoretical overview of living polymerization is presented. The principles of living anionic polymerization and living radical polymerization techniques are outlined. Furthermore, recent developments in the field of anionic polymerization and reports on the combination of anionic polymerization with living free radical polymerization are summarized.

Chapter 3 deals with the first step in the conversion of living anionic chains into macromolecular chain transfer agents. This step consists of the addition of a suitable radical leaving group to anionic polybutadiene by endcapping with various styrenic compounds.

After the addition of the leaving group, the chain end needs to be converted into the eventual chain transfer agent. Halides and mercaptans are the starting materials in the synthesis of trithiocarbonates, which are highly efficient RAFT-agents. **Chapter 4** describes the conversion of the chain-end carbanion into a halide or mercapto-functionality.

Chapter 5 focuses on a slightly more conventional approach to obtain macromolecular RAFT-agents. This approach consists of a two-step esterification procedure. The macromolecular RAFT-agents obtained via this approach were then employed in the RAFT-mediated copolymerization of styrene and maleic anhydride in order to obtain the desired block copolymers. Chapter 5 also describes the results for these copolymerizations.

To provide an alternative for the sequential approach described before, some feasibility studies on the use of "click chemistry" to obtain the desired block copolymers were performed. In this approach an alkyne-functional polymer is coupled to an azide-functional polymer via copper(I) catalyzed cycloaddition of the alkyne and azide groups. The results of the studies on click chemistry are presented in **Chapter 6.**

The **epilogue** highlights the most important findings described in this thesis. Also some recommendations for future research on this subject will be given.

References

1 http://en.wikipedia.org
2 Holden, G.; Kricheldorf, H.; Quirk, R. P. *Thermoplastic elastomers*; Munich: Hanser: **2004**.
3 Holden, G. Elastomers, Thermoplastic; *Encyclopedia of Polymer Science and Technology*; on-line publication **2002.**
4 Szwarc, M.; Levy, M.; Milkovich, R. *Journal of the American Chemical Society* **1956**, *78*, 2656-2657.
5 http://www.iisrp.com
6 Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559-5562.
7 Hawker, C. J.; Bosman, A. W.; Harth, E. *Chemical Reviews (Washington, D.C.)* **2001**, *101*, 3661-3688.
8 Matyjaszewski, K.; Xia, J. *Chemical Reviews (Washington, D.C.)* **2001**, *101*, 2921-2990.
9 Kamigaito, M.; Ando, T.; Sawamoto, M. *Chemical Reviews (Washington, D.C.)* **2001**, *101*, 3689-3745.
10 De Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 3596-3603.
11 Zhu, M. Q.; Wei, L. H.; Du, F. S.; Li, Z. C.; Li, F. M.; Li, M.; Jiang, L. *Chemical Communications (Cambridge, United Kingdom)* **2001**, 365-366.
12 Du, F. S.; Zhu, M. Q.; Guo, H. Q.; Li, Z. C.; Li, F. M.; Kamachi, M.; Kajiwara, A. *Macromolecules* **2002**, *35*, 6739-6741.
13 Chernikova, E.; Terpugova, P.; Bui, C.; Charleux, B. *Polymer* **2003**, *44*, 4101-4107.

2

Living polymerization

Living polymerization:
"A chain polymerization that proceeds in the absence
of chain transfer and termination steps"
(R.P.Quirk, 1992)[3]

2.1 Introduction

The first description of a living polymerization dates back to 1956, when Szwarc and coworkers[1] described the living nature of anionic styrene and diene polymerizations. Although anionic polymerization was the first system to be characterized as living, soon after, many different mechanisms for living polymerization were developed including cationic, radical, Ziegler-Natta and ring opening metathesis polymerization.
Living polymerizations offer versatile methodologies for the preparation of polymers with well-defined structures. A variety of molecular and structural parameters can be controlled such as molecular weight, molecular weight distribution, copolymer composition, stereochemistry and chain-end functionality.

In this chapter the main criteria that define a polymerization as living will be evaluated. The first and best-known living polymerization technique, living anionic polymerization, is discussed, followed by a description of several living radical polymerization techniques. These techniques have been developed during the last decade in order to combine the advantages of radical polymerization with those of living polymerization. Finally some approaches to combine living anionic polymerization with controlled radical polymerization techniques are discussed.

2.2 Criteria for living polymerization

Seven criteria[2;3] are used in practice to decide whether a polymerization can be classified as living. Those seven criteria are discussed briefly in the following section.

1. Polymerization proceeds until all monomer is consumed. Upon addition of a fresh amount of monomer, all chains continue to grow.

This criterion is the basis of the definition of living polymerization. Experimentally it can be verified by the determination of molecular weight and molecular weight distribution before and after the addition of the fresh amount of monomer. Normally, size exclusion chromatography (SEC) is used for these analyses.

If a polymerization is living, the molecular weight of the chains increases upon addition of monomer, and therefore elution times in SEC decrease. Furthermore, no residual starting polymer should be detected. Both termination and chain transfer reactions result in the presence of dead polymer, which will not grow and therefore is detected at lower molecular weight. In order to be able to interpret the SEC result properly, the final molecular weight distribution should not overlap with the distribution before the second monomer addition.

2. $\overline{M}_n$ (or degree of polymerization $\overline{P}_n$) increases linearly with conversion.

In a living polymerization, $\overline{M}_n$ is controlled by the stoichiometry and the degree of monomer conversion. $\overline{M}_n$ can be calculated according to Equation 2.1 when a polymerization is living:

$$\overline{M}_n = X \times \frac{m_{monomer}}{n_{initiator}} \qquad \textit{Eq 2.1}$$

Where $\overline{M}_n$ is the number average molecular weight, X is the fractional monomer conversion, $m_{monomer}$ is the total monomer mass and $n_{initiator}$ is the number of moles of initiator. This means that a linear relation between conversion and $\overline{M}_n$ should be observed. However, if termination occurs, the number of chains that are present will still be constant and the equation still holds.[4] Therefore, a linear relation of $\overline{M}_n$ with conversion can be used to indicate the absence of chain transfer reactions, but does not exclude termination. Hence, in itself this criterion can not be used to prove that a polymerization is living.

3. The number of polymer molecules is a constant, independent of conversion.

This criterion is not sensitive to termination reactions but just to chain transfer reactions in the same way as Criterion 2. Both criteria (2 and 3) are necessary but not sufficient to determine whether a system can be classified as living. They should be used in combination with a criterion that is sensitive to termination.

4. The molecular weight can be controlled by the stoichiometry of the reaction.

For a living polymerization system, equation 2.1 should hold, so the molecular weight is predetermined by the ratio of monomer to initiator. A prerequisite is the quantitative consumption of initiator before all monomer is polymerized. Deviations of the experimentally determined molecular weight from the theoretical molecular weight based on the stoichiometry can be caused by the presence of impurities, which would decrease the number of active centers. Moreover, termination by combination increases the experimentally determined molecular weight as compared to the

theoretical molecular weight, whereas chain transfer reactions decrease the experimental molecular weight.
The use of experimental molecular weight as criterion is limited by the error limits of the analytical methods used to determine its value.

5. Narrow molecular weight distribution polymers are produced.

Generally, it is possible to prepare a polymer with a narrow molecular weight distribution using a living polymerization when the rate of initiation is competitive with the rate of propagation. This condition ensures that all chains start growing at the same time. Slow initiation will broaden the molecular weight distribution. Another, more subtle, requirement for obtaining narrow molecular weight distribution polymers is that all active chain ends should be equally susceptible to reaction with monomer. So, if there is more than one type of active center and each type has a different propagation rate constant, the different species should be in rapid dynamic equilibrium so that all chains grow uniformly.
To obtain a narrow molecular weight distribution, no termination or chain transfer should occur. This is the *only* requirement directly related to the livingness of a polymerization. That means that even when a system is living, if one of the other requirements is not fulfilled, no narrow molecular weight distribution will be obtained. Therefore, the inability to produce polymers with a narrow molecular weight distribution does not necessarily mean that a polymerization is not living.

6. Block copolymers can be prepared by sequential monomer addition.

Next to being one of the most important synthetic applications, the ability to produce block copolymers is an experimental test for the livingness of polymers. This test is similar to the one described in Criterion 1. The result of the chain extension can also be verified via SEC.

7. Chain-end functionalized polymers can be prepared in quantitative yield.

In principle, in a living polymerization system all chains can be functionalized. However, most functionalization reactions do not proceed to give quantitative yield of functional polymer. Moreover, at high molecular weights, the accurate analysis of endgroups may be problematic.

In conclusion, different criteria have different sensitivities towards termination and chain transfer events, therefore a combination of several criteria is the best way of assessing the livingness of a polymerization.

2.3 Timescale of living polymerizations

A living polymerization does not necessarily have to retain its livingness indefinitely. It is generally assumed that the classification of a polymerization system as living is based on a laboratory timescale. That means no significant termination or chain transfer reactions occur within the normal time required to complete the polymerization and carry out any chemical reaction with the active chain ends, such as functionalization or chain extension.

Matyjaszewski[5] proposed some quantitative kinetic requirements:

$k_p/k_t > 10^4\ \mathrm{mol^{-1}L}$

$k_p/k_{tr} > 10^4$

where k_p is the propagation rate constant, k_t is the termination rate constant and k_{tr} is the chain transfer rate constant.

This implies that less than 10% of the chains would be deactivated in a time period of $t = 1000$ s.

2.4 Living anionic polymerization

2.4.1 Development of living anionic polymerization

The first reports describing processes which are currently recognized as anionic polymerization, appeared at the end of the nineteenth century. Several authors reported the formation of gums and resins produced under the influence of alkali metals. Deliberate activities in this field began in the first decades of the last century. A patent by Matthews and Strange[6] claimed polymerization of dienes initiated by metallic sodium.

In the next year there were a couple of reports on anionic polymerization (Harries,[7] Schlenk[8]). However, the mechanisms were not yet known, so the products of these polymerizations were described in vague terms.

During the following years, research on chain addition reactions was mainly directed to free radical polymerizations and interest in anionic polymerization was rather limited. However, two groups (Ziegler and Lebedev) continued their research on styrene and diene polymerization initiated by sodium metal, resulting in the production of synthetic rubber in the 1930s.

Sudden interest in anionic polymerization was raised in 1956 when two important papers were published. First, Szwarc[1] described the homogeneous electron-transfer-initiated polymerization of styrene and isoprene and demonstrated the absence of termination and chain transfer in this process, which led to the introduction of the concept of living polymerization. In the same year, Stavely[9] reported the discovery of the stereospecific polymerization of isoprene, initiated by metallic lithium in hydrocarbon solvents.

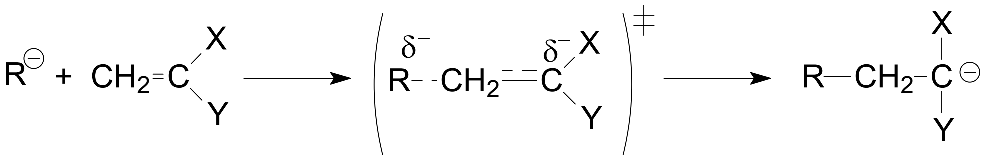
Today, living anionic polymerization still is a unique method for the synthesis of a wide variety of polymeric materials in a controlled way. The main drawback is that the high reactivity of carbanions towards contaminants such as oxygen, moisture and carbon dioxide requires ultra-pure reactants and solvents, specially designed equipment and appropriate techniques in order to avoid undesired termination of living chains

2.4.2 Principles of living anionic polymerization[2;10]

An anionic polymerization is classified as a living polymerization if any spontaneous termination and chain transfer steps are absent. In order to obtain polymers with predictable molecular weights and narrow molecular weight distributions it is required that the reaction is homogeneous throughout the polymerization, that the rate of initiation is higher than the rate of propagation and that all possible terminating impurities are excluded from the system.

Monomers

The monomers that are susceptible to anionic polymerization are the ones that form stable carbanionic species under polymerization conditions. For the most studied monomers, styrenes and dienes, this means that the double bond must have substituents X and Y (Scheme 2.1) that can stabilize the negative charge, making the anions stable to possible nucleophilic attack of other species.



Scheme 2.1. Living anionic polymerization

Moreover, the substituents themselves should be stable towards the anionic chain ends. Consequently, strongly electrophilic groups or relatively acidic proton-donating groups must be avoided or suitably protected. Polar substituents, such as carbonyl or cyano groups, may react with the initiator or with the propagating anionic species. Therefore, the living anionic polymerization of monomers that contain such groups is only possible under very specific reaction conditions including low temperatures and the use of bulky initiators. Monomers that have been successfully polymerized using anionic polymerization include styrenes, dienes, (meth)acrylates and vinylpyridines (the latter two at low temperatures), cyclic siloxanes, epoxides and lactones.

Initiators

The most versatile and widely used anionic initiators are alkyllithium compounds. Most of them are commercially available; they can be prepared relatively easily and they are soluble in various solvents, such as hydrocarbons.

The unique characteristic of the organolithium compounds is that the C-Li bond shows properties of both covalent and ionic bonds. The covalent character of the C-Li bond and the strong aggregation of the ionic pairs are responsible for the higher solubility of organolithium compounds in hydrocarbon solvents, compared to the solubility of the anions with other alkali metals as the counterion. However, it was found that in solution, organolithium compounds form aggregates. The structure of the organic moiety strongly influences the degree of aggregation. The degree of aggregation is also influenced by the nature of the solvent, the solution concentration and the temperature.

It was shown that the reactivity of the alkyllithium initiators is directly related to the degree of aggregation: the lower the degree of association, the higher the reactivity of the initiator. This is demonstrated by a comparison of the reactivity of various alkyllithium initiators for styrene and diene polymerizations. Between brackets the degree of aggregation is shown:

Menthyllithium (2) > *sec*-BuLi (4) > *i*-PrLi (4-6) > *t*-BuLi (4) > *n*-BuLi (6)

Initiation kinetics

The mechanism of initiation of anionic polymerization of vinyl monomers with alkyllithiums is complicated by association and cross-association phenomena in hydrocarbon solvents and by the presence of a wide variety of ionic species in polar solvents.

The rates of initiation of vinyl monomers in hydrocarbon solvents using alkyllithium initiators depend on the monomer, the initiator, the solvent and the temperature. Aromatic solvents increase the rate of initiation as compared to aliphatic ones. Generally, rates of initiation are increased by the addition of Lewis bases that facilitate the dissociation of alkyllithium aggregates.

Propagation kinetics

Like initiation kinetics, propagation kinetics are also complicated by the association of the polymeric chain ends into different aggregates. The aggregates are assumed to be unreactive towards monomer, while the small concentration of unaggregated species present is responsible for chain propagation. Lewis bases promote dissociation of the aggregates and thereby increase the rate of propagation. The addition of alkali metal oxides, except for lithium alkoxide, also accelerates propagation.

2.4.3 Recent progress in living anionic polymerization

During the last couple of years, research in the field of anionic polymerization has focused on four main areas:

1. Living anionic polymerization of (meth)acrylates[11-24]

   New initiator and ligand systems have been developed to enhance the control over polymerization and reactors were designed to facilitate the scale-up of the polymerization processes.

2. Use of functional monomers[25-46]

   The use of protection-deprotection strategies has received a lot of attention in order to broaden the range of monomers that can be used. Furthermore some advanced initiator systems were developed for the polymerization of functional monomers.

3. Chain-end and in-chain functionalization of (living) polymers[47-58]

   In the field of chain-end functionalization, functional initiators as well as functional terminating agents are employed, preferably without the need of a protecting group.

   In-chain functionalization is achieved either by using post-polymerization functionalization reactions, or functional monomers.

4. Macromolecular architectures[54;59-74]

   Many architectures were designed, including (multi)block copolymers, graft (co)polymers, star-branched (co)polymers and dendritic structures. Strategies developed include the use of multifunctional initiators and coupling agents.

2.5 Controlled radical polymerization

2.5.1 Development of controlled radical polymerization

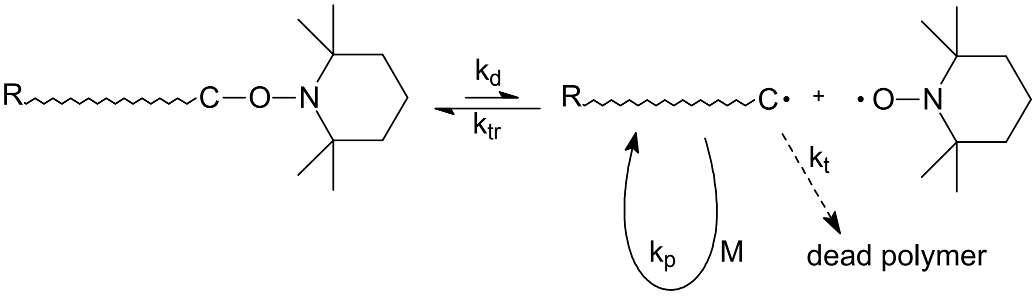
Free radical polymerization is one of the leading methods to produce polymers. It is a powerful and cheap technique, but it offers very little control over the molecular weight distribution and architecture of the polymers. For many applications it is desirable to have control over the polymer characteristics mentioned before. Therefore, the development of polymerization methods that combine the versatility and robustness of a free radical process with the control of living anionic polymerization has been a longstanding goal in polymer chemistry.

During the last two decades several techniques, referred to as controlled (or living) radical polymerizations have emerged, which are able to provide the desired control, using a free radical process. All of these methods are based on establishing a rapid dynamic equilibrium between a small amount of growing radicals and a large amount of dormant species. Since radicals are still present, next to propagation reactions, also termination reactions will occur. However, under appropriate conditions, the contribution of termination will be small and the radical polymerizations behave as nearly living systems.

Three important methods can be distinguished, Nitroxide-Mediated Polymerization (NMP)[75] and Atom Transfer Radical Polymerization (ATRP),[76;77] both based on reversible termination; and Reversible Addition-Fragmentation chain Transfer (RAFT) mediated polymerization,[78] based on reversible transfer. These methods will be described in the following sections.

2.5.2 Nitroxide-Mediated Polymerization

Nitroxide-mediated polymerization (NMP) was first introduced in 1985 by Solomon and Rizzardo,[79] but it really started to emerge as a new technique for radical polymerization in 1993 by the work of Georges[80] and Hawker.[81] NMP is based on the reversible trapping of carbon-centered radicals by nitroxides. A general mechanism is depicted in Scheme 2.2.



Scheme 2.2. Nitroxide-Mediated Polymerization, with k_d the dissociation rate constant, k_{tr} the trapping rate constant, k_p the propagation rate constant and k_t the termination rate constant.

The carbon-oxygen bond of the dormant alkoxyamine is thermally labile and at high temperatures can be homolytically cleaved to form a nitroxide and a carbon-centered radical. That radical can propagate or undergo termination or transfer reactions until it is trapped again by a nitroxide.

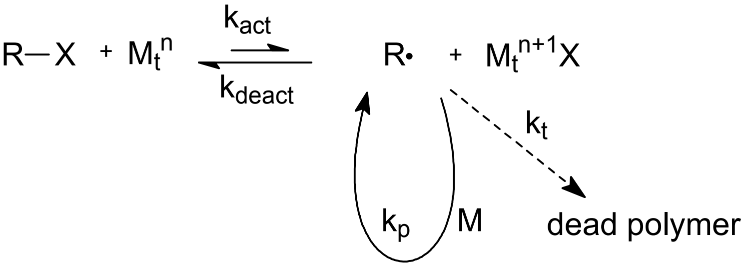
There are two ways of carrying out a nitroxide-mediated polymerization, either by using a conventional free-radical initiator and free nitroxide or by using an alkoxyamine, which acts as initiator and trapping agent. The control over the polymerization depends on different parameters, including the rates of activation and deactivation, the concentration of nitroxides, temperature and monomer type.

The main disadvantages of NMP are the elevated reaction temperatures that are often required (typically 120 °C) and the limited monomer range that can be polymerized in a controlled way, although recently some newly designed alkoxyamines have been used in the controlled polymerization of acrylates and dienes.[75]

2.5.3 Atom Transfer Radical Polymerization

Atom Transfer Radical Polymerization (ATRP) is based on atom transfer radical addition, a well-known reaction in organic chemistry. The first reports on ATRP date from 1995 by Matyjaszewski[82] and Sawamoto.[83]

In ATRP (Scheme 2.3) a halogen atom from an organic halide initiator is transferred to a transition-metal complex, which yields an organic radical and a transition-metal complex in a higher oxidation state. The radical formed can react with monomer or be reversibly deactivated by the transfer of halogen back from the metal complex. Of course, the radical can also undergo (undesired) termination or chain transfer reactions.



Scheme 2.3. Atom Transfer Radical Polymerization, with R-X an alkyl halide, M_t^n a metal complex, k_{act} the activation rate constant, k_{deact} the deactivation rate constant, k_p the propagation rate constant and k_t the termination rate constant

The fast exchange of the halogen between the complex and the propagating polymer in comparison with chain propagation, provides control over the polymerization.

Effective transition-metal couples include Cu(I)/Cu(II), Ru(II)/Ru(III), Fe(II)/Fe(III) and Ni(II)/Ni(III).[76;77] The metals are complexed by ligands to solubilize them and to establish a rapid equilibrium between active and dormant species.

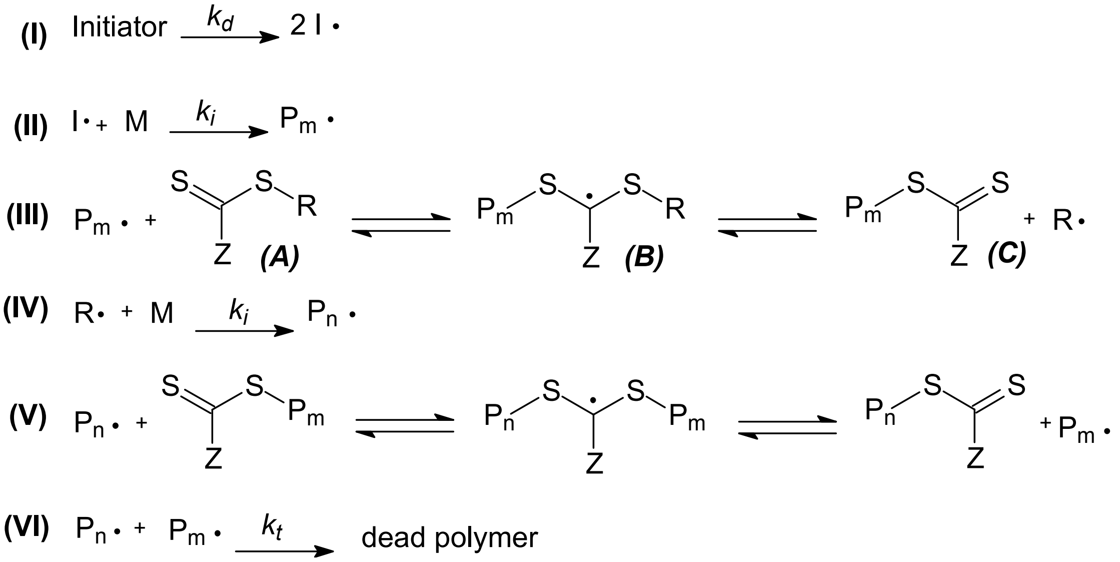
Organic halides that are often used as initiators include haloesters, (haloalkyl)benzenes and sulfonyl halides.

For ATRP the monomer range is broader than for NMP, but there are still some limitations, such as monomers that poison or complex the metal catalyst system, *e.g.* acid group containing monomers and maleic anhydride. A major drawback of ATRP is the contamination of the polymer with the metal catalyst. Removal of the catalyst is required for environmental and stability reasons, which makes the process less attractive for industry.

2.5.4 Reversible Addition-Fragmentation chain Transfer mediated polymerization

In 1998 the Reversible Addition Fragmentation chain Transfer (RAFT) process was reported by Rizzardo et al.[78;84] RAFT-mediated polymerization is based on a reversible chain transfer process by means of addition-fragmentation sequences. The discovery of thiocarbonylthio compounds as efficient transfer agents was the major breakthrough in the development of the RAFT-process.

The mechanism for RAFT-mediated polymerization is depicted in Scheme 2.4.



Scheme 2.4. Reversible Addition-Fragmentation chain Transfer mediated polymerization

Step I is the initiation step, which makes use of a classical free-radical initiator. The radical produced in the initiation step can directly add to chain transfer agent *(A)* or first add to monomer to form a propagating radical (step II). That radical can then add to RAFT-agent *(A)* (step III), forming an intermediate radical *(B)*. This intermediate radical can either fragment back to the starting materials or form a new propagating radical R· and a dormant polymer species *(C)*. The R radical reinitiates polymerization (step IV) to form a new propagating polymer chain. The dormant polymer species that still contains the thiocarbonylthio group acts as a chain transfer agent similarly as the initial RAFT-agent *(A)* (step V).

Because of the high transfer constants of the thiocarbonylthio compounds there is a fast exchange between dormant and active species and the radicals are exchanged among all polymer chains present in the system.

The structure of the initial RAFT-agent is essential for achieving a controlled polymerization. The leaving group R has to produce a radical R· that is more stable than the propagating radical in order to shift the pre-equilibrium (step III) to the right side. On the other hand the R· radical should be able to reinitiate polymerization rapidly.

The activating Z-group influences the stability of the intermediate radical and consequently the rate of addition of a growing radical to the transfer agent.

Excellent reviews on the role of the Z and R groups were published recently by Rizzardo et al.[85;86]

For a polymerization to behave in a living fashion, every polymer chain should grow at the same rate. In the case of RAFT-mediated polymerization, this means that the transfer of the thiocarbonylthio group should be fast as compared with propagation. Fast transfer ensures that a radical is exchanged rapidly among all polymer chains in the system, so that every chain has equal probability of addition to monomer. Therefore, all chains grow at the same rate.

Another important feature of a living polymerization is that the number of chains is constant during the course of the reaction. Since new chains are constantly created by means of initiator decomposition, the total amount of initiator should be low in comparison with the amount of RAFT-agent. For a RAFT-mediated polymerization equation 2.2. holds:

$$[\text{chains}] = [\text{RAFT}]_0 + 2f\left([\text{I}]_0 - [\text{I}]_t\right) \qquad \textit{Eq. 2.2}$$

So if $[I]_0$ is low compared to $[RAFT]_0$ the second term at the right side of the equation can be neglected and the number of chains can be assumed to be constant and equal to $[RAFT]_0$. The theoretical number average molecular weight is then given by equation 2.3:

$$\overline{M}_n = m_{RAFT} + \frac{[M]_0 \times m_{mon} \times X}{[RAFT]_0} \qquad \textit{Eq. 2.3}$$

Where $\overline{M}_n$ is the number average molecular weight, m_{RAFT} and m_{mon} are the molecular weight of the RAFT-agent and the monomer, $[M]_0$ and $[RAFT]_0$ are the initial monomer and RAFT-agent concentration and X is the fractional monomer conversion.

To obtain a narrow molecular weight distribution, all chains should start to grow at the same time. This implies that consumption of the initial RAFT-agent (*A*) should be fast to yield the dormant polymer species (*C*). Furthermore, the expelled radical R· should rapidly reinitiate polymerization to establish the main equilibrium (step V) as soon as possible.

RAFT-mediated polymerization is probably the most versatile of the commonly used controlled radical polymerization techniques. Polymerization of a wide range of monomers is possible in conjunction with a vast range of reaction conditions, even heterogeneous systems, such as emulsions.[87] Drawbacks of RAFT-mediated polymerization are the tedious procedures for the synthesis and purification of some of the RAFT-agents and the inhibition[88-91] and retardation[92-103] phenomena that are observed for some commonly used combinations of RAFT-agents and monomers.

2.6 Combination of living anionic polymerization and controlled radical polymerization

Traditionally, controlled macromolecular architectures such as block and graft (co)polymers are prepared by ionic polymerizations. The advent of controlled radical polymerization offers an alternative way to obtain these controlled structures and expand the monomer range that can be used. Many architectures can be obtained by using only controlled radical polymerization for the entire structure, so for all monomers. However, some monomers can not be polymerized via (controlled) radical polymerization. Designing a suitable combination of ionic and controlled radical polymerization can yield materials which incorporate these specific monomers. Usually, the first monomer is polymerized via an ionic mechanism followed by the conversion of the chain end (for block copolymers) or in-chain groups (for graft polymers) into functional groups that can act as initiating sites for the polymerization of the second monomer via a controlled radical mechanism.

Several examples of the combination of anionic polymerization with different controlled radical polymerizations can be found in recent literature.

Combination of living anionic polymerization with NMP has yielded block copolymers of anionically polymerized polybutadiene and poly(hexamethylcyclotrisiloxane) chain extended with styrene via NMP[104]. Block copolymers of anionically polymerized polystyrene, chain extended with acrylates using a specially designed alkoxyamine are reported as well.[105]

Graft copolymers have also been produced by combination of living anionic polymerization and NMP.[106] First, NMP is used to (co)polymerize p-chloromethylstyrene (with styrene) to yield a backbone polymer with a defined number of chlorine functionalities. Then, living poly(isoprenyl)lithium, polymerized by living anionic polymerization, is grafted onto this backbone, yielding various grafted structures.

The combination of living anionic polymerization with ATRP offers more possibilities than the combination with NMP with respect to the range of monomers that can be employed and various examples have been reported, ranging from the synthesis of block copolymers to more complex star-like structures.

Block copolymers have been prepared, using anionically polymerized and hydrogenated polybutadiene with a hydroxyl endgroup (Kraton L-1203).[107;108] This polymer was converted into a macro-initiator for ATRP by esterification with 2-bromoisobutyrylbromide. The initiator was used for the ATRP polymerization of methyl methacrylate to yield the block copolymer. In a slightly different approach to obtain block copolymers,[109;110] one starts with living anionic polystyrene, poly(styrene-*block*-butadiene) or poly(styrene-*block*-isoprene) which are endcapped with ethylene oxide or styrene oxide to produce the corresponding lithium alkoxides. These alkoxides are then esterified with compounds such as 2-bromoisobutyryl bromide and trichloroacetyl chloride[111] to yield the corresponding macro-initiators for ATRP. The macro-initiators are mainly used to polymerize methyl methacrylate. However, methyl acrylate, butyl acrylate, styrene/acrylonitrile and styrene are also reported as monomers for the ATRP polymerizations.

Liu et al.[112] report another strategy, which consists of the endcapping of living anionic polystyrene with α-methylstyrene and subsequent bromination of the chain end. The macro-initiator thus obtained is used to polymerize methyl methacrylate.

Very recently, some reports have been published on more exotic monomers and more complex structures. Some examples are di-, triblock, and star copolymers containing anionically polymerized poly(ethylene oxide) blocks,[113-117] block copolymers with a poly(ferrocenylsilane) block[118] and with poly(dimethylsiloxane) blocks.[119] In most cases these blocks are chain extended via ATRP with (meth)acrylates, but styrenic blocks are reported as well.

Combination of living anionic polymerization of vinylic monomers with RAFT-mediated polymerization would extend the monomer range even further. However, to our knowledge, this combination has only been reported once by De Brouwer et al.[120] This report describes the chain extension of anionically polymerized and hydrogenated polybutadiene with a hydroxyl endgroup (Kraton L-1203) with styrene/maleic anhydride via RAFT-mediated polymerization. Esterification of the OH-functional block with 4-cyano-4-[(thiobenzoyl)sulfanyl]pentanoic acid yielded a macromolecular chain transfer agent, which was used in subsequent RAFT-mediated polymerization.

References

1 Szwarc, M.; Levy, M.; Milkovich, R. *Journal of the American Chemical Society* **1956**, *78*, 2656-2657.

2 Hsieh, H. L.; Quirk, R. P. *Anionic polymerization: Principles and practice*; New York: Dekker: **1996**.

3 Quirk, R. P.; Lee, B. *Polymer International* **1992**, *27*, 359-367.

4 Penczek, S.; Kubisa, P.; Szymanski, R. *Makromolekulare Chemie, Rapid Communications* **1991**, *12*, 77-80.

5 Matyjaszewski, K. *Journal of Polymer Science, Part A: Polymer Chemistry* **1993**, *31*, 995-999.

6 Matthews, F. E. and Strange, E. H. **1910**, GB Patent 1024790.

7 Harries, C. *Ann.* **1911**, *383*, 157-227.

8 Schlenk, W.; Appenrodt, J.; Michael, A.; Thal, A. *Ber.* **1914**, *47*, 473-490.

9 Stavely, F. W. *Journal of Industrial and Engineering Chemistry (Washington, D.C.)* **1956** , *48*, 778-783.

10 Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 3211-3234.

11 Yu, Y.; Dubois, P.; Teyssie, P.; Jerome, R. *Macromolecules* **1997**, *30*, 4254-4261.

12 Baskaran, D.; Sivaram, S. *Macromolecules* **1997**, *30*, 1550-1555.

13 Jerome, R.; Teyssie, P.; Vuillemin, B.; Zundel, T.; Zune, C. *J.Polym.Sci., Part A: Polym.Chem.* **1999**, *37*, 1-10.

14 Marchal, J.; Gnanou, Y.; Fontanille, M. *Polym.Prepr.(Am.Chem.Soc., Div.Polym.Chem.)* **1997**, *38*, 473-474.

15 Nugay, N.; Nugay, T.; Jerome, R.; Teyssie, P. *J.Polym.Sci., Part A: Polym.Chem.* **1997**, *35*, 1543-1548.

16 Schlaad, H.; Schmitt, B.; Muller, A. H. E. *Angew.Chem., Int.Ed.* **1998**, *37*, 1389-1391.

17 Schmitt, B.; Schlaad, H.; Mueller, A. H. E. *Macromolecules* **1998**, *31*, 1705-1709.

18 Zundel, T.; Teyssie, P.; Jerome, R. *Macromolecules* **1998**, *31* , 2433-2439.

19 Ruckenstein, E.; Zhang, H. *Macromolecules* **1998**, *31*, 9127-9133.

20 Baskaran, D. *Progress in Polymer Science* **2003**, *28*, 521-581.

21 Raghunadh, V.; Baskaran, D.; Sivaram, S. *Journal of Polymer Science, Part A: Polymer Chemistry* **2004**, *42*, 875-882.

22 Liu, F.; Eisenberg, A. *Angewandte Chemie, International Edition* **2003**, *42*, 1404-1407.

23 Baskaran, D. *Macromolecular Chemistry and Physics* **2000**, *201* , 890-895.

24 Zhang, H.; Ruckenstein, E. *Macromolecules* **1998**, *31*, 7575-7580.

25 Foerster, S.; Kraemer, E. *Macromolecules* **1999**, *32*, 2783-2785.

26 Jankova, K.; Chen, X.; Kops, J.; Batsberg, W. *Macromolecules* **1998**, *31*, 538-541.

27 Hirao, A.; Nakahama, S. *Acta Polym.* **1998**, *49*, 133-144.

28 Hirao, A.; Loykulnant, S.; Ishizone, T. *Progress in Polymer Science* **2002**, *27*, 1399-1471.

29 Kitayama, T.; Katsukawa, K. i. *Polymer Bulletin (Heidelberg, Germany)* **2004**, *52*, 117-124.

30 Elkins, C. L.; Long, T. E. *Macromolecules* **2004**, *37*, 6657-6659.

31 Hirao, A.; Kitamura, M.; Loykulnant, S. *Macromolecules* **2004**, *37*, 4770-4775.

32 Ahn, J. H.; Shin, Y. D.; Kim, S. Y.; Lee, J. S. *Polymer* **2003**, *44*, 3847-3854.

33 Ishizone, T.; Han, S.; Okuyama, S.; Nakahama, S. *Macromolecules* **2003**, *36*, 42-49.

34 Ochiai, B.; Tomita, I.; Endo, T. *Macromolecular Rapid Communications* **2002**, *23*, 493-496.

35 Hirao, A.; Negishi, Y.; Hayashi, M.; Sako, K.; Ryu, S. W.; Loykulnant, S.; Matsuo, A.; Sugiyama, K. *Macromolecular Chemistry and Physics* **2001**, *202*, 3590-3605.

36 Loykulnant, S.; Yamashiro, M.; Hirao, A. *Macromolecular Chemistry and Physics* **2001**, *202*, 1791-1798.

37 Nossarev, G. G.; Hogen-Esch, T. E. *Macromolecules* **2001**, *34*, 5373-5375.

38 Hirao, A.; Kubota, S.; Sueyoshi, T.; Sugiyama, K. *Macromolecular Chemistry and Physics* **2001**, *202*, 1044-1052.

39 Peng, W.; Xie, Z. *Macromolecular Chemistry and Physics* **2000**, *201*, 1292-1294.

40 Ito, H.; Knebelkamp, A.; Lundmark, S. B.; Nguyen, C. V.; Hinsberg, W. D. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 2415-2427.

41 Sudo, A.; Uchino, S.; Endo, T. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 1073-1082.

42 Lehmann, O.; Forster, S.; Springer, J. *Macromolecular Rapid Communications* **2000**, *21*, 133-135.

43 Takeuchi, D.; Nakamura, T.; Aida, T. *Macromolecules* **2000**, *33*, 725-729.
44 Zhang, H.; Ruckenstein, E. *Macromolecules* **1999**, *32*, 5495-5500.
45 Sudo, A.; Uchino, S.; Endo, T. *Macromolecules* **1999**, *32*, 1711-1713.
46 Matsumoto, K.; Deguchi, M.; Nakano, M.; Yamaoka, H. *Journal of Polymer Science, Part A: Polymer Chemistry* **1998**, *36*, 2699-2706.
47 Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219-231.
48 Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J.Am.Chem.Soc.* **1995**, *117*, 3380-3388.
49 Hayashi, M.; Nakahama, S.; Hirao, A. *Macromolecules* **1999**, *32*, 1325-1331.
50 Hirao, A.; Hayashi, M. *Macromolecules* **1999**, *32*, 6450-6460.
51 Hirao, A.; Tohoyama, M.; Nakahama, S. *Macromolecules* **1997**, *30*, 3484-3489.
52 Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1998**, *31*, 3759-3763.
53 Tohyama, M.; Hirao, A.; Nakahama, S.; Takenaka, K. *Macromol.Chem.Phys.* **1996**, *197*, 3135-3148.
54 Jagur-Grodzinski, J. *Journal of Polymer Science, Part A: Polymer Chemistry* **2002**, *40*, 2116-2133.
55 Haraguchi, N.; Sakaguchi, Y.; Sugiyama, K.; Hirao, A. *Macromolecular Chemistry and Physics* **2001**, *202*, 2221-2230.
56 Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1997**, *30*, 5213-5219.
57 Hayashi, M. *Macromolecular Symposia* **2004**, *215*, 29-40.
58 Quirk, R. P.; Kim, H.; Polce, M. J.; Wesdemiotis, C. *Macromolecules* **2005**, *38*, 7895-7906.
59 Hirao, A.; Higashihara, T. *Macromolecular Symposia* **2004**, *215*, 57-65.
60 Higashihara, T.; Hirao, A. *Journal of Polymer Science, Part A: Polymer Chemistry* **2004** , *42*, 4535-4547.
61 Knauss, D. M.; Huang, T. *Macromolecules* **2003**, *36*, 6036-6042.
62 Hirao, A.; Hayashi, M.; Matsuo, A. *Polymer* **2002**, *43*, 7125-7131.
63 Hirao, A.; Higashihara, T. *Macromolecules* **2002**, *35*, 7238-7245.
64 Hirao, A.; Haraguchi, N. *Macromolecules* **2002**, *35*, 7224-7231.
65 Hirao, A.; Kawano, H.; Ryu, S. W. *Polymers for Advanced Technologies* **2002**, *13*, 275-284.
66 Higashihara, T.; Hayashi, M.; Hirao, A. *Macromolecular Chemistry and Physics* **2002**, *203*, 166-175.
67 Knauss, D. M.; Huang, T. *Macromolecules* **2002**, *35*, 2055-2062.
68 Hirao, A.; Hayashi, M.; Higashihara, T. *Macromolecular Chemistry and Physics* **2001**, *202*, 3165-3173.
69 Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chemical Reviews (Washington, D.C.)* **2001**, *101*, 3747-3792.
70 Hirao, A.; Tokuda, Y.; Morifuji, K.; Hayashi, M. *Macromolecular Chemistry and Physics* **2001**, *202*, 1606-1613.
71 Hirao, A.; Hayashi, M.; Haraguchi, N. *Macromolecular Rapid Communications* **2000**, *21*, 1171-1184.
72 Endo, T.; Ohshima, A.; Nomura, R.; Mizutani, Y. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 2543-2547.
73 Knauss, D. M.; Al Muallem, H. A.; Huang, T.; Wu, D. T. *Macromolecules* **2000**, *33*, 3557-3568.
74 Rye, S. W.; Hirao, A. *Macromolecular Chemistry and Physics* **2001**, *202*, 1727-1736.
75 Hawker, C. J.; Bosman, A. W.; Harth, E. *Chemical Reviews (Washington, D.C.)* **2001**, *101*, 3661-3688.
76 Matyjaszewski, K.; Xia, J. *Chemical Reviews (Washington, D.C.)* **2001**, *101*, 2921-2990.
77 Kamigaito, M.; Ando, T.; Sawamoto, M. *Chemical Reviews (Washington, D.C.)* **2001**, *101*, 3689-3745.
78 Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559-5562.
79 Solomon, D. H.; Rizzardo, E.; Cacioli, P. **1984**, EP 135280.
80 Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987-2988.
81 Hawker, C. J. *Journal of the American Chemical Society* **1994**, *116*, 11185-11186.
82 Wang, J. S.; Matyjaszewski, K. *J.Am.Chem.Soc.* **1995**, *117*, 5614-5615.
83 Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721-1723.
84 Chiefari, J.; Mayadunne, R. T.; Moad, G.; Rizzardo, E.; Thang, S. H. **1999**, WO 9931144.

85 Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273-2283.

86 Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256-2272.

87 Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromolecular Symposia* **2000**, *150*, 33-38.

88 Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. *Macromolecules* **2002**, *35*, 8300-8306.

89 McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2004**, *37*, 2383-2394.

90 McLeary, J. B.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Chemical Communications (Cambridge, United Kingdom)* **2004**, 1950-1951.

91 McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2005**, *38*, 3151-3161.

92 Monteiro, M. J.; De Brouwer, H. *Macromolecules* **2001**, *34*, 349-352.

93 Calitz, F. M.; Tonge, M. P.; Sanderson, R. D. *Macromolecules* **2003**, *36*, 5-8.

94 Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026-3029.

95 Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849-7857.

96 Coote, M. L.; Radom, L. *Journal of the American Chemical Society* **2003**, *125*, 1490-1491.

97 Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromolecular Theory and Simulations* **2002**, *11*, 823-835.

98 Calitz, F. M.; Tonge, M. P.; Sanderson, R. D. *Macromolecular Symposia* **2003**, *193*, 277-288.

99 Toy, A. A.; Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromolecules* **2004**, *37*, 744-751.

100 Kwak, Y.; Goto, A.; Fukuda, T. *Macromolecules* **2004**, *37*, 1219-1225.

101 Coote, M. L. *Macromolecules* **2004**, *37*, 5023-5031.

102 Feldermann, A.; Stenzel, M. H.; Davis, T. P.; Vana, P.; Barner-Kowollik, C. *Macromolecules* **2004**, *37*, 2404-2410.

103 Calitz, F. M.; McLeary, J. B.; McKenzie, J. M.; Tonge, M. P.; Klumperman, B.; Sanderson, R. D. *Macromolecules* **2003**, *36*, 9687-9690.

104 Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1998**, *31*, 3735-3739.

105 Yoshida, E.; Ishizone, T.; Hirao, A.; Nakahama, S.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3119-3124.

106 Tsoukatos, T.; Pispas, S.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 9504-9511.

107 Schellekens, M. A. J.; Klumperman, B.; van der Linde, R. *Macromolecular Chemistry and Physics* **2001**, *202*, 1595-1601.

108 Waterson, C.; Haddleton, D. M. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **1999**, *40*, 1045-1046.

109 Liu, B.; Liu, F.; Luo, N.; Ying, S. K.; Liu, Q. *Chinese Journal of Polymer Science* **2000**, *18*, 39-43.

110 Acar, M. H.; Matyjaszewski, K. *Macromol.Chem.Phys.* **1999**, *200*, 1094-1100.

111 Liu, F.; Ying, S.; Luo, N.; Liu, B.; Liu, Q. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **1999**, *40*, 1032-1033.

112 Liu, F.; Liu, B.; Luo, N.; Ying, S.; Liu, Q. *Chemical Research in Chinese Universities* **2000**, *16*, 72-77.

113 Mahajan, S.; Renker, S.; Simon, P. F. W.; Gutmann, J. S.; Jain, A.; Gruner, S. M.; Fetters, L. J.; Coates, G. W.; Wiesner, U. *Macromolecular Chemistry and Physics* **2003**, *204*, 1047-1055.

114 Mahajan, S.; Cho, B. K.; Allgaier, J.; Fetters, L. J.; Coates, G. W.; Wiesner, U. *Macromolecular Rapid Communications* **2004**, *25*, 1889-1894.

115 Peleshanko, S.; Jeong, J.; Shevchenko, V. V.; Genson, K. L.; Pikus, Y.; Ornatska, M.; Petrash, S.; Tsukruk, V. V. *Macromolecules* **2004**, *37*, 7497-7506.

116 Hou, S.; Chaikof, E. L.; Taton, D.; Gnanou, Y. *Macromolecules* **2003**, *36*, 3874-3881.

117 Grubbs, R. B. *Macromolecular Chemistry and Physics* **2005**, *206*, 625-627.

118 Korczagin, I.; Hempenius, M. A.; Vancso, G. J. *Macromolecules* **2004**, *37*, 1686-1690.

119 Pyun, J.; Jia, S.; Kowalewski, T.; Matyjaszewski, K. *Macromolecular Chemistry and Physics* **2004**, *205*, 411-417.

120 De Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 3596-3603.

3

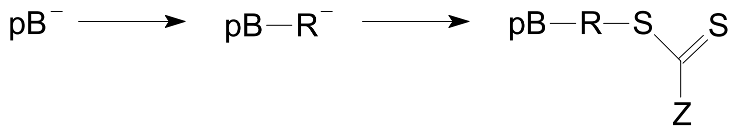
Chain end modification of living anionic polybutadiene with diphenylethylenes and styrenes

This chapter is based on:

Donkers, E. H. D.; Willemse, R. X. E.; Klumperman, B. *Journal of Polymer Science, Part A: Polymer Chemistry* **2005**, *43*, 2536-2545.[1]

3.1 Introduction

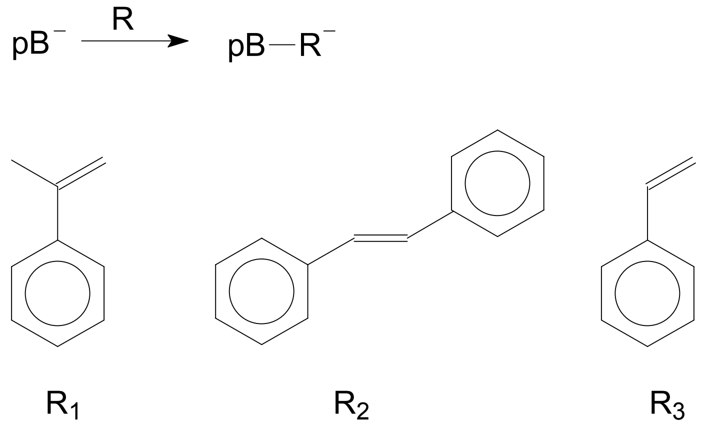
As described in Chapter 1, the objective of our work is to make block copolymers by combination of living anionic polymerization and living radical polymerization.
Our first approach to obtain these block copolymers is sequential living anionic polymerization and RAFT-mediated polymerization. This approach requires one or more transition steps *i.e.* chain end modifications, to change from anionic to RAFT-mediated polymerization. In our case, this means that the chain end carbanion has to be converted into a RAFT-group. More specifically, for polybutadiene, (anionically polymerized and initiated by *sec*-butyllithium) the first step is the modification of the poly(butadienyl) anion into a good leaving/reinitiating group for RAFT-mediated polymerization (first step in Scheme 3.1). Subsequently, one or more chain end modification steps are required to eventually obtain the desired RAFT-agent.



Scheme 3.1. Multi-step chain end modification of polybutadiene (PB)

The capping of poly(butadienyl)lithium with a styrenic group would be very suitable to introduce a good leaving group at the chain end. The capping reaction with styrene (derivatives) would lead to a good leaving group at the chain end while maintaining a highly reactive carbanion at the chain end that can participate in subsequent modification steps to yield a macromolecular RAFT-agent with a polymeric leaving group.

We investigated three different capping agents, which are shown in Scheme 3.2.



Scheme 3.2. Capping agents used for the modification of anionic polybutadiene, R_1: α-methylstyrene, R_2: *trans*-stilbene, R_3: styrene

The choice of the capping agents shown in Scheme 3.2 was based on two main criteria. Most importantly, the endcapping efficiency should be high to obtain a high yield of macromolecular RAFT-agent and, eventually, of block copolymer. Furthermore, it should be noted that compounds used as capping agents preferably do not polymerize under the conditions used for the capping reactions.

The three different chain end modifications, with α-methylstyrene, 1,2-diphenylethylenes and styrene, are discussed in this chapter. For each modification reaction, the influence of Lewis bases on the progress of the reaction is evaluated.

Lewis bases are known to have a very strong influence on reaction rates in anionic polymerization because they change the association behavior of organolithium compounds.[2] Two Lewis bases of different strength were used: THF (tetrahydrofuran) and TMEDA (N,N,N',N'-tetramethylethenediamine).

In the analysis of the polymers we used MALDI-ToF-MS as the main technique to determine the molar mass, the endgroups[3-6] and the chemical composition distribution[7] of the polymers obtained. The results for each functionalization agent will be discussed separately, starting with α-methylstyrene, followed by the diphenylethylenes and finally styrene.

3.2 α-Methylstyrene

Earlier results from literature[8] about the use of α-methylstyrene as capping agent for living anionic polystyrene indicate that one α-methylstyrene unit can be added to living anionic polybutadiene, in such a way that all chains bear one α-methylstyrene unit at the chain end and a narrow molecular weight distribution is retained. However, α-methylstyrene can be polymerized anionically below the ceiling temperature of 60 °C. We therefore investigated the capping reaction of living anionic polybutadiene with α-methylstyrene at temperatures above the ceiling temperature for α-methylstyrene.

Liu *et al.*[8] report on the use of α-methylstyrene in endcapping polystyrene. The authors report that the addition of THF as Lewis base theoretically should increase reaction rates. However, they did not find the expected rate enhancement experimentally. Based on ^{1}H-NMR analysis, Liu *et al.* conclude that the capping reaction was completed within 30 minutes, regardless of the presence of THF. We investigated the reaction of poly(butadienyl)lithium with α-methylstyrene under the reaction conditions displayed in Table 3.1.

Table 3.1. Reaction conditions for the endcapping of poly(butadienyl)lithium with α-methylstyrene

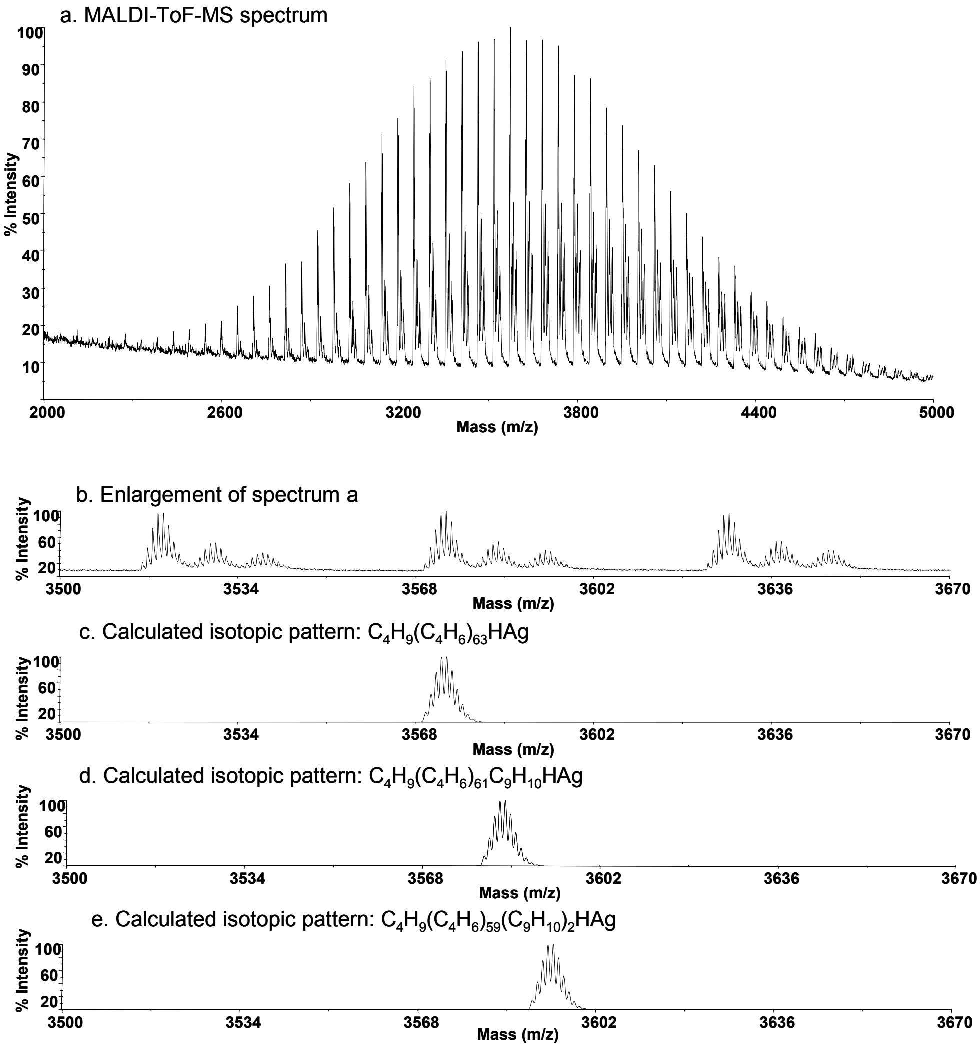
Entry	**Lewis base**	**[α-methylstyrene]/ [s-BuLi]**	**[Lewis base]/ [s-BuLi]**	**Temperature (°C)**
MS-1	-	2	-	65
MS-2	THF	2	2	65
MS-3	THF	2	2	75
MS-4	THF	2	3	75
MS-5	TMEDA	2	2	65

All samples were analyzed with MALDI-ToF-MS to determine the chemical composition of the polymers. A typical mass spectrum is shown in Figure 3.1a.
Careful analysis of the MALDI-ToF-MS spectra revealed that when no Lewis base was added (MS-1, Table 3.1) no α-methylstyrene endgroups could be observed. This result corresponds with earlier reports on the endcapping reaction with 1,1-diphenylethylene,[9] which proceeds readily for poly(styryl)lithium, but requires the addition of a Lewis base for poly(butadienyl)lithium. Adding THF (MS-2, 3 and 4, Table 3.1) led to a small number of chains with one α-methylstyrene unit at the chain end, but also to chains with two, three or four α-methylstyrene units. A relatively large amount of non-functional polybutadiene was also detected. Performing the endcapping reaction in the presence of TMEDA (MS-5, Table 3.1) resulted in more functionalized material. TMEDA is expected to have a larger effect on the endcapping reaction than THF, since it is a more powerful ligand for organolithium compounds.[2] Figure 3.1a shows the mass spectrum for polybutadiene after endcapping with α-methylstyrene in the presence of TMEDA.

The spectrum is built up of three individual distributions. In order to resolve the structures of the reaction products corresponding to these distributions, the theoretical masses of the most likely reaction products were calculated according to Equation 3.1.

$$m_{th} = x_a M_a + E_1 + E_2 + M^+ \qquad \textit{Eq 3.1}$$

This equation calculates the mass of a single charged polymer via summation of the mass of the number (x_a) of monomer units (M_a), the masses of the endgroups (E_1 and E_2) and the mass of the cationization agent (M^+).


a. MALDI-ToF-MS spectrum

b. Enlargement of spectrum a

c. Calculated isotopic pattern: $C_4H_9(C_4H_6)_{63}HAg$

d. Calculated isotopic pattern: $C_4H_9(C_4H_6)_{61}C_9H_{10}HAg$

e. Calculated isotopic pattern: $C_4H_9(C_4H_6)_{59}(C_9H_{10})_2HAg$

Figure 3.1.

a. MALDI-ToF-MS mass spectrum of polybutadiene after reaction with α-methylstyrene (MS-5, Table 3.1). Ag^+ was used as the cationization agent

b. an enlargement of Figure 3.1a between 3500 and 3670 g/mol

c-e. calculated isotopic patterns for polybutadiene, polybutadiene with an α-methylstyrene endgroup and polybutadiene with two units of α-methylstyrene at the chain end

The theoretical isotopic patterns were compared with the measured spectrum in order to get an insight into the composition of the reaction products (Figure 3.1b-e). In addition to the desired product with one α-methylstyrene unit at the chain end (compare Figure 3.1b and d), a significant amount of unmodified polybutadiene was still detected (compare Figure 3.1b and c) and products with more than one α-methylstyrene unit were also found (compare Figure 3.1b and e). So, addition of a Lewis base as strong as TMEDA did improve the reaction, but still no quantitative degree of functionalization could be obtained and oligomerization of α-methylstyrene was observed. The ceiling temperature for α-methylstyrene is 60 °C, so reactions were carried out above that temperature, but this did not completely prevent polymerization of α-methylstyrene, causing the formation of chains with more than one α-methylstyrene unit at the chain end. Because reactions had to be carried out at these high temperatures, the effect of the Lewis base is not as strong as at lower temperatures.[2] This may explain the relatively low degree of functionalization.

3.3 Diphenylethylenes

The second capping reaction we investigated makes use of 1,2-diphenylethylenes, more commonly known as *cis*-stilbene and *trans*-stilbene. These compounds are members of the class of diphenylethylenes, just like 1,1-diphenylethylene. It is known that diphenylethylenes do not homopolymerize under normal conditions for living anionic polymerizations.[10-12] However, *trans*-stilbene does participate as a comonomer in living anionic polymerization.[10;12] In the chain-end functionalizations no other monomer is present, so the stilbenes are supposed to react in a similar way as 1,1-diphenylethylene with polymeric organolithium compounds, *i.e.* quantitatively and with complete selectivity for addition of only one stilbene unit.[9;13;14] Therefore, the addition of 1,2-diphenylethylenes to *s*-butyllithium initiated living anionic polybutadiene should yield polybutadiene with one 1,2-diphenylethylene unit at each chain end, implying that a dienyl anion is quantitatively transformed into a styryl-like anion.

Different Lewis bases were added to promote the reaction, and temperature was adjusted to optimize the effect of the added Lewis base. Reaction conditions are collected in Table 3.2.

Table 3.2. Reaction conditions for the endcapping of poly(butadienyl)lithium with *trans*-stilbene

Entry	**Lewis base**	**[*trans*-stilbene]/ [s-BuLi]**	**[Lewis base]/ [s-BuLi]**	**Temperature (°C)**
TS-6	-	2	-	65
TS-7	THF	2	2	65
TS-8[a]	TMEDA	2.5	2	25
TS-9	TMEDA	2.5	2	40
TS-10	TMEDA	2.5	2	50
TS-11	TMEDA	5	2	50
TS-12	TMEDA	2	5	50
TS-13	TMEDA	2	1	50
TS-14	PMDETA	2	2	50

[a] In entries TS 8-14, *trans*-stilbene was dissolved in THF before addition to the living polymer solution

All samples were analyzed with MALDI-ToF-MS in the same way as the α-methylstyrene experiments. Figure 3.2 shows a typical MALDI-ToF-MS spectrum.

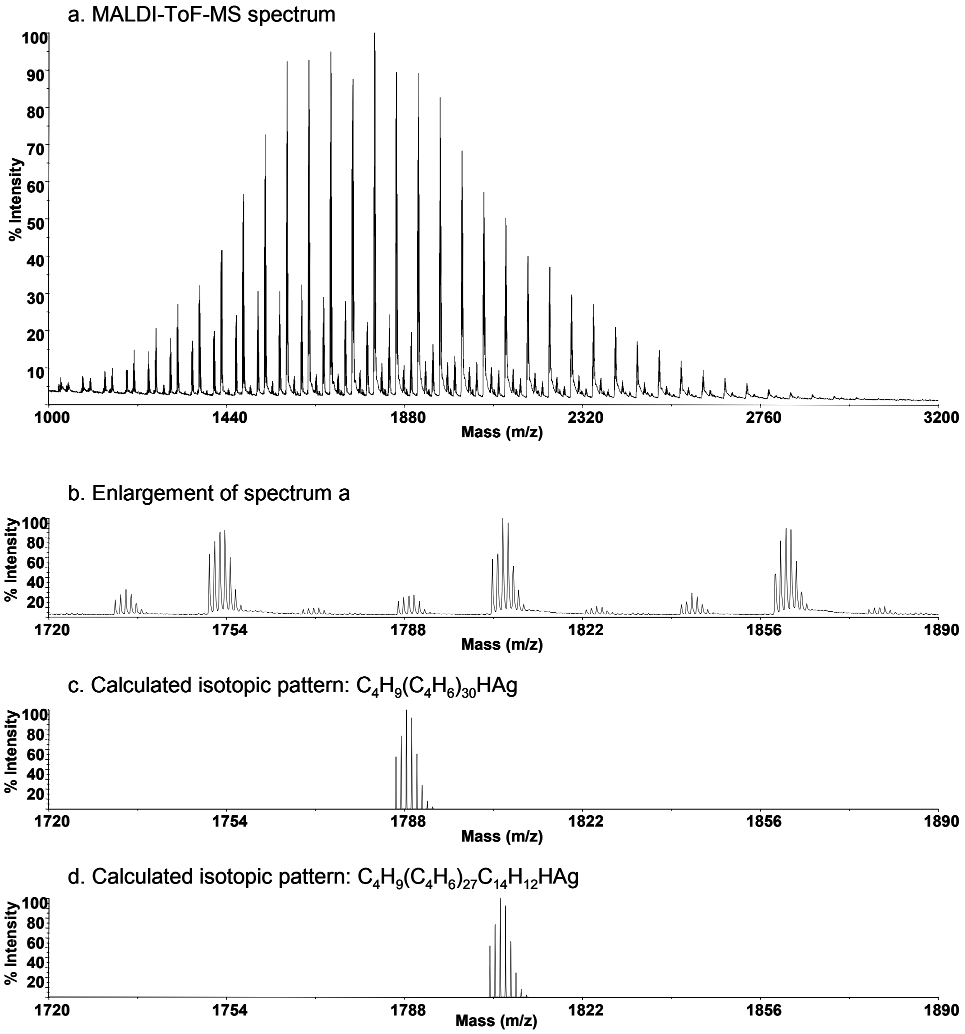


Figure 3.2.

a. MALDI-ToF-MS mass spectrum of polybutadiene after endcapping reaction with *trans*-stilbene (TS-12, Table 3.2)

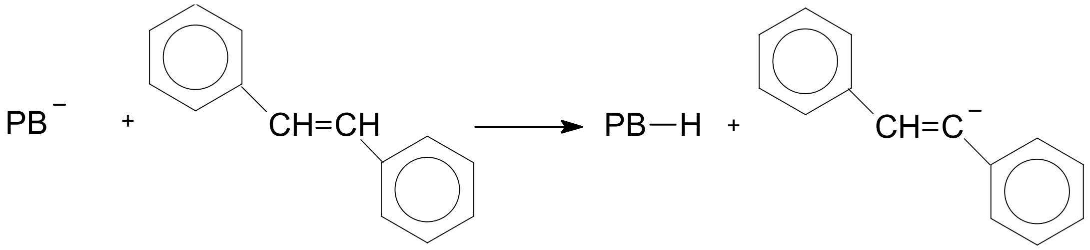
b. an enlargement of Figure 3.2a between 1720 and 1890 g/mol

c-d. calculated isotopic patterns of polybutadiene and polybutadiene with *trans*-stilbene endgroup

Two overlapping distributions can be observed (Figure 3.2a). Again, we compared the experimentally obtained masses with the theoretical masses of the most likely reaction products. In addition to the signals corresponding to polybutadiene with one *trans*-stilbene unit attached to the chain (compare Figures 3.2b and d), some non-functional polybutadiene was also detected (compare Figures 3.2b and c). As expected, no oligomerization of *trans*-stilbene was observed. We tried to optimize the reaction conditions by choosing the most effective Lewis base (TS 6-8 and 14, Table 3.2).

TMEDA gave the best results, although PMDETA is expected to be a stronger ligand. Further optimization by variation of temperature and reactant concentrations (TS 8-13, Table 3.2) did not result in quantitative functionalization *i.e.* no residual non-functional polybutadiene. Reactions with *cis*-stilbene gave similar results, whereas control reactions with 1,1-diphenylethylene in the presence of TMEDA, yielded quantitative functionalization in a couple of hours.

A striking feature of the reactions with 1,2-diphenylethylenes was a gradual color change from red at short reaction times to deep purple at longer reaction times (typically more than two hours). This color change was reported previously for reactions of *trans*-stilbene with *n*-butyllithium in THF[11] and for copolymerizations of *trans*-stilbene and styrene in THF.[12] When using benzene for the same reactions no change in color was observed.[15] A proposed cause for the observed color change is the abstraction of one of the relatively acidic methine protons from *trans*-stilbene by the anion. In the case of a *trans*-stilbene/styrene copolymerization, this results in chain transfer. In our case, where *trans*-stilbene was the only monomer present, proton abstraction means termination of the living chains (Scheme 3.3).



Scheme 3.3. Hydrogen abstraction from *trans*-stilbene by living anionic polybutadiene (PB)

As mentioned earlier, this reaction is observed in THF but not in benzene. Since we used cyclohexane as the solvent, we expected a behavior similar to that in benzene. However, significant amounts of Lewis base (TMEDA and/or THF) were added, which may have promoted the transfer reaction. If this reaction did indeed occur, it competes with the addition of *trans*-stilbene to the anionic chain ends and is a possible explanation for the fact that we were not able to achieve complete endcapping.

3.4 Styrene

The third capping agent we used, was styrene. Our results for α-methylstyrene and 1,2-diphenylethylene in the presence of TMEDA indicated that it should be possible to obtain a living polymer with a very short polystyrene block (approximately five styrene units) at the chain end of living polybutadiene. The block copolymer should be formed in such a way that all polybutadiene chains bear at least one styrene unit at the chain end, while the molecular weight distribution remains narrow. This short polystyrene block will yield chain ends with modified reactivity, but is not expected to have a significant influence on the properties of the final material.

From anionic copolymerization of styrene and butadiene it is known that styrene propagation is much faster than the crossover reaction from butadiene to styrene.[2] This is a problem when the desired product is a random copolymer or when the objective is to obtain a block copolymer with well-defined block lengths and a narrow molecular weight distribution (*e.g.* styrene-butadiene-styrene rubber). However, the relative reaction rates can be modified by addition of a Lewis base. If it would be possible to drastically increase the crossover rate from butadiene to styrene without increasing styrene propagation rate too much, a very short styrene block could be attached to poly(butadienyl)lithium. TMEDA proved to have a strong effect on the reactions with α-methylstyrene and 1,2-diphenylethylene, so we also used it in our attempts to increase the crossover rate from butadiene to styrene. The reaction conditions are listed in Table 3.3.

Table 3.3. Reaction conditions for the endcapping of poly(butadienyl)lithium with a short polystyrene block

Entry	**Lewis base**	**[styrene]/ [s-BuLi]**	**[Lewis base]/ [s-BuLi]**	**Temperature (°C)**
S-15	TMEDA	4	2	40
S-16	TMEDA	5	2	40
S-17	TMEDA	3	2	40

The polymers obtained were analyzed with MALDI-ToF-MS. In this case we were not aiming at adding only one molecule of styrene to the polybutadiene chain end, but a small polystyrene block, which leads to a narrow chain length distribution of the styrene block. This makes the mass spectra more difficult to interpret because of complicated isotopic patterns (Figure 3.3a-b).

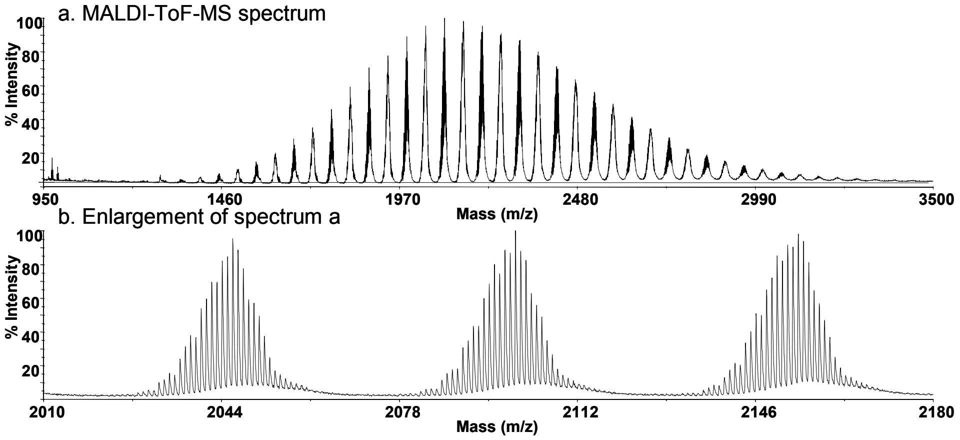


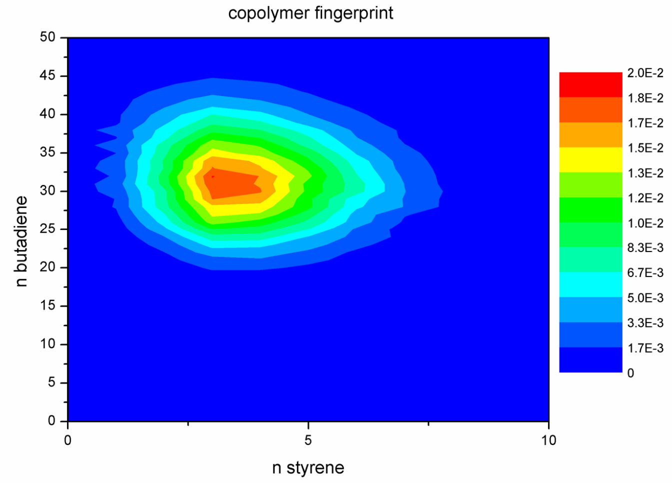
Figure 3.3.

a. MALDI-ToF-MS mass spectrum of poly(butadiene-*b*-styrene) (S-15, Table 3.3)
b. an enlargement of Figure 3.3a between 2010and 2180 g/mol

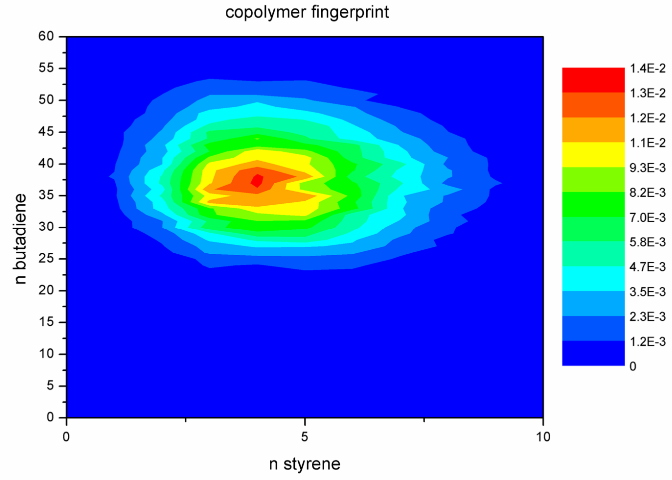
The mass spectra can be represented in a different way to make interpretation easier. This is done by using software developed in-house by Willemse *et al.*[16]; the resulting so called copolymer fingerprints are displayed in Figure 3.4.

A copolymer fingerprint (or contourplot) is a two-dimensional representation of a three-dimensional plot of a normalized matrix of the MALDI-ToF-MS mass spectrum. The construction of the normalized matrix from the MALDI-ToF-MS spectrum is described in detail by Willemse *et al.*[16]

a. Copolymer fingerprint S-15



b. Copolymer fingerprint S-16



c. Copolymer fingerprint S-17

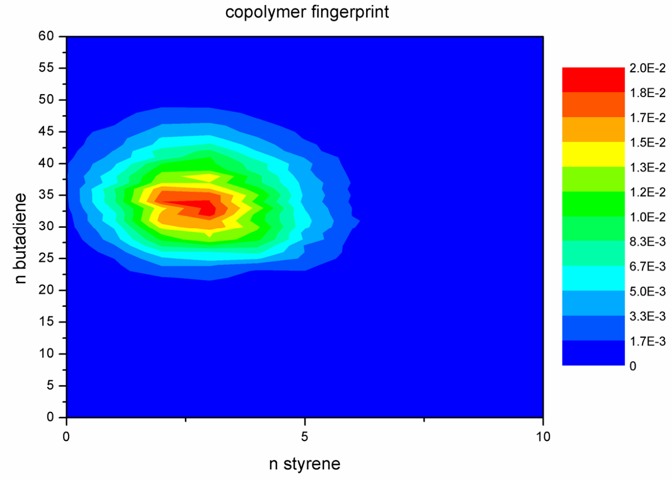


Figure 3.4. Copolymer fingerprints for poly(butadiene-*b*-styrene) (a. S-15, b. S-16 and c. S-17, Table 3.3)

The copolymer fingerprints give an overview of the chain length distribution and the chemical composition distribution of the copolymers; on the y-axis the number of butadiene units is displayed and on the x-axis the number of styrene units. For example, in Figure 3.4a it can be seen that polybutadiene chain length ranges from approximately 20 to 45 monomer units. The highest intensity can be found at about 30 units. For styrene, chain length ranges from one to eight monomer units, with the highest intensity at four units. From these copolymer fingerprints, the individual block distributions can be obtained. We are interested in the chain length and chain length distribution of the styrene block, therefore styrene distributions are plotted in Figure 3.5.

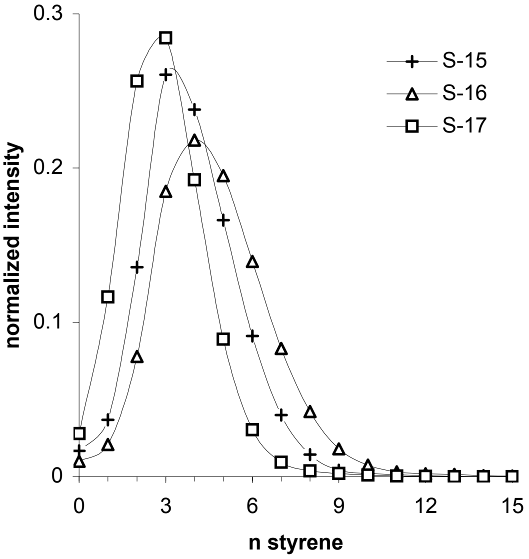


Figure 3.5. Chain length distributions for styrene blocks obtained from the corresponding copolymer fingerprints

Figures 3.4 and 3.5 clearly demonstrate that for S-15 and S-16 hardly any non-functional polybutadiene is present. However, for S-17 a larger amount of non-functional material can be observed. The individual block characteristics can be calculated from the styrene block distributions. Table 3.4 shows these characteristics.

Table 3.4. Individual styrene block properties, calculated from the individual distributions

Entry	Pn	Pw	PDI	$PDI_{Poisson}$
S-15	3.87	4.59	1.19	1.16
S-16	4.64	5.47	1.18	1.15
S-17	2.97	3.70	1.25	1.19

These results indicate that a well-defined polystyrene block can be formed, with a minimum average block size of approximately four. Recipes for smaller block sizes lead to significant amounts of residual polybutadiene. The PDI values are close to the theoretical values of a Poisson distribution with the same number average degree of polymerization (Pn). This indicates that initiation of the styrene block is faster than propagation.[2]

3.5 Conclusions

The modification of the anionic chain end of living poly(butadienyl)lithium with different capping agents was investigated in order to modify the poly(butadienyl) anion into a suitable leaving group for RAFT-mediated polymerization. This chain end modification is the first step in converting the polymeric carbanion into a macromolecular RAFT-agent with the polymer as the leaving group. α-Methylstyrene, 1,2-diphenylethylene and styrene were used as capping agents. α-Methylstyrene was found to undergo oligomerization and to yield a non-quantitative degree of functionalization. Even the addition of a strong Lewis base (TMEDA) was not sufficient to yield the desired polybutadiene with one α-methylstyrene endgroup. 1,2-diphenylethylene could be attached to the chain ends in a mono-additional way. Addition of TMEDA led to an increase in the degree of functionalization, but no quantitative addition was achieved. Probably, proton abstraction from *trans*-stilbene, which leads to termination of living poly(butadienyl)lithium, competes with the addition of *trans*-stilbene to the chains. Attempts to attach a very short polystyrene block to poly(butadienyl)lithium were successful as is demonstrated by the advanced MALDI-ToF-MS analysis of the block copolymers. The short polystyrene block provides the desired endgroup. Subsequent chain end modifications to obtain a macromolecular RAFT-agent by converting the carbanion into a mercapto or halide functionality are reported in Chapter 4.

3.6 Experimental procedures

3.6.1 Materials

1,3-Butadiene (Shell Chemicals Europe, 99.5%), styrene (VWR, 99%), α-methylstyrene (Aldrich, 99%), cyclohexane (VWR, high purity) and tetrahydrofuran (THF, Aldrich, AR) were passed over an activated alumina column prior to use. N,N,N',N'-tetramethylethenediamine (TMEDA, Aldrich, >99.5%) and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were stored over molecular sieves under inert atmosphere. *sec*-Butyllithium (*s*-BuLi, Acros, 1.3 M solution in cyclohexane/hexane (92/8)), *trans*-stilbene (Merck, >97%), *cis*-stilbene (Aldrich, 96%), 1,1-diphenylethylene (Aldrich, 97%) were all used without further purification and stored under inert atmosphere.

3.6.2 Polymerizations

Butadiene polymerizations were carried out under nitrogen atmosphere in a 2 L stainless steel autoclave reactor equipped with a screw stirrer. The reactor was charged with 1 kg of cyclohexane and heated to 60 °C. Butadiene (50 g, 0.99 mol) and s-BuLi (25 mL of 1 M solution in cyclohexane, 0.025 mol) were added. Polymerization was allowed to reach complete conversion, which corresponds to approximately 90 minutes reaction time. After completion, a sample was withdrawn and quenched in an excess of methanol. Living polybutadiene solutions were kept in the reactor for the *in situ* functionalization reactions.

3.6.3 *In situ* functionalizations

Typical procedures are given for each type of functionalization agent, using living polybutadiene with a M_n of 2500 g/mol as the starting material.
All reactions were carried out *in situ* directly after butadiene polymerization.

α-methylstyrene

After butadiene polymerization, the reactor contents were heated to 65 °C.
α-Methylstyrene (3.68 g, 0.03 mol, α-methylstyrene/*s*-BuLi = 2) and TMEDA (3.62 g, 0.03 mol, TMEDA/s-BuLi = 2) were weighed under inert atmosphere into a glass vial capped with a rubber septum and added successively to the reactor via an autoinjector. Reaction was allowed to continue for 4 hours at 65 °C. Samples were taken at regular time intervals and quenched in methanol.

Diphenylethylenes (DPEs)

After butadiene polymerization, the reactor contents were cooled to 50 °C. 1,2-Diphenylethylene (5.62 g, 0.03 mol, DPE/*s*-BuLi = 2) was weighed under inert atmosphere into a glass vial and dissolved in 5 mL of THF before capping the vial with a rubber septum. TMEDA (3.62 g, 0.03 mol., TMEDA/*s*-BuLi = 2) was also weighed under inert atmosphere into a glass vial, which was capped with a rubber septum. The DPE solution and TMEDA were added successively to the reactor via an autoinjector. The reaction mixture was kept at 50 °C for 4 hours. Samples were taken at regular time intervals and quenched in methanol.

Styrene

After butadiene polymerization, the reactor contents were cooled to 40 °C. TMEDA (3.62 g, 0.03 mol, TMEDA/*s*-BuLi = 2) and styrene (6.49 g, 0.06 mol, styrene/*s*-BuLi = 4) were weighed under inert atmosphere into a glass vial, which was capped with a rubber septum. Then TMEDA and styrene were added successively to the reactor via an autoinjector. Reaction was allowed to continue at 40 °C for 30 minutes. After that a sample was withdrawn from the reactor and quenched in methanol.

3.6.4 Characterization

Size Exclusion Chromatography (SEC)

Molar mass and molar mass distributions were measured by size exclusion chromatography using a Waters GPC equipped with a Waters model 590 pump, a Spectra Physics model SP6040 XR differential refractive index detector (40 °C), a Waters WISP 717 autoinjector (50 µL injection volume) and a PL gel (5 µm pore size) 300 ×7.5 mm column (50 °C). THF was used as eluent (flow rate 0.95 mL/min). Narrow polystyrene standards (range 2400 g/mol-73000 g/mol) were used for calibration. The resulting apparent molar masses were converted into “real” molar masses, using an empirical equation. MALDI-ToF-MS was used to obtain absolute values for the molar mass.

MALDI-ToF-MS

MALDI-ToF-MS measurements were carried out on a Voyager-DE-STR (Applied Biosystems) equipped with a 337 nm nitrogen laser. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonononitrile (DCTB)[17] was used as the matrix. The matrix was dissolved in THF at a concentration of approximately 40 mg/mL. Silver trifluoroacetate (Aldrich, 98%) was used as the cationization agent and was added to THF at a concentration of 1 mg/mL. The polymer sample was dissolved in THF at a concentration of 2 mg/mL. In a typical measurement, the matrix, cationization agent and sample solutions were premixed in a 10:1:5 volume ratio. Approximately 0.5 µL of the mixture obtained was hand spotted on the target plate and left to dry. Mass spectra were recorded in the reflector mode. For each spectrum, 5000 laser shots were accumulated. Data Explorer© software (Applied Biosystems) was used for data interpretation. Additionally, data obtained from the styrene functional samples were analyzed using an in house developed software package written in Visual Basic 6.0. The principles used in this program are outlined in a recent paper by Willemse et al.[16]

References

1 Donkers, E. H. D.; Willemse, R. X. E.; Klumperman, B. *Journal of Polymer Science, Part A: Polymer Chemistry* **2005**, *43*, 2536-2545.
2 Hsieh, H. L.; Quirk, R. P. *Anionic polymerization: Principles and practice*; New York: Dekker: **1996**.
3 Keki, S.; Nagy, M.; Deak, G.; Herczegh, P.; Zsuga, M. *Journal of Polymer Science, Part A: Polymer Chemistry* **2004**, *42*, 587-596.
4 Llauro, M. F.; Loiseau, J.; Boisson, F.; Delolme, F.; Ladaviere, C.; Claverie, J. *Journal of Polymer Science, Part A: Polymer Chemistry* **2004**, *42*, 5439-5462.
5 Quirk, R. P.; Guo, Y.; Wesdemiotis, C.; Arnould, M. A. *Journal of Polymer Science, Part A: Polymer Chemistry* **2003**, *41*, 2435-2453.
6 Quirk, R. P.; Gomochak, D. L.; Wesdemiotis, C.; Arnould, M. A. *Journal of Polymer Science, Part A: Polymer Chemistry* **2003**, *41*, 947-957.
7 Venkatesh, R.; Vergouwen, F.; Klumperman, B. *Journal of Polymer Science, Part A: Polymer Chemistry* **2004**, *42*, 3271-3284.
8 Liu, F.; Liu, B.; Luo, N.; Ying, S.; Liu, Q. *Chemical Research in Chinese Universities* **2000**, *16*, 72-77.
9 Quirk, R. P.; Yoo, T.; Lee, Y.; Kim, J.; Lee, B. *Advances in Polymer Science* **2000**, *153*, 67-162.
10 Balas, Jaroslav G. **1963**, US 3448176.
11 Okamoto, Y.; Kato, M.; Yuki, H. *Bulletin of the Chemical Society of Japan* **1969**, *42*, 760-765.
12 Yuki, H.; Kato, M.; Okamoto, Y. *Bulletin of the Chemical Society of Japan* **1968**, *41*, 1940-1944.
13 Quirk, R. P.; Takizawa, T.; Lizarraga, G.; Zhu, L. F. *J.Appl.Polym.Sci.: Appl.Polym.Symp.* **1992**, *50*, 23-41.
14 Wakefield, B. J. *The chemistry of organolithium compounds*; S.I. Pergamon Press: **1974**.
15 Wyman, D. P.; Altares, T., Jr. *Makromolekulare Chemie* **1964**, *72*, 68-75.
16 Willemse, R. X. E.; Staal, B. B. P.; Donkers, E. H. D.; van Herk, A. M. *Macromolecules* **2004**, *37*, 5717-5723.
17 Ulmer, L.; Mattay, J.; Torres-Garcia, H. G.; Luftmann, H. *European Journal of Mass Spectrometry* **2000**, *6*, 49-52

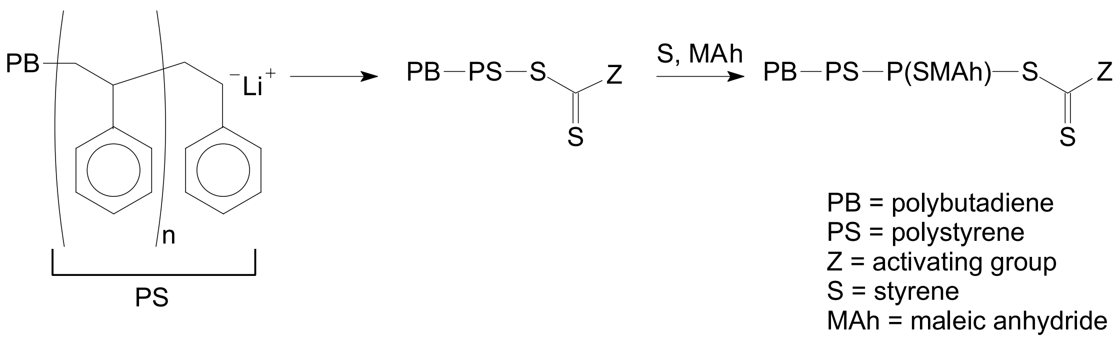
4

Reactions at the anionic chain end: Towards macromolecular RAFT-agents

4.1 Introduction

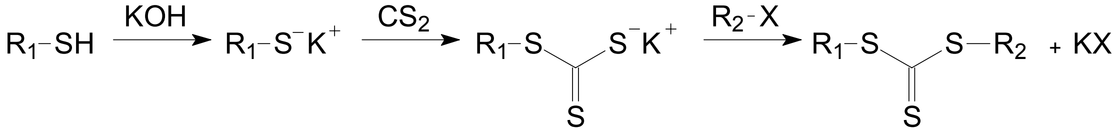
The first step in our sequential approach to obtain block copolymers was described in Chapter 3. The objective of that first step was the attachment of a good leaving/reinitiating group for RAFT-mediated polymerization to the polymer chain end of living anionic polybutadiene. A short polystyrene block with a well-defined length was found to be very suitable for that purpose.

To obtain the desired block copolymers by combination of living anionic polymerization and RAFT-mediated polymerization, two steps are still required (Scheme 4.1): The transformation of the anionic chain end into a RAFT-agent and subsequent RAFT-mediated copolymerization of styrene and maleic anhydride leading to the desired block copolymer.



Scheme 4.1. Reaction steps for the transformation of the anionic chain end into the desired block copolymer

In this chapter, our investigations on the transformation of anionic poly(butadiene-*b*-styrene) chains into macromolecular RAFT-agents are described. We primarily focused on trithiocarbonates as RAFT-agents because of their high transfer constants and their relatively easy synthesis.[1;2] The synthetic procedure for a trithiocarbonate, which is shown in Scheme 4.2, consists of the deprotonation of a thiol to form a sulfide, and the subsequent coupling of the sulfide with carbon disulfide leading to the trithiocarbonate salt. The final step is the reaction of the trithiocarbonate salt with an alkyl halide, which yields the RAFT-agent, thereby splitting off the halide anion.

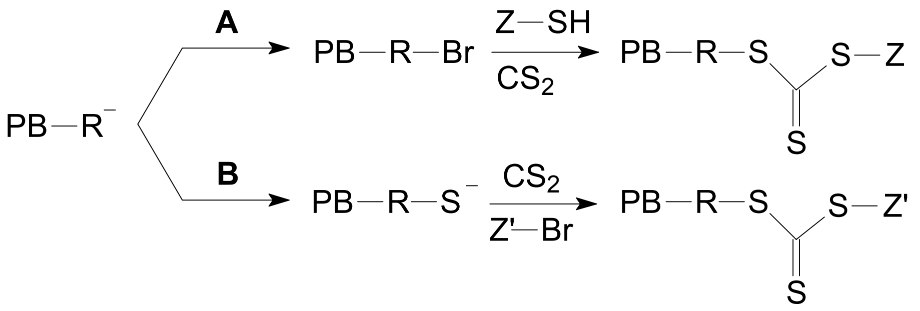


$$R_1{-}SH \xrightarrow{KOH} R_1{-}S^-K^+ \xrightarrow{CS_2} R_1{-}S{-}C({=}S){-}S^-K^+ \xrightarrow{R_2{-}X} R_1{-}S{-}C({=}S){-}S{-}R_2 + KX$$

Scheme 4.2. Trithiocarbonate synthesis

Since the starting materials for the synthesis of trithiocarbonates are thiols (or sulfides) and halides, the anionic chain end of poly(butadiene-*b*-styrene) can either be converted into a sulfide or into a halide functional group.

A general scheme for the synthesis of trithiocarbonates starting from living anionic polybutadiene (PB) with a short polystyrene block (R) at the chain end is depicted in Scheme 4.3.



PB = polybutadiene
R = short polystyrene block
Z, Z' = alkyl groups

Scheme 4.3. Trithiocarbonates from living polybutadiene (PB) with a short polystyrene block (R) at the chain end

Route **A**, which involves conversion of the carbanion into a bromide, is described in Section 4.2. Route **B**, which comprises the conversion of the carbanion into a sulfide anion, is evaluated in Section 4.3.

Route **A** as well as route **B** are suitable for a one-pot procedure without intermediate polymer isolation or purification steps.

4.2 From carbanion to bromide

Three ways to introduce a bromide-functionality starting from a carbanion with a lithium counterion are reported in literature:

- Addition of bromine (Br_2)[3;4]
- Addition of α,ω-dihaloalkane[3;5;6]
- Lithium-halogen exchange[7-9]

In our system, addition of bromine is not a viable route, since the polybutadiene block contains many double bonds. Addition of Br_2 to these double bonds would compete with addition to the anionic chain end, leading to incomplete chain end functionalization and to the presence of undesired in-chain bromide-functionalities.

Introduction of a bromide endgroup by means of reaction with an α,ω-dihaloalkane is no suitable pathway either, since this reaction leads to the chain-end structure shown in Figure 4.1

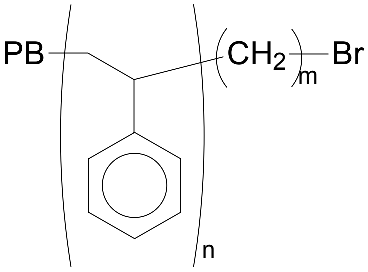
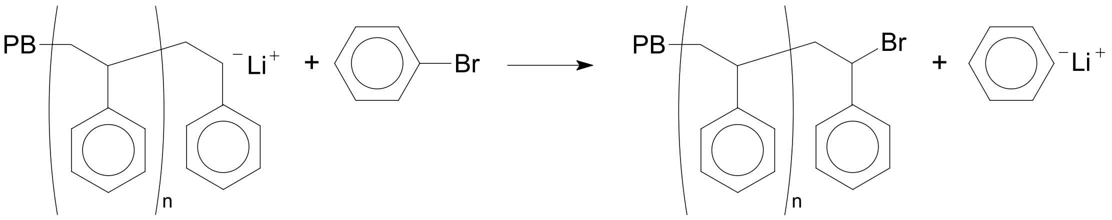


Figure 4.1. Chain-end structure after reaction with α,ω-dibromoalkane

The styrenic group that was attached to the polybutadiene chain end to obtain a good leaving group for RAFT-mediated polymerization is now coupled to an alkyl group, which in its turn is a very poor leaving group. Therefore, an effective RAFT-agent with a polymeric leaving group can not be obtained via reaction of the carbanion with an α,ω-dihaloalkane.

The third, and final, route to obtain a bromide-functionality at the chain end is lithium-halogen exchange, which is a well-known method to prepare aryllithium compounds. Scheme 4.4 shows the lithium-bromide exchange reaction at the polymer chain end.



Scheme 4.4. Lithium-bromide exchange reaction

The bromide-functionality is attached directly to the ultimate styrene repeat unit, which implies that the leaving group ability of the chain end is retained. Therefore, lithium-halogen exchange appears to be a suitable method to obtain a bromide endgroup.

In Table 4.1 the reaction conditions for the lithium-halogen exchange reactions are listed.

Table 4.1. Reaction conditions for lithium-halogen exchange reactions, see Scheme 4.4

Entry	**Polymer**[a]	**[C_6H_5Br]/[anions]**	**Reaction time (hours)**	**Temperature (°C)**
PBS-1	PBS	1.1	1	50
PBS-2	PBS	10	1	50
PBD-1	PBD	1.5	1	25

[a] PBS is living polybutadiene with a short polystyrene block at the chain end and PBD is living polybutadiene with 1,1-diphenylethylene at the chain end

The SEC-chromatograms of the starting material (PBS) and the product of reaction PBS-1 are shown in Figure 4.2.

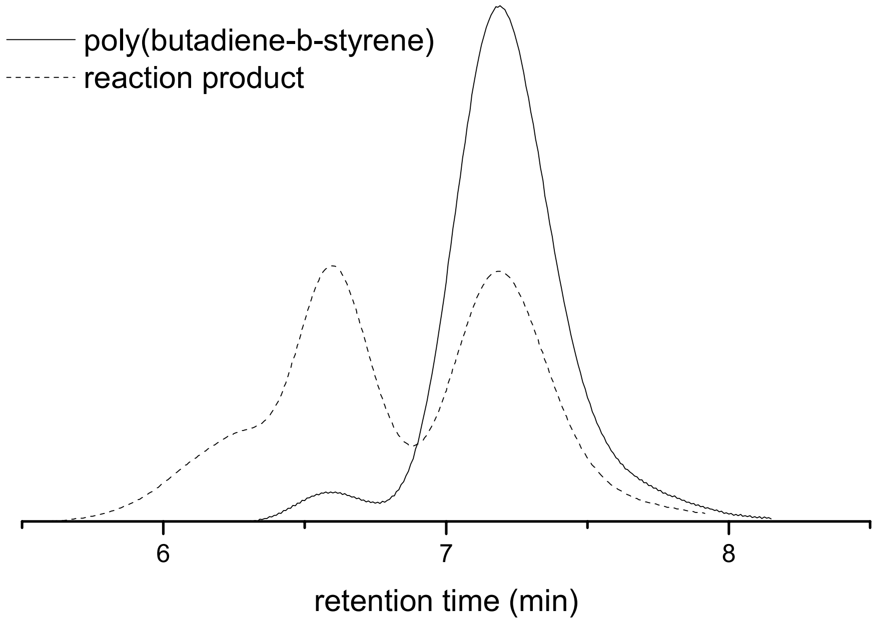
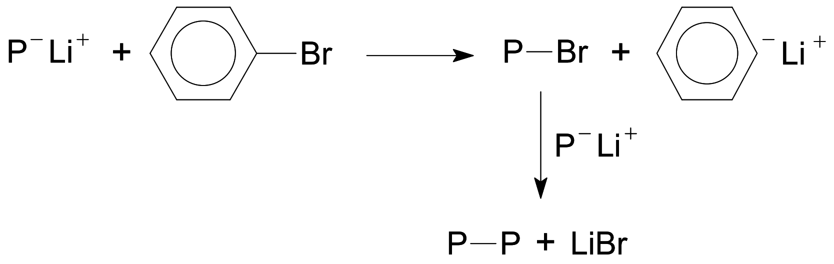


Figure 4.2. SEC-chromatograms of poly(butadiene-*b*-styrene) and the reaction product of

PBS-1 (Table 4.1)

In case of a successful lithium-halogen exchange reaction, hardly any change in the molecular weight distribution is expected, since only the endgroup is modified. However, Figure 4.2 clearly shows that polymeric material with at least twice the molecular weight of the starting polymer is formed. Possibly the desired product is subject to a coupling reaction with the initial anionic poly(butadiene-*b*-styrene) as shown in Scheme 4.5.



Scheme 4.5. Lithium-halogen exchange reaction followed by polymer-polymer coupling

We observed that the lithium-halogen exchange reaction proceeded very fast. After only ten minutes of reaction time, no further change in the SEC-chromatograms could be observed. We tried to take advantage of the high reaction rate, by using a larger excess of bromobenzene (Table 4.1, PBS-2). The presence of a large excess of bromobenzene increases the rate of lithium-halogen exchange reaction, whereas the rate coefficient of the polymer-polymer coupling reaction is expected to be unaffected. This should lead to a high degree of functionalization and a decrease in coupled material. Figure 4.3 shows the SEC-chromatograms of reaction PBS-2 where a tenfold excess of bromobenzene was used.

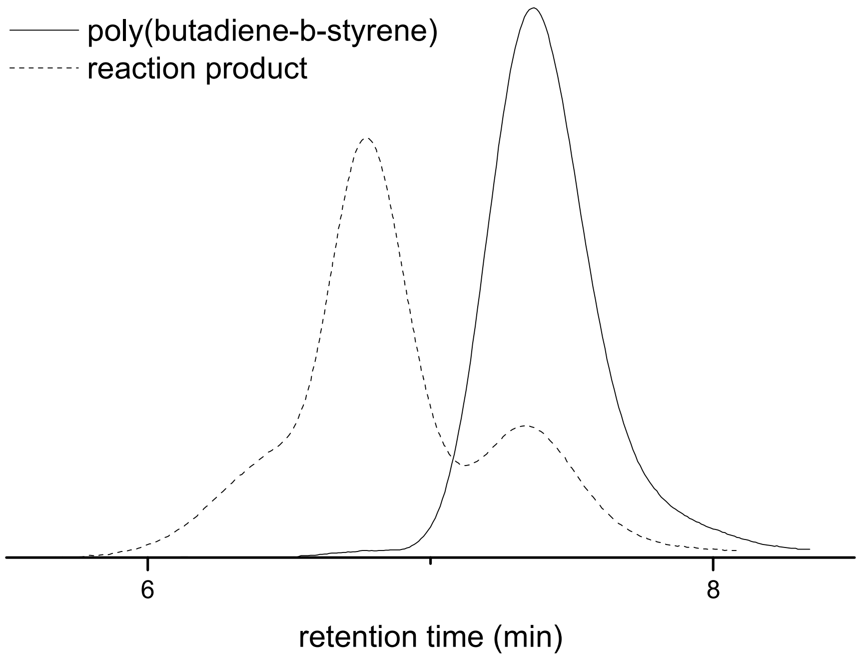
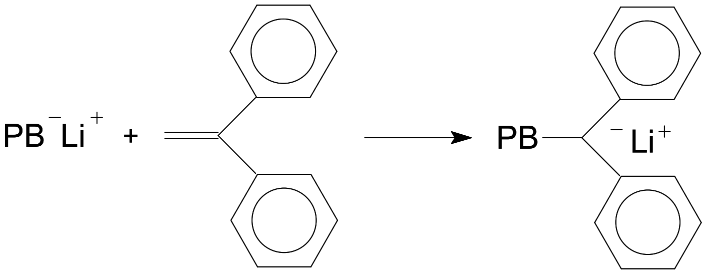


Figure 4.3. SEC-chromatograms of poly(butadiene-*b*-styrene) and the reaction product of PBS-2 (Table 4.1)

The result does not differ significantly from reaction PBS-1 where only a 1.1-fold excess of bromobenzene was used, which indicates that the reactivity towards the living anionic chain ends is much higher for the bromide-functional chain end than for bromobenzene. Therefore, even though a large excess of bromobenzene is used, the polymer-polymer coupling reaction is still taking place.

A reduction of chain-end reactivity should lead to a decrease of the undesired coupling reaction. Reduction of reactivity and increase of steric hindrance at the chain end by endcapping with 1,1-diphenylethylene is reported[3;6] to reduce the contribution of coupling reactions. 1,1-Diphenylethylene endcapping has been used to suppress coupling reactions during functionalization of living anionic polymers with α,ω-dihaloalkanes. We used the endcapping with 1,1-diphenylethylene (Scheme 4.6) to suppress the contribution of the coupling reactions which dramatically decrease the selectivity of the lithium-halogen exchange reaction.



Scheme 4.6. Endcapping of anionic polybutadiene with 1,1-diphenylethylene

The reaction conditions for the lithium-bromide exchange reaction with polybutadiene endcapped with 1,1-diphenylethylene are listed in Table 4.1, reaction PBD-1.
The SEC-result for this reaction is shown in Figure 4.4.

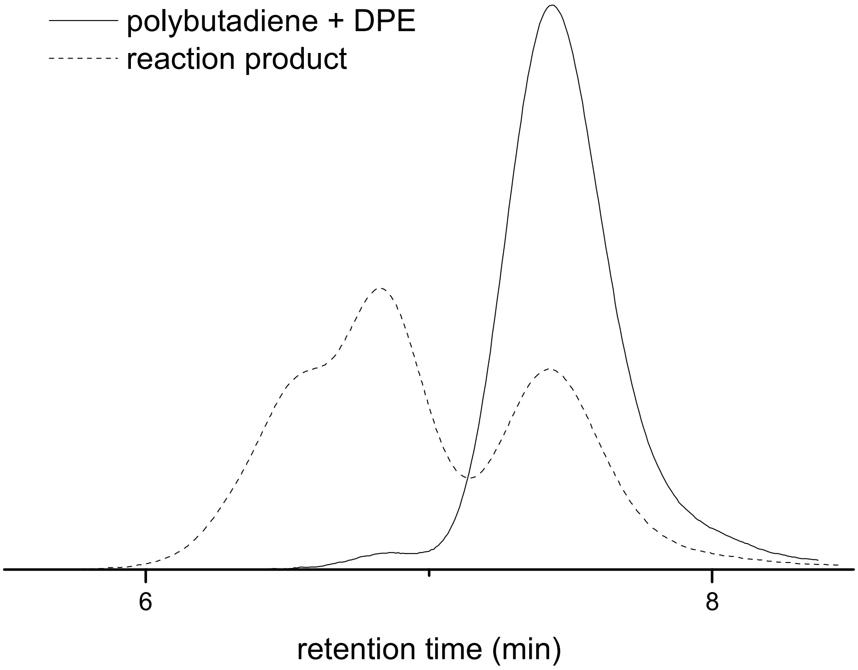
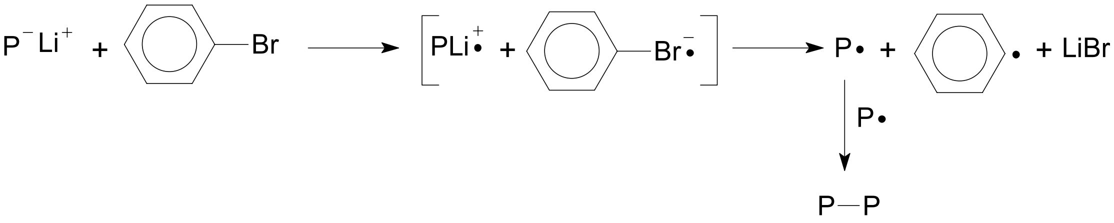


Figure 4.4. SEC-chromatograms of polybutadiene endcapped with 1,1-diphenylethylene and the reaction product of PBD-1 (Table 4.1)

In contrast to the reported effectiveness of 1,1-diphenylethylene in reducing coupling reactions, also here a significant formation of high molecular weight material is observed. In comparison with PBS-1 and PBS-2, the amount of coupled product decreased, but the amount of material with a molecular weight higher than two times that of the desired product increased.

The formation of coupled products for PBD-1 and the formation of higher molecular weight products in reaction PBS-1, PBS-2 and PBD-1 can not be explained by the mechanism for coupling as shown in Scheme 4.5. This suggests that another mechanism governs the coupling reactions. One mechanism that has been reported before[3] involves radical-ion intermediates (Scheme 4.7).



Scheme 4.7. Coupling reaction via radical mechanism

The formation of a polymeric radical could provide an explanation for the formation of dimers, trimers or even higher molecular weight material. Dimeric material can be formed via radical-radical combination as shown in Scheme 4.7. For higher degrees of coupling, one could also imagine a mechanism which involves hydrogen abstraction from the polybutadiene present in our system.

If these radical reactions occur, the introduction of a bulky group, such as 1,1-diphenylethylene, at the chain end does not prevent coupling reactions, which corresponds to our observations. The occurrence of radical reactions forces us to conclude that lithium-halogen exchange is not suitable to introduce a bromide-functionality at the chain end of anionic polybutadiene with a short polystyrene block. Therefore, a successful direct transformation of the chain-end carbanion into a halide is very unlikely within the scope of our work.

4.3 From carbanion to thiol

Two methods for the direct transformation of living anionic polymers into thiol-terminated polymers are reported in literature.[10] The first method is the addition of elemental sulfur (S_8) to living anionic polymers. The second method is the addition of an episulfide to the living system resulting in ring-opening of the episulfide. Both methods would yield a sulfide anion at the chain end. The product can be used directly for the synthesis of trithiocarbonates or protonated to form a thiol.
We investigated both the addition of elemental sulfur and episulfides for our system. Additionally, we attempted to obtain the S-functionality via heterolytic cleavage of the S-S bond in disulfides. In the following sections, the functionalization reactions of carbanionic chain ends with elemental sulfur, episulfides and disulfides are described.

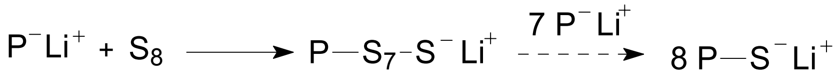
4.3.1 Elemental sulfur

The reaction conditions for the functionalization reactions with elemental sulfur are collected in Table 4.2. In all cases living anionic polybutadiene with a short polystyrene block was used as the starting material and the reaction time was 24 hours. After that time the reaction mixture was quenched in methanol to protonate the chain end.

Table 4.2. Reaction conditions for reactions of anionic poy(butadiene-*b*-styrene) with elemental sulfur

Entry	S_8/anions	Temperature (°C)
PBS-3	1/8	25
PBS-4	1/8	50
PBS-5	1	25
PBS-6	1	50

Ideally, one sulfur atom is attached to each chain end. Since S_8 is the reactant, a one-step reaction is highly unlikely, but probably a more complicated process takes place, which is schematically represented in Scheme 4.8.



$$P^{-}Li^{+} + S_8 \longrightarrow P{-}S_7{-}S^{-}Li^{+} \xrightarrow{7\,P^{-}Li^{+}} 8\,P{-}S^{-}Li^{+}$$

Scheme 4.8. Addition of elemental sulfur to an anionic polymer

The process proposed in Scheme 4.8 involves the formation of oligosulfide followed by several chain-breaking steps, which eventually lead to the desired thiol-functionality. As can be derived from Scheme 4.8, the ideal ratio of S_8 to anions is 1/8. For comparison, we also carried out two experiments with an equimolar amount of S_8, *i.e.* an eightfold excess of sulfur.

The SEC-chromatograms of the products of the reactions with a stoichiometric amount of sulfur (Table 4.2, PBS-3 and PBS-4) are presented in Figure 4.5.

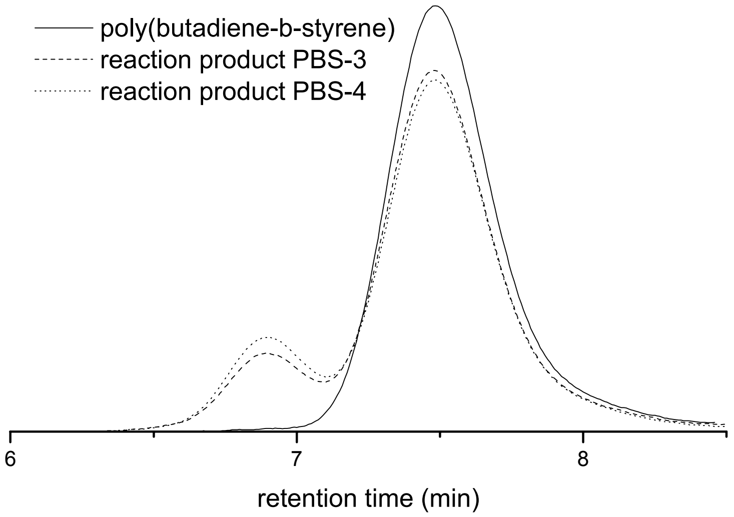


Figure 4.5. SEC-chromatograms of poly(butadiene-*b*-styrene) and the reaction products of PBS-3 and PBS-4 (Table 4.2)

The SEC-results demonstrate that the reaction temperature has no significant influence on the outcome of the reaction. The reaction products have a bimodal molecular weight distribution, indicating the formation of dimeric product by polymer-polymer coupling. After deconvolution, the amount of coupled material is estimated to be approximately 15 weight % based on the total amount of reaction product.

The SEC-results for PBS-5 and PBS-6 (Figure 4.6) where a large excess of sulfur was used, reveal that more coupled material (approximately 70% by weight) is formed in these cases. The reaction temperature has no significant influence.

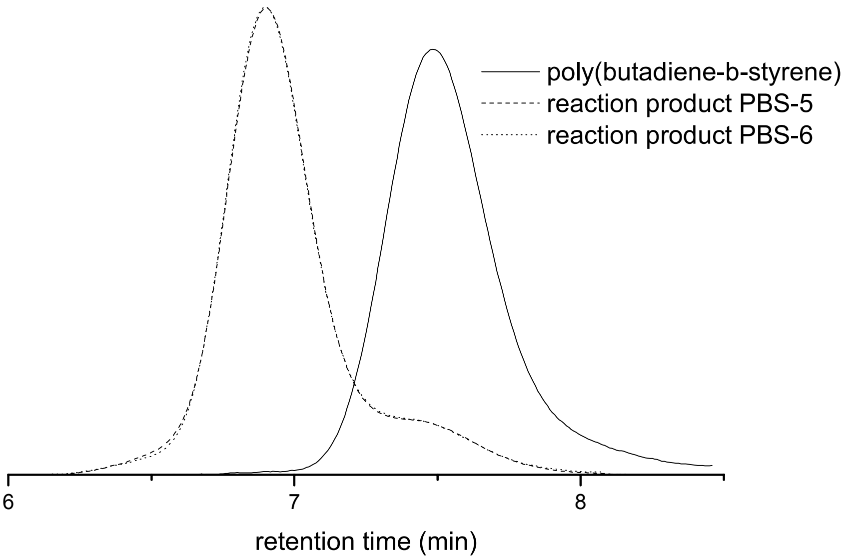
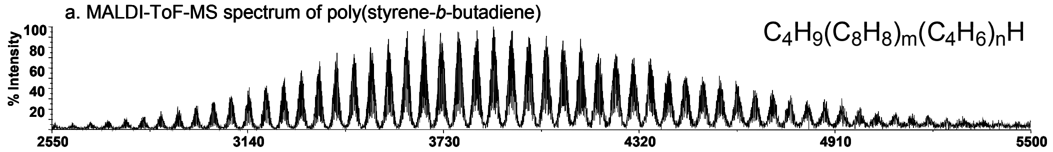


Figure 4.6. SEC-chromatograms of poly(butadiene-*b*-styrene) and the reaction products of PBS-5 and PBS-6 (Table 4.2)

The products of the experiments PBS-3 and PBS-4 were analyzed by MALDI-ToF-MS and compared with the starting material, poly(butadiene-*b*-styrene).

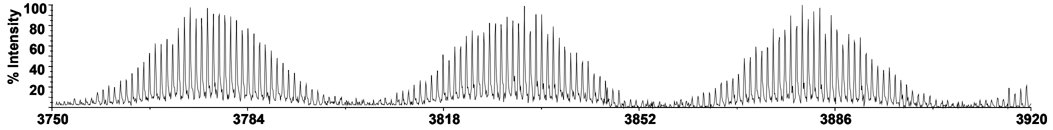
Figure 4.7a shows the MALDI-ToF-MS mass spectrum of poly(butadiene-*b*-styrene), prepared by living anionic polymerization which was initiated by *s*-butyllitium and terminated by protonation, resulting in a hydrogen endgroup. An enlargement of the spectrum (Figure 4.7b) shows the complicated isotopic patterns for this block copolymer. These isotopic patterns are difficult to assign to a specific copolymer composition and endgroups. With the aid of advanced simulations using an in-house developed software-package[11] in combination with existing Data Explorer software (Applied Biosystems, version 4.0.0.0), we were able to unravel the complicated mass spectrum. Part of the simulated mass spectrum with the assumed endgroups (*s*-butyl and hydrogen) is shown in Figure 4.7c and corresponds very well with the measured spectrum (Figure 4.7b). As already demonstrated in Chapter 3, the interpretation of complicated mass spectra of block copolymers can be facilitated by representing the mass spectrum as a copolymer fingerprint (Figure 4.7d). The maximum intensity in the fingerprint, representing the highest number of chains, is located at block lengths of 36 butadiene units and 4 styrene units.

a. MALDI-ToF-MS spectrum of poly(styrene-*b*-butadiene)

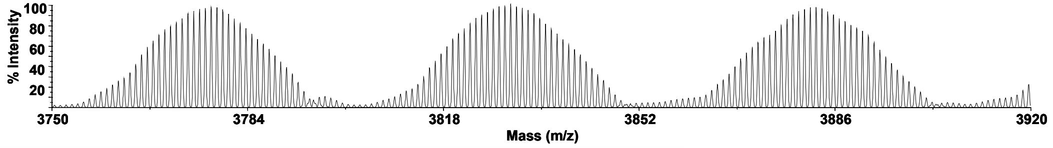


$C_4H_9(C_8H_8)_m(C_4H_6)_nH$

b. Enlargement of spectrum a



c. Calculated isotopic pattern



d. Copolymer fingerprint

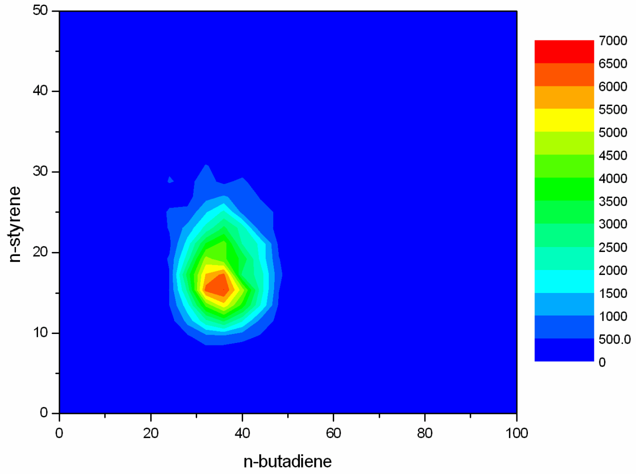


Figure 4.7.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated poly(butadiene-*b*-styrene)

b. an enlargement of spectrum (a) between 3750 and 3920 g/mol

c. calculated isotopic patterns

d. the copolymer fingerprint for poly(butadiene-*b*-styrene)

The MALDI-ToF-MS mass spectrum of the reaction product of PBS-4 is displayed in Figure 4.8a

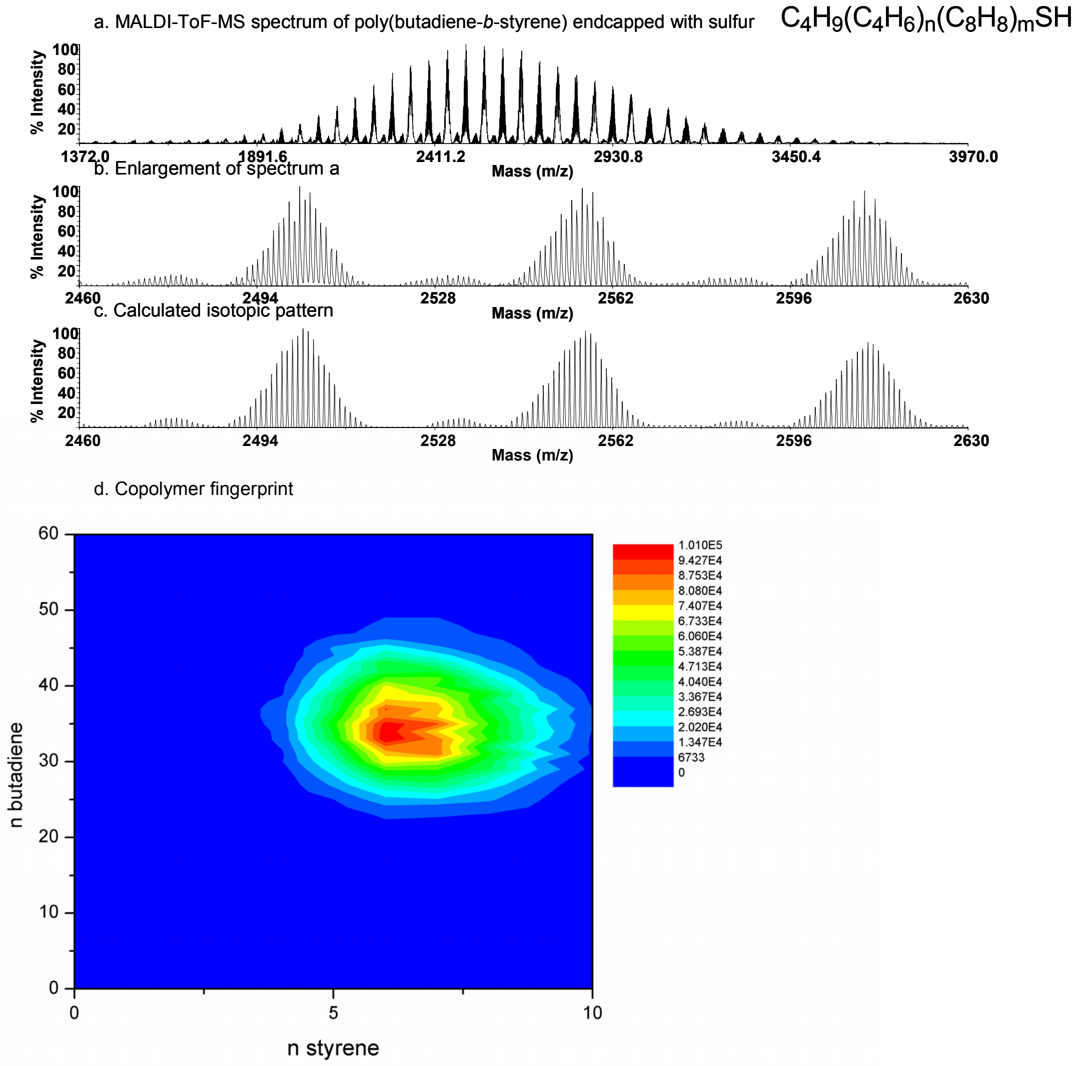


Figure 4.8.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated poly(butadiene-*b*-styrene) after reaction with elemental sulfur

b. an enlargement of spectrum (a) between 2460 and 2630 g/mol

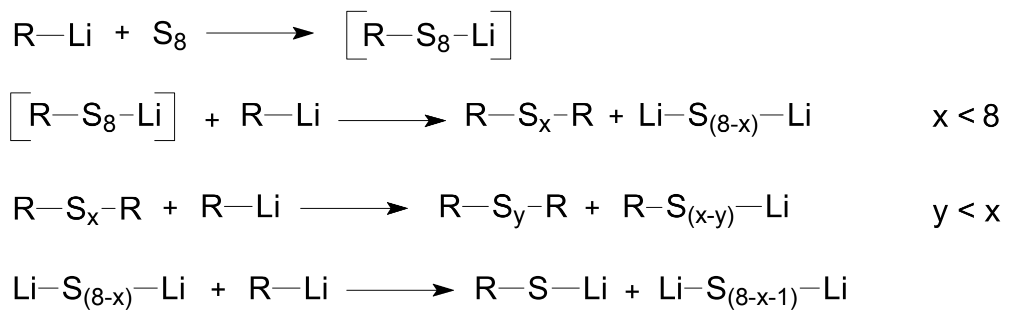
c. calculated isotopic patterns

d. the copolymer fingerprint for poly(butadiene-*b*-styrene) after reaction with elemental sulfur

In Figure 4.8b an enlargement of the mass spectrum is shown, which can be compared with the simulated isotopic patterns assuming *s*-butyl and thiol endgroups (Figure

4.8c). The measured spectrum corresponds well with the calculated spectrum, indicating successful functionalization of the chain ends with one sulfur atom. However, analysis of the copolymer fingerprint (Figure 4.8d) shows that the maximum intensity corresponds with block lengths of 35 butadiene units and 6 styrene units. These block lengths are not in agreement with the block lengths that were calculated for the polymer before reaction with sulfur. The discrepancy in the copolymer composition before and after reaction raises doubts about the reliability of the measured spectrum. It is known that sulfur-containing compounds are difficult to characterize using MALDI-ToF-MS. The difficulties in the characterization can be caused by fragmentation of the sample and reaction with the cationization agents that are used. Therefore we suppose that Figure 4.8a does not show all products that are formed. Probably some non-functional polymer and/or some polymer functionalized with oligosulfide chains are present as reaction products as well. The SEC-chromatograms (Figure 4.5) that show the presence of coupled polymeric material, also indicate that the addition of sulfur was partially successful, but not selective, resulting in the formation of significant amounts of side products.

A reaction scheme proposed in literature[12] for the reaction of elemental sulfur with organolithium compounds demonstrates a range of possible reaction products (Scheme 4.9)



$$R{-}Li + S_8 \longrightarrow [R{-}S_8{-}Li]$$

$$[R{-}S_8{-}Li] + R{-}Li \longrightarrow R{-}S_x{-}R + Li{-}S_{(8-x)}{-}Li \qquad x < 8$$

$$R{-}S_x{-}R + R{-}Li \longrightarrow R{-}S_y{-}R + R{-}S_{(x-y)}{-}Li \qquad y < x$$

$$Li{-}S_{(8-x)}{-}Li + R{-}Li \longrightarrow R{-}S{-}Li + Li{-}S_{(8-x-1)}{-}Li$$

Scheme 4.9. Reactions of organolithium compounds with elemental sulfur[12]

According to Scheme 4.9, many different products can be formed, and the authors report that even when an exact stoichiometric amount of sulfur is used, oligosulfides and dimeric, coupled, products are formed.

In conclusion, the addition of elemental sulfur to living anionic polymers is not a suitable route to obtain thiol-functional chain ends in high yield. First of all, coupling reactions and sulfur oligomerization can not be excluded and secondly, working stoichiometrically is a prerequisite. This prerequisite is very difficult to obey in the case of polymeric organolithium compounds, since it demands exact determination of the molecular weight. Note that an accurate prediction of this molecular weight relies on the initiation efficiency of the *s*-butyllithium.

4.3.2 Episulfides

Ethylene sulfide and propylene sulfide are known to provide the desired sulfide-functionality at the chain end of living anionic polybutadiene by ring-opening.[10;13;14] However, the resulting chain-end structures (Figure 4.9) do not yield a proper radical leaving group for RAFT-mediated polymerization.

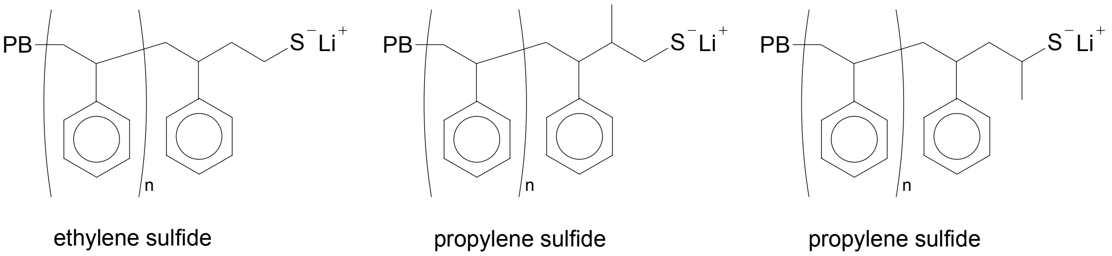


Figure 4.9. Chain-end structures after reaction of anionic poly(butadiene-*b*-styrene) with lithium counterion and ethylene sulfide or propylene sulfide

The simultaneous incorporation of a good leaving group and a thiol-functionality could be achieved by the use of an episulfide with phenyl substituents, such as styrene sulfide or stilbene sulfide. The chain-end structures that are obtained via these episulfides are shown in Figure 4.10.

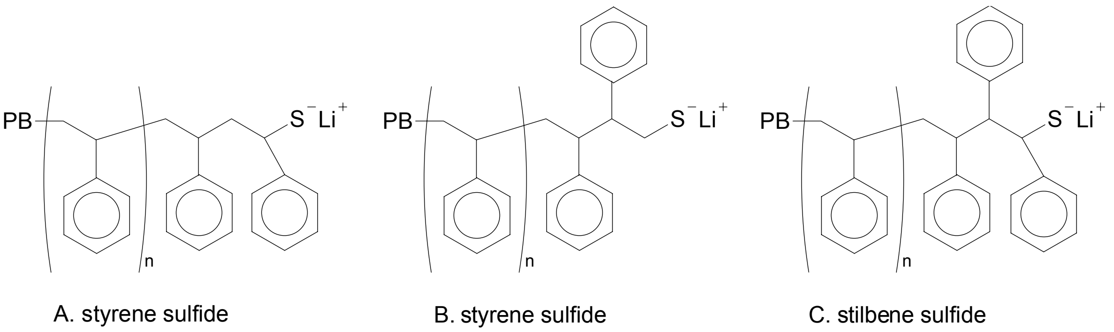


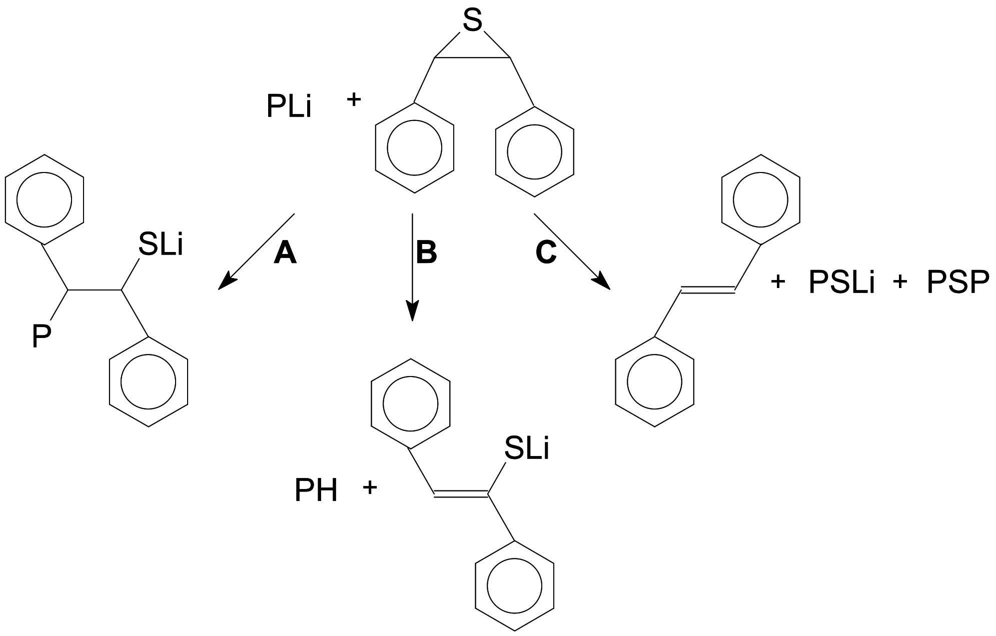
Figure 4.10. Chain-end structure after reaction of anionic poly(butadiene-*b*-styrene) with lithium counterion with styrene sulfide and stilbene sulfide

As can be seen from Figure 4.10, if styrene episulfide or stilbene episulfide are used, the short polystyrene block at the chain end of the polybutadiene would not be required anymore to obtain a good leaving group at the chain end.

Figure 4.10 demonstrates that styrene sulfide can add to the anionic chain end in two different ways, which yield two different reaction products, A and B. Product A results in a good leaving group Product B, however, results in a CH_2 group next to the sulfur, which is a poor leaving group. Although the probability of the formation of product B is relatively low because of steric hindrance, this way of addition to anionic chains is reported in literature[15-17] for styrene oxide.

Additional problems can be expected because of the poor stability of styrene sulfide, which is very susceptible to polymerization.[18]

Stilbene sulfide is expected to yield only one reaction product (Figure 4.10 C), because of its symmetrical structure. However, also for stilbene sulfide, poor stability is reported. Desulfurization results in the formation of stilbene. Moreover, stilbene sulfide is reported[19;20] to react with organolithium compounds in three different ways (Scheme 4.10). Next to the desired ring-opening reaction (**A**), hydrogen abstraction, yielding a thiolate anion (**B**) and desulfurization leading to the formation of stilbene and coupled polymeric material (**C**) are possible side reactions.



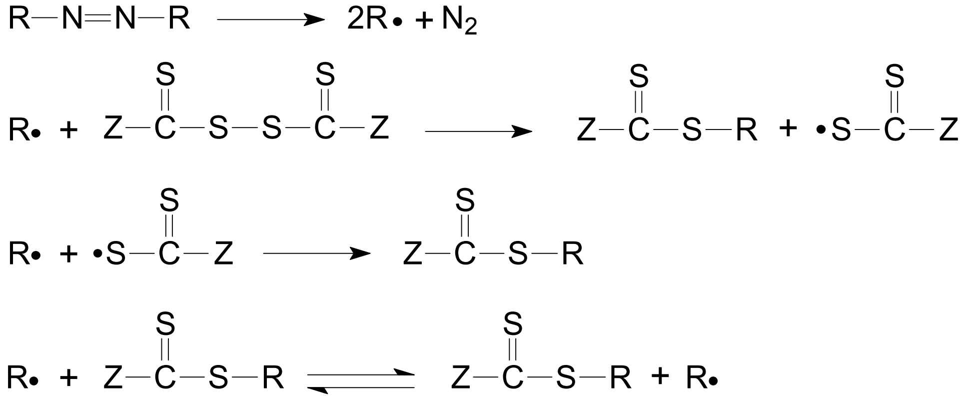
Scheme 4.10. Reactions of stilbene episulfide with organolithium compounds

The reported instability of the episulfides and the low selectivity of the reaction with organolithium compounds, prompted us to conclude that the use of episulfides was not a viable route to obtain thiol-functional polymers. Therefore, we did not pursue experimental investigations of this route.

4.3.3 Disulfides

Symmetrical disulfides

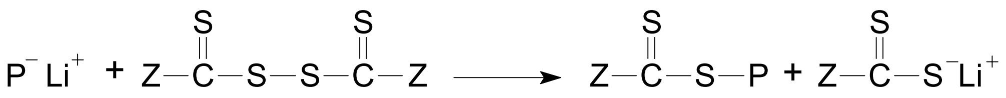
One of the methods that are widely used for the synthesis of dithioesters, which are commonly used RAFT-agents, proceeds via a radical mechanism, using azo-compounds and disulfides (Scheme 4.11)[21;22]



Scheme 4.11. Radical mechanism for the synthesis of dithioesters

Thiophilic attack of the radical at the C=S bond leads to homolytic cleavage of the S-S bond. A dithioester and a dithio-radical are formed. The dithio-radical can react with another radical (R·) to form a second dithioester molecule.

A similar mechanism as in Scheme 4.11 could also be applicable to our system, but instead of radicals, anions would be the attacking species. The nucleophilic attack would then result in heterolytic cleavage of the S-S bond instead of homolytic cleavage (Scheme 4.12).



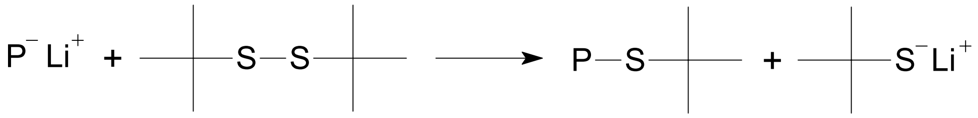
Scheme 4.12. Heterolytic cleavage of the S-S bond via nucleophilic attack

We used bis(thiobenzoyl)disulfide (Z = phenyl) to yield a RAFT-agent with a good activating group and reacted it with living poly(butadiene-*b*-styrene) with lithium counterion to obtain a macromolecular RAFT-agent with a polymeric leaving group.

Unfortunately, the reaction did not proceed in a controlled way, judging from the visual inspection of the reaction mixture (dark-brown color) and the MALDI-ToF-MS results. Most likely, side reactions such as attack at the carbon-side of the C=S bond play a significant role.

However, heterolytic cleavage of the S-S bond in a simple disulfide should be possible according to literature.[23] The S-S bond can be cleaved by direct attack at one of the two sulfur atoms by a radical, nucleophile, electrophile or a combination of the latter two. In our case, the anionic polymer is the nucleophilic species. The lithium counterion is the electrophilic species.

To investigate whether we could indeed prevent side reactions and selectively cleave the S-S bond, we replaced bis(thiobenzoyl)disulfide with a simple disulfide, namely di-*tert*-butyl disulfide. The reaction of di-*tert*-butyl disulfide with anionic polymer is displayed in Scheme 4.13.



Scheme 4.13. Heterolytic cleavage of the S-S bond in di-*tert*-butyl disulfide

The reaction as shown in Scheme 4.13 leads to the formation of a *tert*-butyl protected sulfide at the polymer chain-end and the formation of lithium *tert*-butyl sulfide.

The SEC-results for the reaction of living poly(butadiene-*b*-styrene) with di-*tert*-butyl disulfide are shown in Figure 4.11

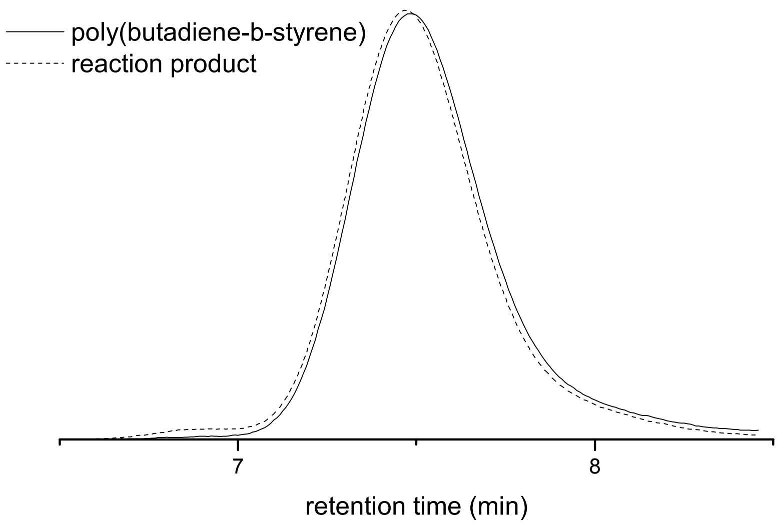


Figure 4.11. SEC-chromatograms of poly(butadiene-*b*-styrene) and the product of the reaction of anionic poly(butadiene-*b*-styrene) with lithium counterion and di-*tert*-butyl disulfide

Hardly any change in the SEC-chromatogram can be observed, indicating that no significant polymer-polymer coupling had taken place. The reaction product was analyzed with MALDI-ToF-MS to reveal the structure of the endgroups. Figure 4.12a shows the MALDI-ToF-MS mass spectrum of the reaction product. In Figure 4.12b an enlargement of spectrum a is shown, which can be compared with the simulated isotopic patterns assuming *s*-butyl and *t*-butyl sulfide endgroups (Figure 4.12c). The isotopic patterns match very well, indicating successful functionalization of the chain end.

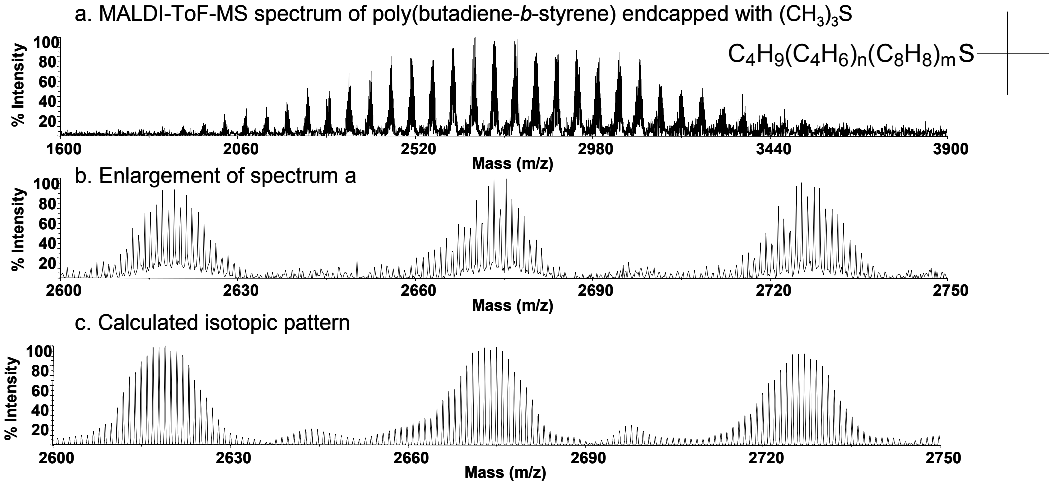


Figure 4.12.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated poly(butadiene-*b*-styrene) after reaction with di-*tert*-butyl disulfide

b. an enlargement of the spectrum between 2600 and 2750 g/mol

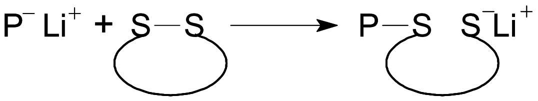
c. calculated isotopic patterns

After functionalization of the chain end with di-*tert*-butyl disulfide, a deprotection step is required to remove the *tert*-butyl group and yield a sulfide anion, or thiol at the chain end. Removal of a *tert*-butyl group from sulfur is not as straightforward as removal of a *tert*-butyl group from oxygen.[24-26] Earlier reports describe partial removal of the *tert*-butyl group under mild conditions. Under more harsh conditions, complete removal of the *tert*-butyl group can be achieved, but sulfur is also partially removed from the chain end under those conditions. In our case, a significant removal of sulfur is not acceptable, since a high degree of sulfide-functionality is required in order to obtain a reasonable yield of block copolymer in the end.

Except for the deprotection problem, the principle of the heterolytic cleavage of the S-S bond worked well. So if we would be able to design a disulfide which does not require a deprotection step after functionalization and which is not susceptible to side reactions, the desired chain-end functionality should be obtained.

Cyclic disulfides (thiiranes)

Cleavage of the S-S bond in a cyclic disulfide would eliminate the need for a deprotection step afterwards, which is demonstrated in Scheme 4.14



Scheme 4.14. Heterolytic cleavage of the S-S bond in a cyclic disulfide

Attack at sulfur results in the formation of a thioether. At the same time, a free sulfide anion at the chain end is formed. The structure of the cyclic disulfide is of utmost importance, since it has to yield a good leaving/reinitiating group for RAFT-mediated polymerization after ring-opening. We have chosen 1,4-dihydro-2,3-benzodithiin (Figure 4.13), which yields a benzylic endgroup, as a suitable cyclic disulfide. Note that the cyclic disulfide provides the required leaving group at the polymer chain end, therefore polybutadiene can be used directly, without the addition of a short polystyrene block.

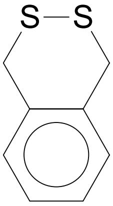
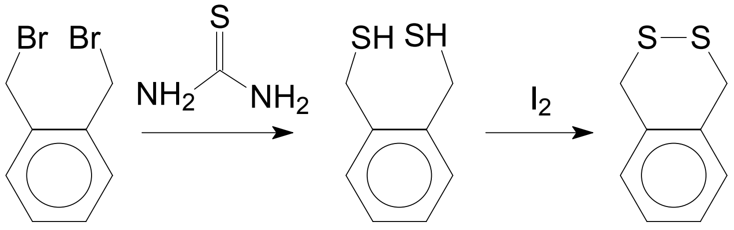


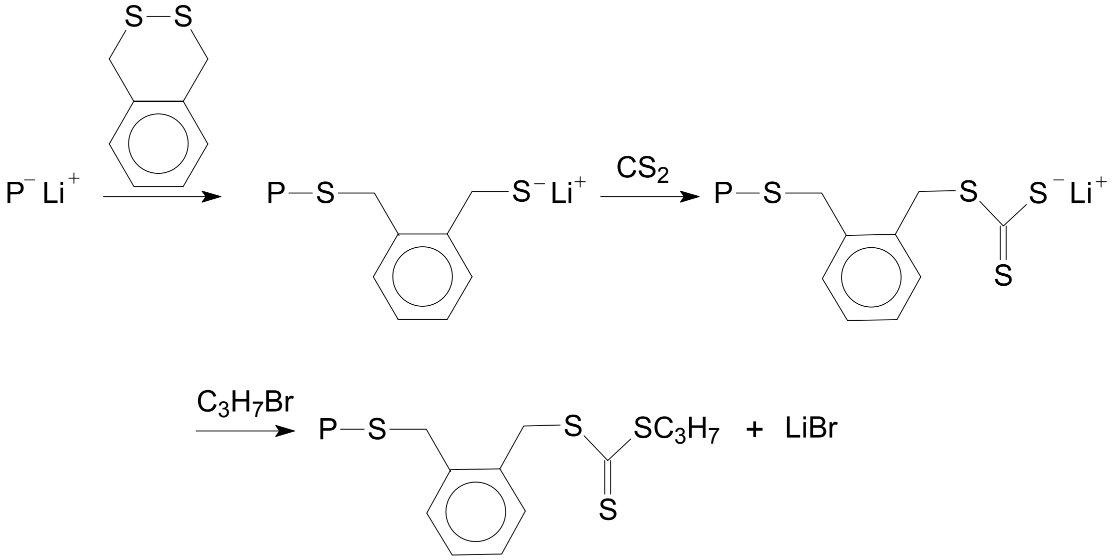
Figure 4.13. 1,4-dihydro-2,3-benzodithiin (DHBD)

1,4-dihydro-2,3-benzodithiin was synthesized from α,α'-dibromo-*o*-xylene and thiourea via the two-step route depicted in Scheme 4.15.[27;28]



Scheme 4.15. Synthesis of 1,4-dihydro-2,3-benzodithiin

Simply adding 1,4-dihydro-2,3-benzodithiin to living anionic polybutadiene should yield the desired sulfide anion at the chain end. From that point, a trithiocarbonate can be obtained by subsequent addition of carbon disulfide and 1-bromopropane to the reaction mixture (Scheme 4.16).



Scheme 4.16. One-pot procedure for the synthesis of a macromolecular RAFT-agent from living anionic polymer

Before investigating the entire procedure proposed in Scheme 4.16, the reaction of living anionic polybutadiene with 1,4-dihydro-2,3-benzodithiin was investigated separately. After the reaction, the product was terminated by quenching in methanol.

The reaction conditions that were used for the addition of 1,4-dihydro-2,3-benzodithiin to the living polymer are listed in Table 4.3. All reactions were carried out by adding a solution of 1,4-dihydro-2,3-benzodithiin immediately after the living anionic polymerization of butadiene.

Table 4.3. Reaction conditions and results for reactions of anionic polybutadiene with 1,4-dihydro-2,3-benzodithiin (DHBD)

Entry	Polymer[a]	DHBD/anions	Temperature (°C)	High MW material (%)
DHBD-a	PB	1	25	10
DHBD-b	PB	1	50	10
DHBD-c	PB	1	-78	5
DHBD-d	PB	1.5	25	55
DHBD-e	PB	0.7	25	15
DHBD-f	PS	1	25	45

[a] PB = polybutadiene, PS = polystyrene

The reaction products of DHBD-a were analyzed by MALDI-ToF-MS to determine the endgroups. Figure 4.14a shows the MALDI-ToF-MS mass spectrum. An enlargement of spectrum a (Figure 4.14b) was compared with the calculated isotopic patterns for polybutadiene with the desired endgroups (Figure 4.14c) and unmodified polybutadiene (Figure 4.14d). Mainly functionalized material can be observed, but also some unmodified polybutadiene can be seen. Furthermore, the 'bumps' in the baseline indicate that fragmentation of the sample occurred during the MALDI-ToF-MS measurement. However, the MALDI-ToF-MS results clearly indicate the formation of the desired product.

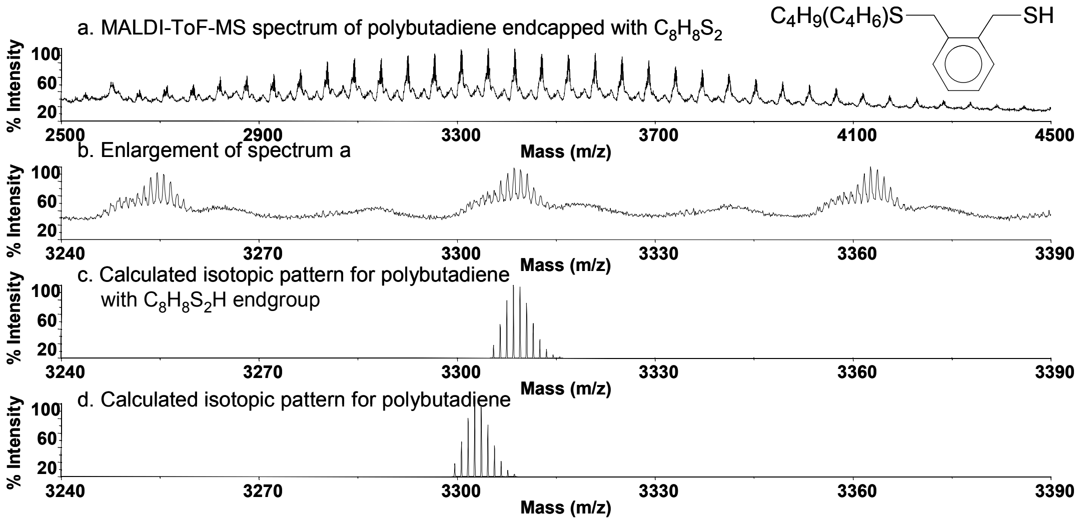


Figure 4.14.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated polybutadiene after reaction with 1,4-dihydro-2,3-benzodithiin

b. an enlargement of the spectrum between 3240 and 3390 g/mol

c. calculated isotopic pattern for polybutadiene with C_4H_9 and $C_8H_8S_2H$ endgroups

d. calculated isotopic pattern for polybutadiene with C_4H_9 and H endgroups

The SEC-results of DHBD-a (Table 4.3) are shown in Figure 4.15 top-left. A high molecular weight shoulder can be seen in the SEC-chromatogram of the reaction product. This shoulder can be assigned to the high molecular weight material formed by polymer-polymer coupling. After deconvolution, the amount of high molecular weight material was calculated to be approximately 10%. We attempted to reduce the amount of high molecular weight material by optimization of the reaction conditions. Variation of the reaction temperature (DHBD-a to c, Table 4.3 and Figure 4.15) showed that a drastic decrease of temperature, resulted in a decrease of the amount of coupled product with approximately a factor 2. A change in the ratio of the 1,4-dihydro-2,3-benzodithiin concentration to the polybutadiene anion concentration (DHBD-a, d and e, Tablle 4.3 and Figure 4.15) revealed that the use of equimolar amounts yielded the lowest amount of high molecular weight material. The influence of the living chain-end structure was investigated by comparison of polybutadiene with polystyrene (DHBD-a and f, Table 4.3 and Figure 4.15). The use of polystyrene instead of polybutadiene led to a dramatic increase in the amount of high molecular weight material.

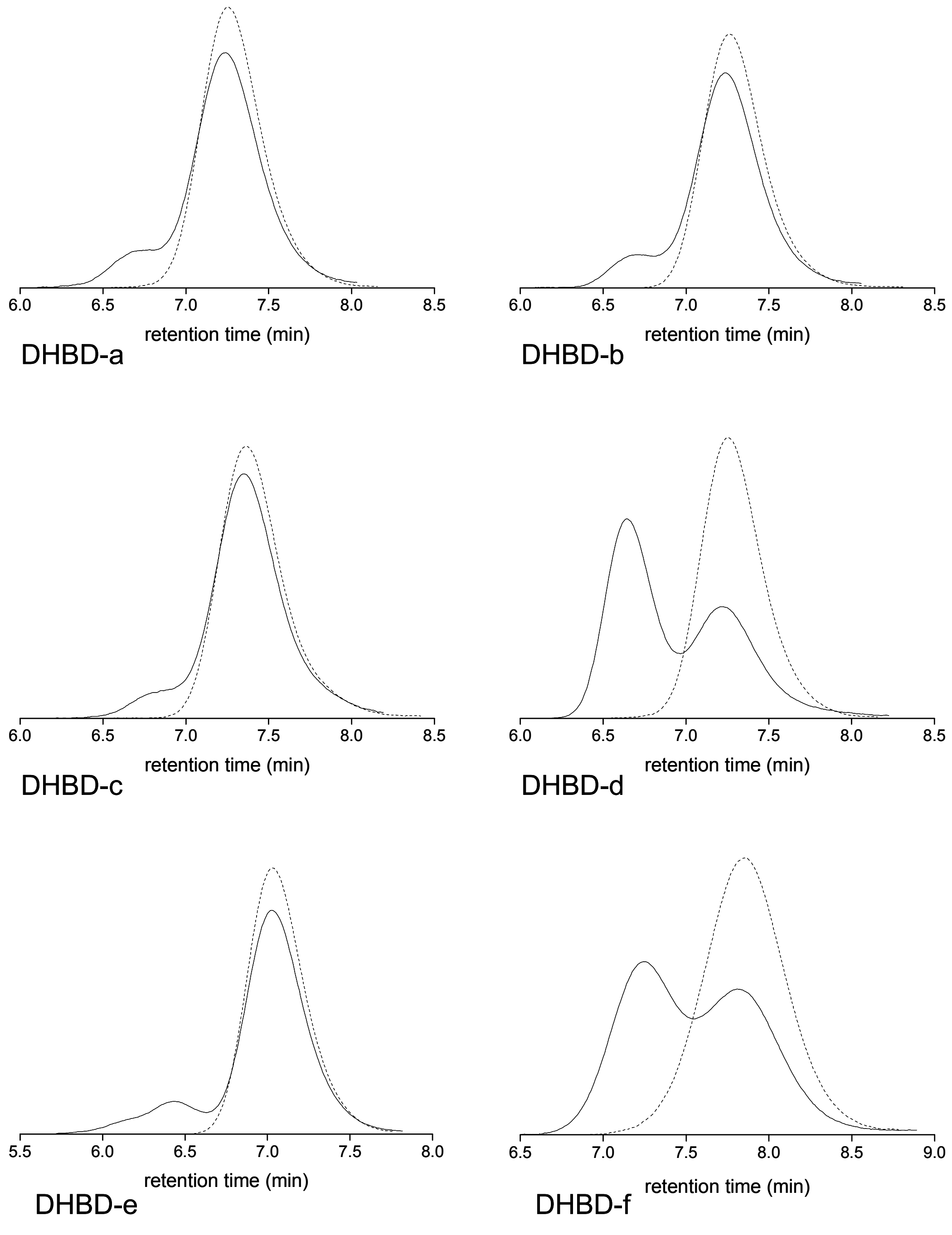
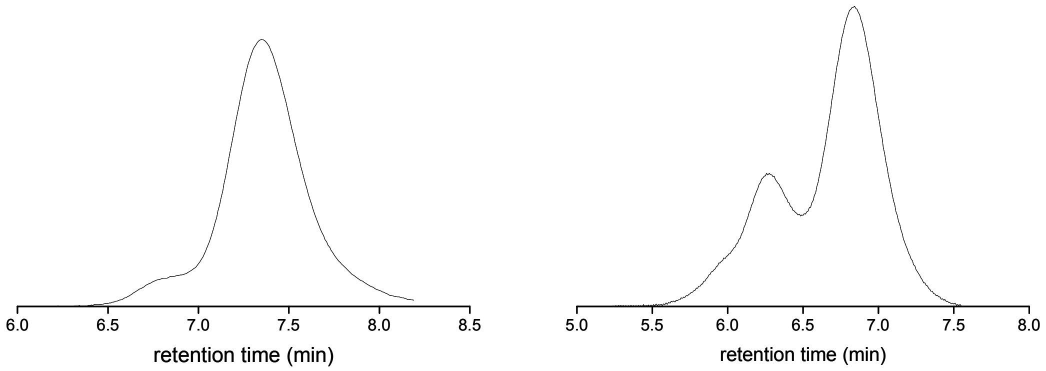


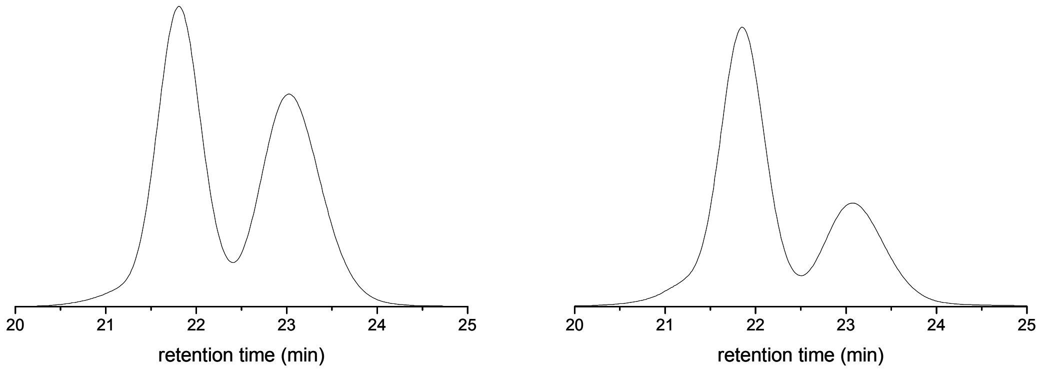
Figure 4.15. SEC-chromatograms of polybutadiene (or polystyrene, DHBD-f) before (---) and after (—) reaction with 1,4-dihydro-2,3-benzodithiin under different reaction conditions (Table 4.3)

In summary, the lowest amount of high molecular weight material was formed in the reaction of polybutadiene with an equimolar amount of 1,4-dihydro-2,3-benzodithiin at -78 °C. However, comparing the results of DRI-detection (Figure 4.16a) with the results of UV-detection (Figure 4.16b) shows a large discrepancy between the two chromatograms. Surprisingly, the UV-chromatogram shows more high molecular weight relative to the lower molecular weight material than the DRI-chromatogram. This means that part of the polybutadiene does not bear a UV-active group at the chain end and therefore does not show any UV-response.



a. DRI, day of reaction

b. **UV,** day of reaction



c. DRI after one week

d. DRI, after one month

Figure 4.16. SEC-chromatograms of polybutadiene after reaction with 1,4-dihydro-2,3-benzodithiin

a. DRI-trace on the day of the reaction (Table 4.3, DHBD-c)

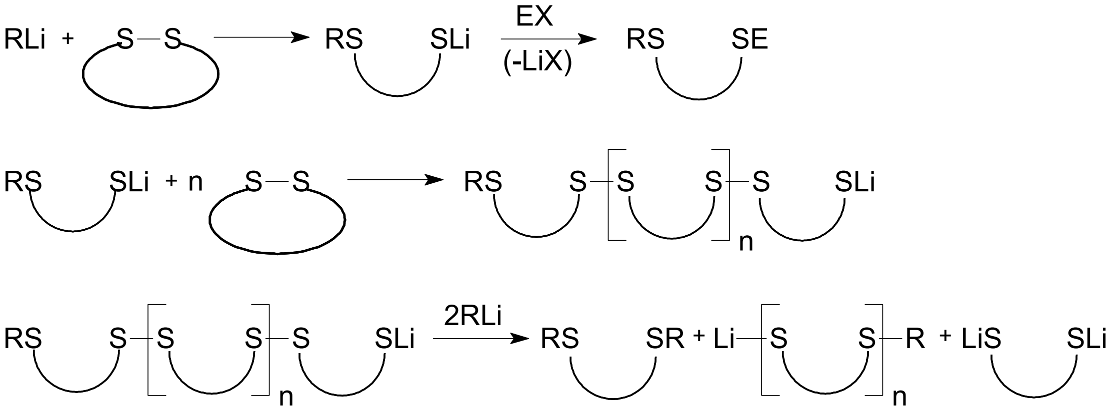
b. UV-trace on the day of the reaction

c. DRI-trace one week after the reaction

d. DRI-trace one month after the reaction

Furthermore, comparison of the DRI-trace measured directly after reaction with the same sample measured one week later and one month later (Figure 4.16 a, c and d), shows a large increase in the relative amount of high molecular weight material, *i.e.* from 5% to 50% after one week and up to 65% after one month.

To the best of our knowledge, hardly any papers have been published on the reaction of cyclic disulfides with organolithium compounds. In 1995, Smith and Tzimas[29] reported on the reaction of 1,2-dithiacycloalkanes and organolithium compounds. These authors treated the products of this reaction with electrophilic reactants to provide unsymmetrical dithia compounds. The reaction mechanism proposed by these authors is shown in Scheme 4.17.



Scheme 4.17. Reaction of cyclic disulfides with organolithium compounds

The first reaction in Scheme 4.17 corresponds with the desired functionalization reaction of the polybutadiene anion with 1,4-dihydro-2,3-benzodithiin. Possibly, the reaction is complicated by reaction of the sulfide anion that is formed with additional cyclic disulfide molecules, forming oligomeric species. These species in their turn give rise to coupled material as demonstrated by the last reaction in Scheme 4.17. Smith and Tzimas report a high yield of the desired product after trapping the sulfide with an electrophile. In our case, the sulfide anions are protonated and may be more susceptible to further reactions, such as oligomerization.

If we would complete the three-step trithiocarbonate synthesis that was shown in Scheme 4.16 instead of protonating the sulfide after the first step to obtain a thiol, we might avoid side reactions such as oligomerization.

We carried out the three-step synthesis by sequential addition of 1,4-dihydro-2,3-benzodithiin, carbon disulfide and 1-bromopropane to living anionic polybutadiene.

Analysis of the product with MALDI-ToF-MS was troublesome. No clear spectrum could be obtained because of fragmentation of the sample during the measurement. The SEC-chromatograms (Figure 4.17) indicate the formation of only a small amount of high molecular weight material and a reasonable agreement of the DRI-trace with the UV-trace.

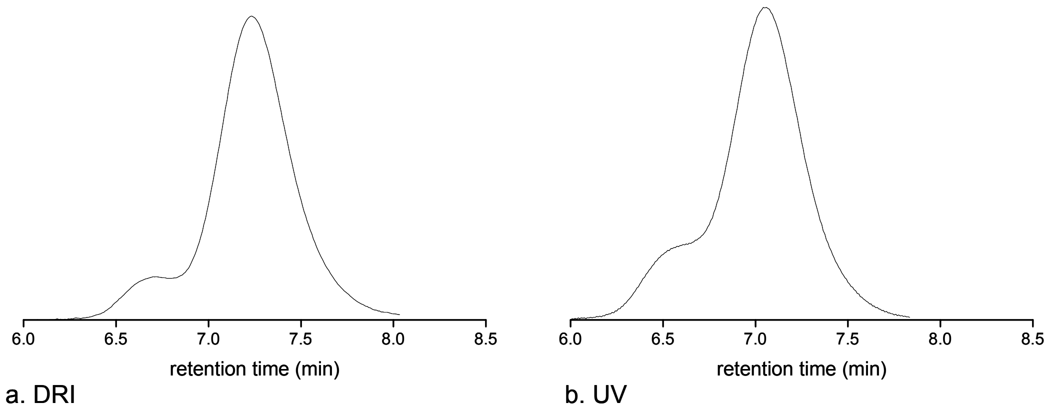


Figure 4.17. SEC-chromatograms of polybutadiene after reaction with 1,4-dihydro-2,3-benzodithiin, carbon disulfide and 1-bromopropane
a. DRI-trace
b. UV-trace

Based on the SEC-results, we tried to perform a chain extension reaction of the macromolecular RAFT-agent with styrene/maleic anhydride. The result of the chain extension could give an indication whether the transformation of polybutadiene into trithiocarbonate was successful or not. Unfortunately, only free radical polymerization of styrene/maleic anhydride was observed, resulting in high molecular weight polymer with a high polydispersity. The lack of control of the polymerization indicates that no, or hardly any, macromolecular RAFT-agent was present in the system. Therefore, we concluded that the conversion of polybutadiene into trithiocarbonate was not successful.

4.4 Conclusions

The chain-end functionalization of living anionic polybutadiene, with or without a short polystyrene block at the chain end was investigated. The ultimate goal was to convert the anionic chains into macromolecular RAFT-agents. In order to obtain the desired RAFT-agents, the chain ends had to be converted into either a bromide or a sulfide.

The introduction of a bromide-functionality at the chain end was attempted by lithium-halogen exchange reactions. A significant contribution of polymer-polymer coupling reactions was observed. These reactions, which probably proceed via a radical-ion intermediate, could not be suppressed sufficiently.

Several methods were employed to introduce a thiol-functionality. Reaction of anionic poly(butadiene-*b*-styrene) with elemental sulfur was partly successful, but not selective since polymer-polymer coupling and sulfur oligomerization could not be suppressed.

Cleavage of the S-S bond in disulfides is another method we used to obtain a thiol-functionality. First we tried to obtain a dithiobenzoate in one step by cleavage of the S-S bond in bis(thiobenzoyl)disulfide. This reaction was not selective resulting in the formation of different side products. Undesired side reactions were not observed when cleaving the S-S bond in di-*tert*-butyl disulfide. However, complete removal of the *tert*-butyl group without partial removal of sulfur is problematic.

The use of a cyclic disulfide, 1,4-dihydro-2,3-benzodithiin, eliminates the need for deprotection, since a free sulfide anion is formed at the chain end. MALDI-ToF-MS results indicate that the reaction was successful. Some polymer-polymer coupling reactions did take place, but they could be suppressed by a decrease of the reaction temperature to -78 °C. However, the SEC-results revealed that a significant amount of unmodified polybutadiene is still present after the reaction. Furthermore, the reaction product is not stable over time, resulting in the formation of more coupled material upon storage.

Finally, we concluded that direct conversion of anionic chain ends into thiol or bromide functionality is not possible in a selective way within the scope of our work. Side reactions, mainly polymer-polymer coupling, prevented high yield chain-end functionalization. Probably, the very reactive carbanions are the main cause for the side reactions. Therefore, attenuation of the chain-end reactivity is required for selective chain-end functionalization.

4.5 Experimental procedures

4.5.1 Materials

Anionic polymerizations: 1,3-Butadiene (Shell Chemicals Europe, 99.5%), styrene (VWR, 99%) and cyclohexane (VWR, high purity) were passed over an activated alumina column prior to use. N,N,N',N'-tetramethylethenediamine (TMEDA, Aldrich, >99.5%) was stored over molecular sieves under inert atmosphere. *sec*-Butyllithium (*s*-BuLi, Acros, 1.3 M solution in cyclohexane/hexane (92/8)) and 1,1-diphenylethylene (Aldrich, 97%), were used without further purification and stored under inert atmosphere.

Chain-end modifications: Bromobenzene (Aldrich, 99%), di-*tert*-butyl disulfide (Aldrich, 97%), carbon disulfide (Fluka, purum, 99+%) and 1-bromopropane (Aldrich, 99%) were all used without further purification and stored under inert atmosphere. Bis(thiobenzoyl)disulfide was synthesized according to literature procedures.[21;22]

1,4-dihydro-2,3-benzodithiin: α,α'-dibromo-*o*-xylene (Fluka, >98.5%), thiourea (Aldrich, 99%), iodine (VWR, >99.8%), sodium bisulfite (Sigma, >99%) , ethanol (Biosolve, AR) and ether (Biosolve, 99%) were all used as received.

All reactions were carried out under inert atmosphere.

4.5.2 Anionic polymerizations

Polybutadiene

Living anionic polymerization of butadiene was carried out in a 2 L stainless steel autoclave reactor equipped with a screw stirrer. The reactor was charged with 1 kg of cyclohexane and heated to 60 °C. Butadiene (50 g, 0.99 mol) and *s*-BuLi [40 mL of a 0.33 M solution in cyclohexane, (13 mmol)] were added. The polymerization was allowed to reach full conversion (approximately 90 min of reaction time).

Short polystyrene block

After butadiene polymerization, the reactor contents were cooled to 40 °C. TMEDA (3.02 g, TMEDA/*s*-BuLi = 2) and styrene (5.42 g, styrene/*s*-BuLi = 4) were weighed under inert atmosphere into glass vials, which were capped with a rubber septum. Then TMEDA and styrene were added successively to the reactor via an autoinjector. Reaction was allowed to continue at 40 °C for 30 minutes. After that time a sample was withdrawn from the reactor and quenched in methanol.

4.5.3 Lithium-halogen exchange reactions

In a typical procedure, the living polymer solution was used directly after polymerization. Approximately one fifth of the reaction mixture (200g, containing 2.6 mmol of polymer) was transferred to an oven-dried and nitrogen-purged glass bottle. Bromobenzene (0.45 g, 2.9 mmol) was added dropwise at room temperature while stirring. The reaction mixture was heated to 50 °C and allowed to react for 1 hour at that temperature. After that time the reaction mixture was quenched in an excess of methanol. After evaporation of the solvents, a sample was taken and used for analysis.

4.5.4 Functionalization with elemental sulfur

In a typical procedure the living polymer solution was used directly after polymerization. Approximately one fifth of the reaction mixture (200g, containing 2.6 mmol of polymer) was transferred to an oven-dried and nitrogen-purged glass bottle. Sulfur powder (83 mg, 0.33 mmol) was added in a glove box at room temperature while stirring. The reaction mixture was stirred overnight at room temperature. After that time the reaction mixture was quenched in an excess of methanol. After evaporation of the solvents, a sample was taken and used for analysis.

4.5.5 Functionalization with bis(thiobenzoyl)disulfide

In a typical procedure the living polymer solution was used directly after polymerization. Approximately one fifth of the reaction mixture (200g, containing 2.6 mmol of polymer) was transferred to an oven-dried and nitrogen-purged glass bottle. Bis(thiobenzoyl)disulfide (0.8 g, 2.6 mmol) was added in a glove box at room temperature while stirring. The mixture was allowed to react for 4 hours at room temperature. After that time the reaction mixture was quenched in an excess of methanol. After evaporation of the solvents, a sample was taken and used for analysis.

4.5.6 Functionalization with di-*tert*-butyl disulfide

In a typical procedure the living polymer solution was used directly after polymerization. Approximately one fifth of the reaction mixture (200g, containing 2.6 mmol of polymer) was transferred to an oven-dried and nitrogen-purged glass bottle. Di-*tert*-butyl disulfide (0.70 g, 3.9 mmol) was added dropwise via a syringe at room temperature while stirring. The reaction was stirred for one hour at room temperature. After that time the reaction mixture was quenched in an excess of methanol. After evaporation of the solvents, a sample was taken and used for analysis.

4.5.7 Functionalization with 1,4-dihydro-2,3-benzodithiin

Synthesis of 1,4-dihydro-2,3-benzodithiin

Synthesis of o-xylene-α,α'-dithiol[27]

α,α'-dibromo-*o*-xylene (10 g, 38 mmol) and thiourea (5.75 g, 76 mmol) were dissolved in a mixture of ethanol (5 mL) and water (30 mL) in an oven-dried three-neck roundbottom flask equipped with a stirrer and condenser. The solution was purged with Argon for 30 min. After that, the reaction mixture was allowed to reflux for 3 hours. Then, a sodium hydroxide solution (6g, 0.15 mol, in 10 mL water) was added dropwise via a syringe. The mixture was kept at reflux for 90 minutes. After that, the reaction mixture was cooled to below 5 °C and acidified to pH 2 by the dropwise addition of 6 M sulfuric acid. The resulting white solid was collected by filtration over a glass filter, washed with 3 M sulfuric acid and washed repeatedly with water. The product was dried under vacuum

^{1}H-NMR: δ (ppm) 7.2 [m, 4H, aromatic ring], 3.86 [d, 4H, CH_2], 1.85 [t, 2H, SH]

Synthesis of 1,4-dihydro-2,3-benzodithiin[28]

o-xylene-α,α'-dithiol (2.08 g, 0.01 mol), water (50 mL) and ether (100 mL) were added to a three-neck roundbottom flask equipped with a stirrer and condenser. The mixture was cooled to 0 °C and a solution of iodine (3 g, 0.01 mol, in 50 mL ether) was added dropwise. The resulting dark-brown solution was stirred for 1 hour at 0 °C and then enough saturated sodium bisulfite solution in water was added to decolorize the solution. The solution was further diluted with water (150 mL) and extracted three times with diethyl ether. The combined organic layers were dried with sodium sulfate, the solvent was evaporated and the product was recrystallized from methanol.

^{1}H-NMR: δ (ppm) 7.2 [m, 4H, aromatic ring], 4.1 [s, 4H, CH_2]

Functionalization with 1,4-dihydro-2,3-benzodithiin

In a typical procedure the living polymer solution was used directly after polymerization. Approximately one fifth of the reaction mixture (200g, containing 2.6 mmol of polymer) was transferred to an oven-dried and nitrogen-purged glass bottle. 1,4-dihydro-2,3-benzodithiin (0.44 g, 2.6 mmol) dissolved in cyclohexane was added dropwise via a syringe at room temperature while stirring. The reaction was stirred for one hour at room temperature. After that time the reaction mixture was quenched in an excess of methanol. After evaporation of the solvents, a sample was taken and used for analysis.

4.5.8 Trithiocarbonate synthesis

In a typical procedure the living polymer solution was used directly after polymerization. Approximately one fifth of the reaction mixture (200g, containing 2.6 mmol of polymer) was transferred to an oven-dried and nitrogen-purged glass bottle. 1,4-dihydro-2,3-benzodithiin (0.44 g, 2.6 mmol) dissolved in cyclohexane was added dropwise via a syringe at 50 °C while stirring. The mixture was allowed to react for one hour and was then cooled to room temperature. A solution of carbon disulfide (0.30 g, 3.9 mmol, in cyclohexane) was added dropwise. The mixture was stirred at room temperature for 30 min. A solution of 1-bromopropane (0.48 g, 3.9 mmol, in cyclohexane) was added dropwise. The mixture was kept at room temperature for 30 min. and then at 50 °C for two hours.

4.5.9 Characterization techniques

^{1}H-NMR

^{1}H-NMR analyses were performed on a Varian Mercury-Vx 400 MHz spectrometer. Samples were dissolved in deuterated chloroform (Cambridge Isotope Laboratories)

Size Exclusion Chromatography (SEC)

Set-up 1 (Kraton Polymers)

Molar mass and molar mass distributions were measured by size exclusion chromatography using a Waters GPC equipped with a Waters model 590 pump, a Spectra Physics model SP6040 XR differential refractive index detector (40 °C), a Waters WISP 717 autoinjector (50 µL injection volume) and a PL gel (5 µm pore size) 300 ×7.5 mm column (50 °C). THF was used as eluent (flow rate 0.95 mL/min). Narrow polystyrene standards (range 2400 g/mol-73000 g/mol) were used for calibration. The resulting apparent molar masses were converted into “real” molar masses, using an empirical equation. MALDI-ToF-MS was used to obtain absolute values for the molar mass.

Set-up 2 (TU Eindhoven)

SEC analyses were performed on a system that consisted of a three-column set (Mixed-C 5µm columns from Polymer Laboratories), with a guard column (PL gel 5µm, Polymer Laboratories), a gradient pump (Waters Alliance 2695, flow rate 1 mL/min isocratic), a photodiode-array detector (Waters 2996) and a differential refractive index detector (Waters 2414), a light-scattering detector (Viscotek) and a viscosity detector (Viscotek, dual detector 250). THF was used as the eluent.

MALDI-ToF-MS

MALDI-ToF-MS measurements were carried out on a Voyager-DE-STR (Applied Biosystems) equipped with a 337 nm nitrogen laser. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonononitrile (DCTB)[30] was used as the matrix. The matrix was dissolved in THF at a concentration of approximately 40 mg/mL. Silver trifluoroacetate (Aldrich, 98%) was used as the cationization agent and was added to THF at a concentration of 1 mg/mL. The polymer sample was dissolved in THF at a concentration of 2 mg/mL. In a typical measurement, the matrix, cationization agent and sample solutions were premixed in a 10:1:5 ratio. Approximately 0.5 μL of the mixture obtained was hand spotted on the target plate and left to dry. Mass spectra were recorded in the reflector mode. For each spectrum, 5000 laser shots were accumulated. Data Explorer© software (Applied Biosystems) was used for data interpretation. Additionally, data obtained from the copolymer samples were analyzed using a in house developed software package written in Visual Basic 6.0.[11] The principles used in this program are outlined in a recent paper by Willemse et al.[31]

References

1 Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754-6756.

2 Degani, I.; Fochi, R.; Gatti, A.; Regondi, V. *Synthesis* **1986**, 894-899.

3 Hirao, A.; Tohoyama, M.; Nakahama, S. *Macromolecules* **1997**, *30*, 3484-3489.

4 Liu, F.; Liu, B.; Luo, N.; Ying, S.; Liu, Q. *Chemical Research in Chinese Universities* **2000**, *16*, 72-77.

5 Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219-231.

6 Jagur-Grodzinski, J. *Reactive & Functional Polymers* **2001**, *49* , 1-54.

7 Rogers, H. R.; Houk, J. *Journal of the American Chemical Society* **1982**, *104*, 522-525.

8 Gilman, H.; Langham, W.; Moore, F. W. *Journal of the American Chemical Society* **1940**, *62*, 2327-2335.

9 Trepka, W. J.; Sonnenfeld, R. J. *Journal of Organometallic Chemistry* **1969**, *16*, 317-320.

10 Tung, L. H.; Lo, G. Y. S.; Griggs, J. A. *Journal of Polymer Science, Polymer Chemistry Edition* **1985**, *23*, 1551-1568.

11 This software package is based on work published in: *Characterization of (co)polymers by MALDI-TOF-MS*; B.B.P.Staal, PhD Thesis; Eindhoven; **2005**.

12 Boscato, J. F.; Catala, J. M.; Franta, E.; Brossas, J. *Makromolekulare Chemie* **1979**, *180*, 1571-1574.

13 McKee, G. E.; Knoll, K.; Guentherberg, N.; Gottschalk, A. **1996,** EP 693510.

14 Bronstert, K.; Walter, H. M.; Schwaben, H. D. **1988,** EP 295675

15 Quirk, R. P.; Lizarraga, G.; Lu, L. M.; Hasegawa, H.; Zhuo, Q. *Macromolecular Symposia* **1997**, *118*, 89-97.

16 Quirk, R. P.; Hasegawa, H.; Gomochak, D. L.; Wesdemiotis, C.; Wollyung, K. *Macromolecules* **2004**, *37*, 7146-7155.

17 Yus, M.; Soler, T.; Foubelo, F. *Tetrahedron* **2002**, *58*, 7009-7016.

18 Communications via e-mail with I. Mohammadpoor-Baltork Esfahan University, Iran, **2003**.

19 Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Zani, P. *Gazzetta Chimica Italiana* **1990**, *120*, 115-121.

20 Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Piccinelli, P. *Tetrahedron Letters* **1979**, 3987-3990.

21 Bouhadir, G.; Legrand, N.; quiclet-Sire, B.; Zard, S. Z. *Tetrahedron Letters* **1999**, *40*, 277-280.

22 Thang, S. H.; Chong, Y. K.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Letters* **1999**, *40*, 2435-2438.

23 Kice, J. L. *Accounts of Chemical Research* **1968**, *1*, 58-64.

24 Callahan, F. M.; Anderson, G. W.; Paul, R.; Zimmerman, J. E. *Journal of the American Chemical Society* **1963**, *85*, 201-207.

25 Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1995**, *51*, 11883-11890.

26 Kudzin, Z. H.; Stec, W. J. *Synthesis* **1983**, 812-814.

27 Mayerle, J. J.; Denmark, S. E.; DePamphilis, B. V.; Ibers, J. A.; Holm, R. H. *Journal of the American Chemical Society* **1975**, *97*, 1032-1045.

28 Juaristi, E.; Cruz-Sanchez, J. S. *Journal of Organic Chemistry* **1988**, *53*, 3334-3338.

29 Smith, K.; Tzimas, M. *Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry* **1995**, 2381-2382.

30 Ulmer, L.; Mattay, J.; Torres-Garcia, H. G.; Luftmann, H. *European Journal of Mass Spectrometry* **2000**, *6*, 49-52.

31 Willemse, R. X. E.; Staal, B. B. P.; Donkers, E. H. D.; van Herk, A. M. *Macromolecules* **2004**, *37*, 5717-5723.

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5

Macromolecular RAFT-agents via esterification Synthesis and chain extension

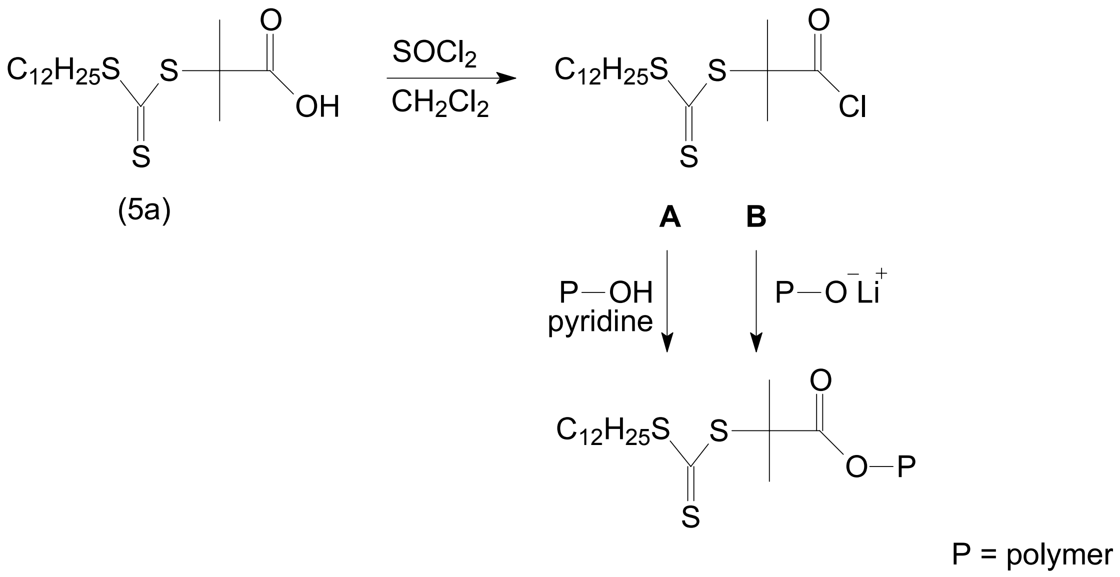
5.1 Introduction

In the previous chapter, attempts to convert poly(butadienyl)lithium and poly(styryl)lithium into macromolecular RAFT-agents were described. In all cases we tried to take advantage of the high reactivity of the polymeric carbanions by performing modification reactions directly at these carbanions.

In this chapter, a slightly more conventional route to obtain macromolecular RAFT-agents is presented.

The endcapping reaction of living anionic polymers with ethylene oxide is a well-known and widely used method to obtain hydroxyl-functional polymers.[1-4] The addition of ethylene oxide is known to proceed quantitatively and without significant oligomerization. Subsequent protonation by quenching in methanol yields the hydroxyl-functional polymer.

The two-step esterification of hydroxyl-functional polymers with S-dodecyl S'-(isobutyric acid) trithiocarbonate (DIBTC)[5] (5a) yields macromolecular RAFT-agents with polymeric leaving groups. The reaction is depicted in Scheme 5.1, route A.[6;7] In an alternative route, the product of the endcapping reaction with ethylene oxide is not protonated, but used immediately in the esterification[8;9] with DIBTC (Scheme 5.1, route B) yielding the same macromolecular RAFT-agent.



P = polymer

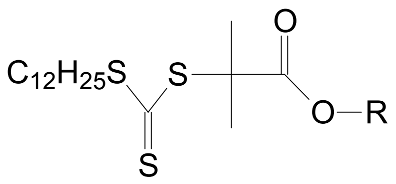
Scheme 5.1. Esterifications with DIBTC (5a)

Route A as well as route B will be evaluated in this chapter; first for different low and intermediate molecular weight RAFT-agents and subsequently for the high molecular weight equivalents. All RAFT-agents were chain extended with styrene and maleic anhydride to attach a polar block to the RAFT-agents, as described in Chapter 1.

5.2 Low molecular weight RAFT-agents

5.2.1 RAFT-agent synthesis

Two RAFT-agents based on DIBTC (5a in Scheme 5.1) were synthesized (Figure 5.1). RAFT-agent 5b is the product of the esterification of DIBTC with *n*-butanol and 5c is produced by the esterification of DIBTC with lithium ethoxide.



5b. R = C_4H_9
5c. R = C_2H_5

Figure 5.1. Low molecular weight RAFT-agents

The efficiencies of these two esterifications were mutually compared in order to determine the most suitable route for the RAFT-agent synthesis. ^{1}H-NMR and LC-MS analyses indicated near-quantitative formation of the ester in both cases. However, a small amount of impurity was observed in the ^{1}H-NMR spectrum, which seems to be an inherent byproduct of the reaction between thiocarbonylthio-compounds and thionyl chloride. From our experience, dithioesters are not stable at all when exposed to thionyl chloride. Trithiocarbonates proved to be reasonably stable, but still degrade to a small extent.

In conclusion, *n*-butanol as well as lithium ethoxide afford the desired RAFT-agent in high yield upon esterification with DIBTC. Our results with *n*-butanol and lithium ethoxide point to polymeric alcohols and polymeric lithium alkoxides as promising starting materials in the synthesis of macromolecular RAFT-agents. However, when polymeric alcohols or lithium alkoxides are used, the concentration of endgroups is lower and therefore the high reactivity of the polymeric lithium alkoxide may be advantageous. An additional advantage of the use of lithium alkoxides over alcohols is the reduced number of intermediate polymer isolation steps, which allows a one-pot procedure for anionic polymerization, endcapping with ethylene oxide and esterification with the acid chloride derivative of DIBTC.

5.2.2 Polymerizations

Both RAFT-agents 5b and 5c were used to control the (co)polymerization of styrene (and maleic anhydride). An overview of the results is given in Table 5.1

As can be seen from Table 5.1, in the case of styrene (S-1), high conversions are not reached in a reasonable time and the polydispersity of the product is rather high (PDI = 1.4). These observations have been made earlier in our laboratory for DIBTC controlled polymerization of styrene under similar reaction conditions.

The copolymerization of styrene and maleic anhydride on the other hand, can be taken to high conversions with good control over the molecular weight (distribution).

Table 5.1. Results of polymerizations with RAFT-agents 5b and 5c, see Figure 5.1

Entry[a]	RAFT -agent	Solvent	Conversion (%)	M_n calc (g/mol)	M_n SEC (g/mol)	PDI
S-1[b]	5b	Toluene	28	9650	13300	1.4
SMA-1[c]	5b	MEK[d]	100	5410	6060	1.2
SMA-2[c]	5c	MEK:toluene (1:2)	93	8180	10430	1.2

[a] [RAFT]/[I] = 10, T = 85 °C, reaction time = 24 hours

[b] styrene homopolymerization, [Sty] = 1 M

[c] styrene-maleic anhydride copolymerization, [Sty] = [MAh] = 1 M

[d] MEK = methyl ethyl ketone

In all cases, M_n found by SEC is slightly higher than M_n calculated. For the copolymerizations, this difference may be attributed to the fact that polystyrene calibration was used to determine the molecular weight. Additionally, for all polymerizations, the RAFT-agents were used without purification, so the actual RAFT-concentration is somewhat lower than calculated on the basis of the amount of RAFT-agent in the recipe, which results in an increased M_n.

5.3 Macromolecular RAFT-agents: Intermediate molecular weight

5.3.1 RAFT-agent synthesis

Before starting investigations on systems of molecular weights that are sufficiently high to obtain useful material properties, first some model systems of intermediate molecular weight were tested. The endgroup modifications can be characterized more thoroughly for these model systems than for their higher molecular weight equivalents. Three different model systems were used:

- Hydroxyl-functional poly(ethylene-*co*-butylene) (pEB-OH, Kraton L-1203, $M_n \approx 3800$ g/mol), which is commercially available from Kraton Polymers.

- Polybutadiene (pB, $M_n \approx 3800$ g/mol), which was prepared by anionic polymerization using *s*-butyllithium as initiator and subsequently endcapped with ethylene oxide. We used this polymer as alcohol (pB-OH) and as lithium alkoxide (pB-OLi)
- Poly(styrene-*block*-butadiene) (pSB, $M_n \approx 3800$ g/mol), which was prepared by anionic polymerization using *s*-butyllithium as initiator and used directly after ethylene oxide endcapping as lithium alkoxide (pSB-OLi)

Each polymer was converted into an ester of DIBTC to obtain the macromolecular RAFT-agents according to the route shown in Scheme 5.1.

The pEB-OH based RAFT-agent was analyzed by ^{1}H-NMR, which revealed that approximately 75% of the chain ends were converted into ester groups.

In case of the pB based RAFT-agents, ^{1}H-NMR analysis is hampered by the presence of different chain-end structures (Figure 5.2).[10]

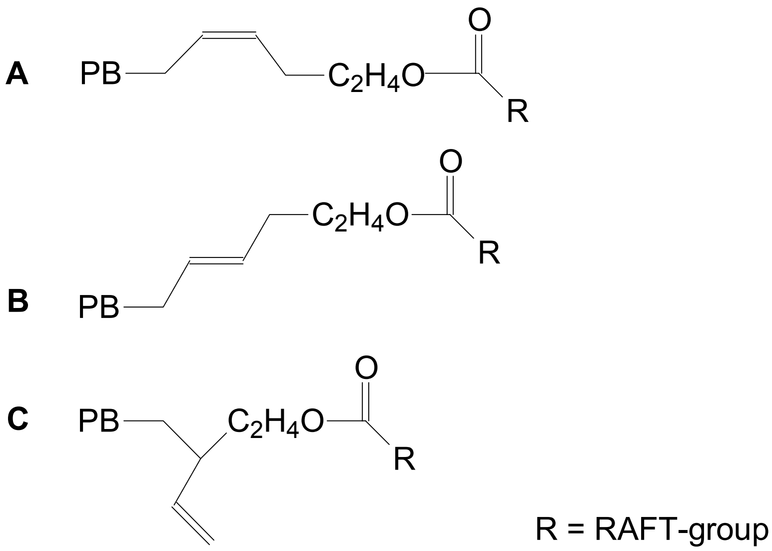


Figure 5.2. Polybutadiene chain ends: A. *cis*-1,4-addition
B. *trans*-1,4-addition
C. 1,2-addition

These three structures, caused by different ways of addition of butadiene in living anionic polymerization, result in a very broad multiplet signal for the C*H*$_2$OCOR protons, leading to inadequate integration. However, the C*H₂*OH signal completely disappears, indicating high conversion of the endgroup.

In addition to ^{1}H-NMR analysis, the reaction products of the three reaction steps in the RAFT-synthesis, being butadiene polymerization, ethylene oxide endcapping and esterification, were analyzed with MALDI-ToF-MS.

Figure 5.3a shows the MALDI-ToF-MS spectrum of *s*-butyllithium initiated polybutadiene, terminated by protonation resulting in a hydrogen endgroup. In Figure 5.3b an enlargement of this spectrum from 3060 to 3240 g/mol is displayed. The enlargement shows three isotopic patterns. The mass difference between each pattern corresponds to the mass of one butadiene unit. Figure 5.3b can be compared with the calculated isotopic pattern for polybutadiene with 55 repeating units and *s*-butyl and hydrogen endgroups, shown in Figure 5.3c. This comparison allows the conclusion that polybutadiene with the expected endgroups is synthesized without the formation of significant amounts of side products.

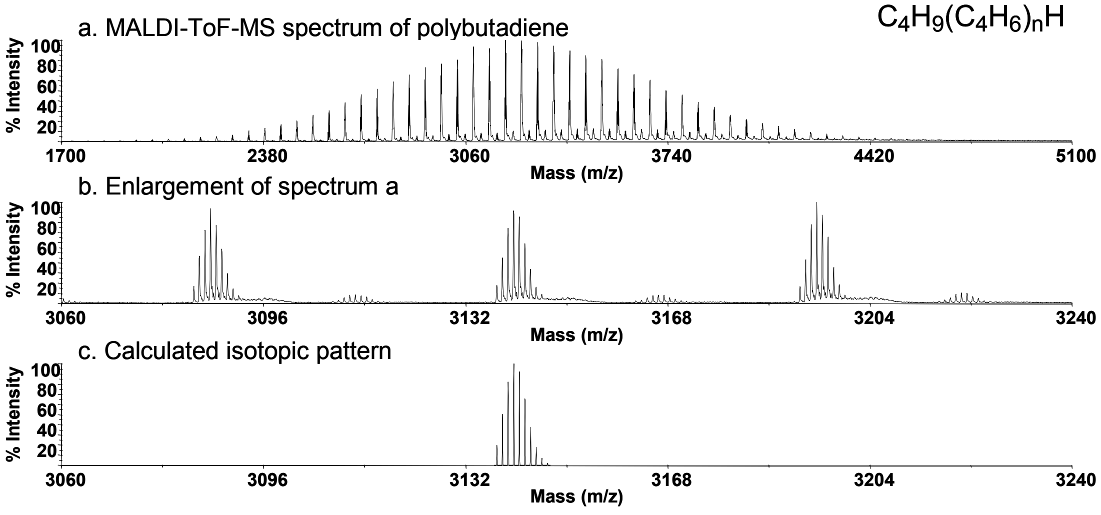


Figure 5.3.

a. MALDI-ToF-MS mass spectrum of polybutadiene with *s*-butyl and hydrogen endgroups

b. an enlargement of the spectrum between 3060 and 3240 g/mol

c. calculated isotopic pattern for polybutadiene: $C_4H_9(C_4H_6)_{55}H$

The MALDI-ToF-MS mass spectrum of poly(butadienyl)lithium after endcapping with ethylene oxide is depicted in Figure 5.4a. Again, comparison of an enlargement of this spectrum (Figure 5.4b) with the calculated isotopic pattern (Figure 5.4c) reveals that polybutadiene with one ethylene oxide unit at the chain end is the main reaction product.

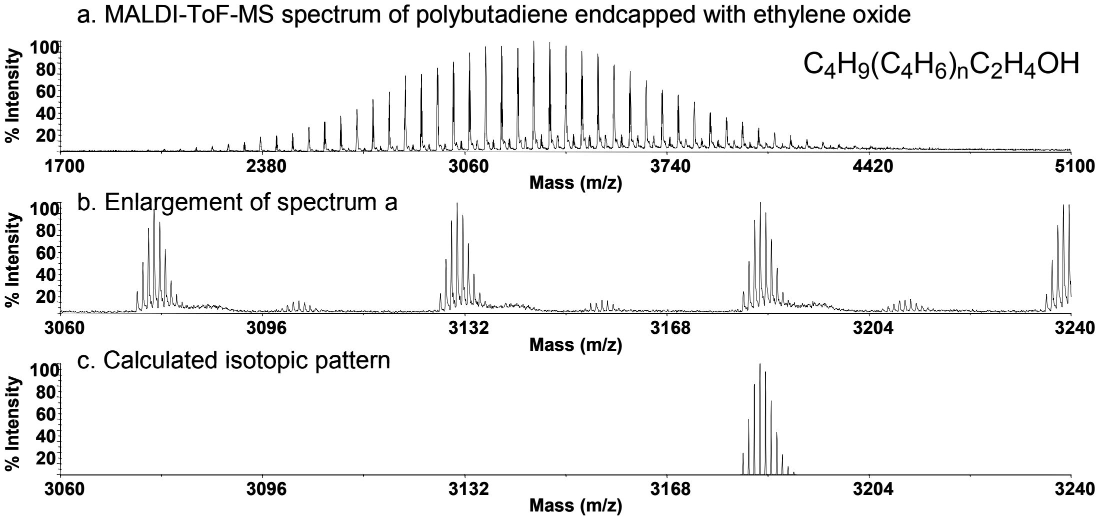


Figure 5.4.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated polybutadiene endcapped with ethylene oxide

b. an enlargement of the spectrum between 3060 and 3240 g/mol

c. calculated isotopic pattern for polybutadiene: $C_4H_9(C_4H_6)_{55}C_2H_4OH$

Finally, the MALDI-ToF-MS mass spectrum of the product of the esterification with DIBTC is shown in Figure 5.5. It can be clearly seen that the main distribution corresponds to the expected distribution of the macromolecular RAFT-agent.

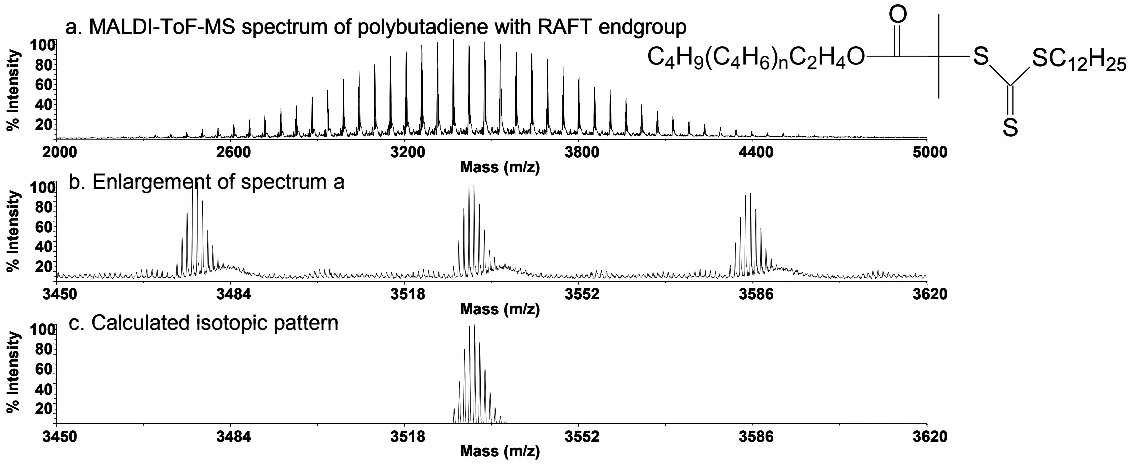


Figure 5.5.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated polybutadiene after ethylene oxide endcapping and esterification with DIBTC

b. an enlargement of the spectrum between 3450 and 3620 g/mol

c. calculated isotopic pattern for polybutadiene:

$C_4H_9(C_4H_6)_{55}C_2H_4OCOC(CH_3)_2CS_3C_{12}H_{25}$

No significant amounts of residual polybutadiene and polybutadiene with hydroxyl-endgroup can be observed in the mass spectrum of the final product. However, it should be noted that even though the MALDI-ToF-MS spectra indicate a high yield of the macromolecular RAFT-agent, MALDI-ToF-MS is not a quantitative method. This is due to the fact that different polymer chains in the sample have different ionization efficiencies, which can lead to a discrepancy between the composition of the actual sample and the distributions as displayed in the MALDI-ToF-MS spectrum.

Another estimation of the conversion of the polymeric alcohol into RAFT-agent was obtained by analyzing the product with gradient polymer elution chromatography (GPEC). With this chromatographic technique polymers can be separated according to their endgroup by applying a suitable eluent gradient. Detection is done by means of an evaporative light scattering detector (ELSD) and a UV-detector. The GPEC-chromatograms (Figure 5.6) of the starting material and the reaction product demonstrate that a DIBTC-polybutadiene ester was formed with high conversion. Some residual pB-OH was detected (Figure 5.6a), which was estimated to be approximately 15% of the total product.

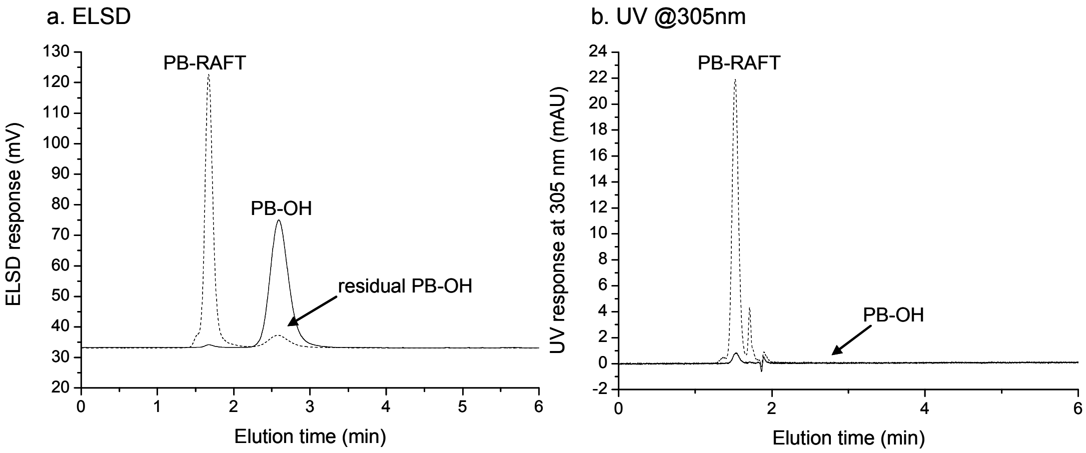


Figure 5.6. GPEC chromatograms for hydroxyl-functional polybutadiene (pB-OH, —) and for the product of the esterification of hydroxyl-functional polybutadiene with DIBTC (pB-RAFT and residual pB-OH, ----)

a. ELSD response

b. UV response at a wavelength of 305 nm

The last intermediate molecular weight RAFT-agent is based on a block copolymer of styrene and butadiene (pSB-RAFT). This means that the same problem as for the polybutadiene based RAFT-agent occurs in ^{1}H-NMR analysis, therefore accurate integration was not possible. MALDI-ToF-MS analysis is complicated by the fact that we are dealing with a block copolymer instead of a homopolymer, which broadens the isotopic distributions significantly. To unravel the complicated mass spectra we employed advanced simulations using an in-house developed software-package[11], partly based on the program mentioned in Chapter 3, in combination with existing Data Explorer software. These two combined programs can calculate a MALDI-ToF-MS mass spectrum based on input values for the molecular weight of the monomers, assumed endgroups and cationization agent. A comparison of the simulated spectrum including calculated isotopic patterns with the spectrum of a product sample provides information about the copolymer composition and can confirm the expected endgroups. For each reaction step in the synthesis of pSB-RAFT the product (mixture) was analyzed with MALDI-ToF-MS. The MALDI-ToF-MS spectra of the polymers were analyzed with the aid of the simulation program.

Poly(styrene-*b*-butadiene) was prepared by living anionic polymerization.

s-Butyllithium was used to initiate the polymerization of styrene. When complete styrene conversion was reached, butadiene was added, resulting in the desired block copolymer. After butadiene polymerization, a sample was withdrawn and quenched in methanol to terminate the living polymer chains by protonation. Figure 5.7a shows the MALDI-ToF-MS mass spectrum of this product. An enlargement of this spectrum (Figure 5.7b) shows the complicated isotopic patterns for this block copolymer, which cannot be assigned easily to specific copolymer compositions and endgroups. Representing the mass spectrum by means of a copolymer fingerprint (Figure 5.7d), as was also demonstrated in Chapter 3, makes interpretation more straightforward. The maximum intensity in the fingerprint, meaning the highest number of chains, can be found at block lengths of 18 styrene units and 36 butadiene units. This is in accordance with the quantities of monomer used, resulting in equal molecular weights for the polystyrene and the polybutadiene blocks.

Part of the simulated mass spectrum with the assumed endgroups (*s*-butyl and hydrogen) is displayed in Figure 5.7c and corresponds very well to the spectrum of the product sample in Figure 5.7b, indicating that the expected block copolymer was formed.

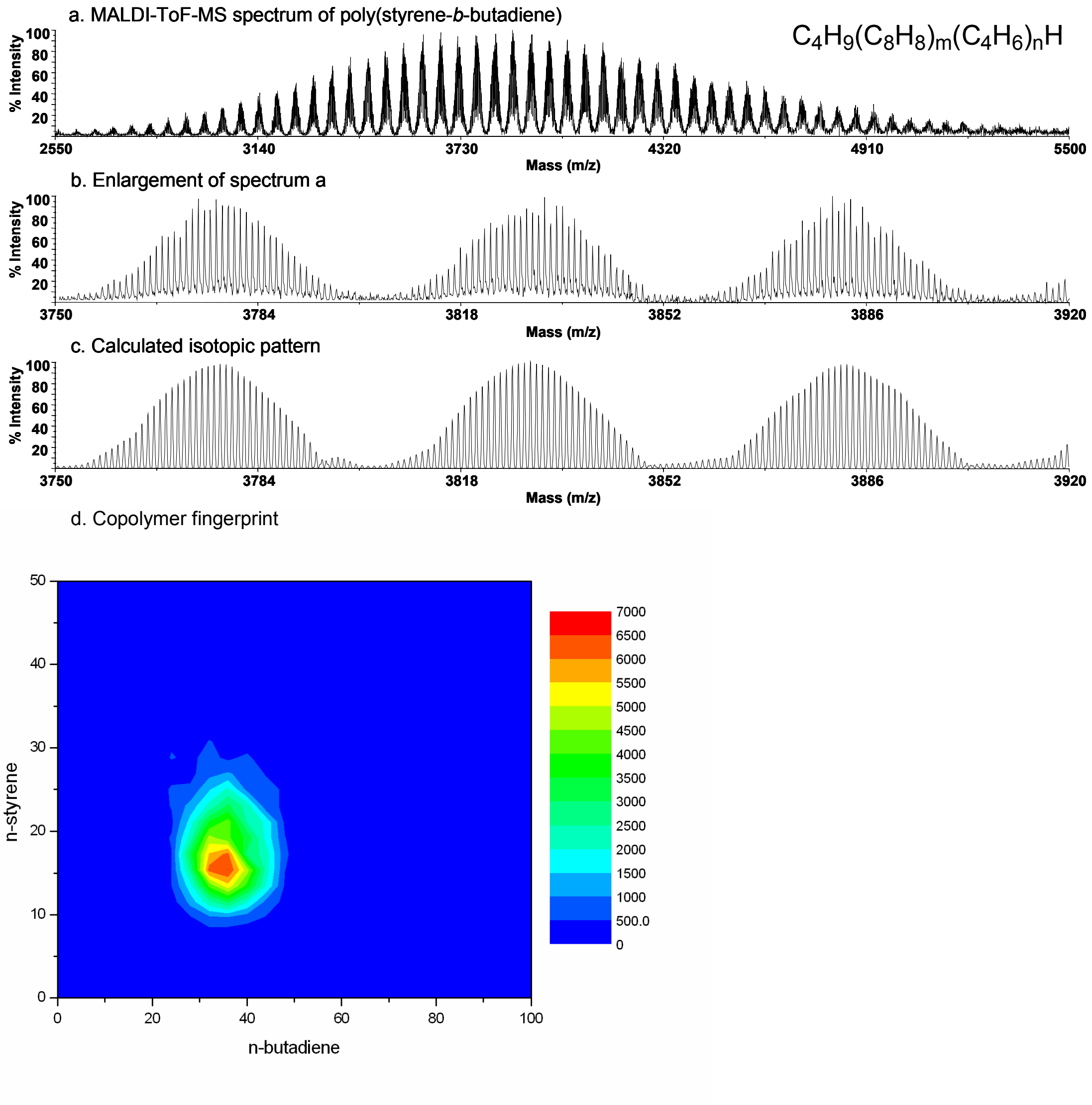


Figure 5.7.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated poly(styrene-*b*-butadiene)

b. an enlargement of the spectrum between 3750 and 3920 g/mol

c. calculated isotopic patterns

d. the copolymer fingerprint for poly(styrene-*b*-butadiene)

After the anionic polymerization of styrene and butadiene, the living polymer was endcapped with ethylene oxide. Again, a sample was withdrawn and quenched in methanol. This procedure yields poly(styrene-*b*-butadiene) with a $-C_2H_4OH$ endgroup. The MALDI-ToF-MS mass spectrum of this polymer is displayed in Figure 5.8a.

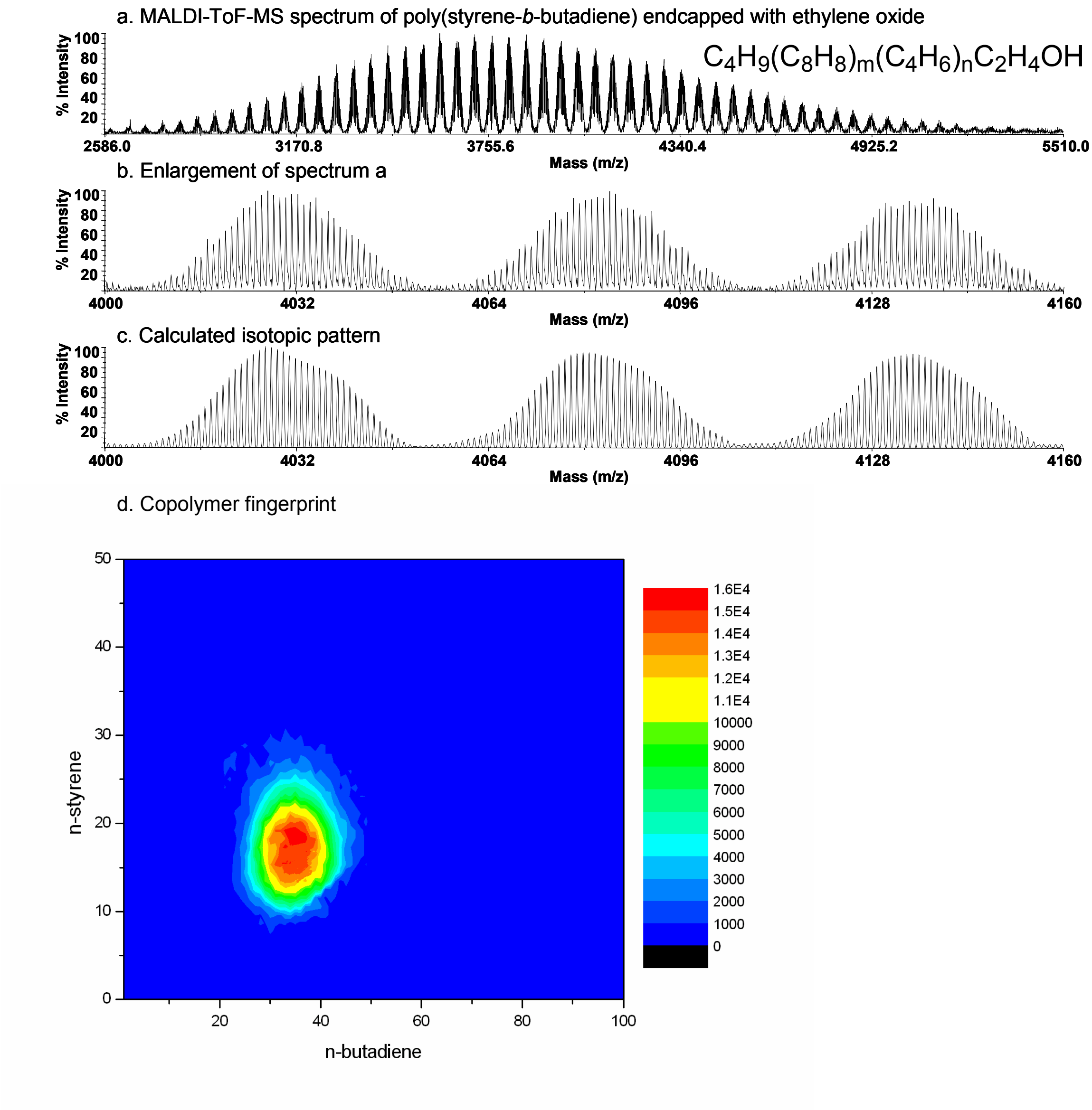


Figure 5.8.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated poly(styrene-*b*-butadiene) endcapped with ethylene oxide

b. an enlargement of the spectrum between 4000 and 4160 g/mol

c. calculated isotopic patterns

d. the copolymer fingerprint for poly(styrene-*b*-butadiene) endcapped with ethylene oxide

Figure 5.8b shows an enlargement of this spectrum, which is almost identical to the simulated spectrum (Figure 5.8c). Furthermore the copolymer fingerprint (Figure 5.8d) shows the same maximum intensity as the fingerprint in Figure 5.7d. This implies that, except for the modified endgroup, the copolymer composition did not change upon modification with ethylene oxide.

The last step in the synthesis of pSB-RAFT was the esterification of ethylene oxide endcapped poly(styrene-*b*-butadiene) with the acid chloride derivative of DIBTC. Figure 5.9a shows the MALDI-ToF-MS mass spectrum of the product. Some fragmentation due to the presence of the RAFT-group occurs during the MALDI-ToF-MS measurement, resulting in poorer quality of the mass spectrum. This makes the simulation more difficult. Therefore, from comparison of the measured spectrum (Figure 5.9b) with the calculated isotopic patterns (Figure 5.9c) only an indication can be obtained for the success of the esterification. The fact that the maximum intensity in the copolymer fingerprint (Figure 5.9d) does not change with respect to the maximum intensity in Figures 5.7d and 5.8d supports this indication.

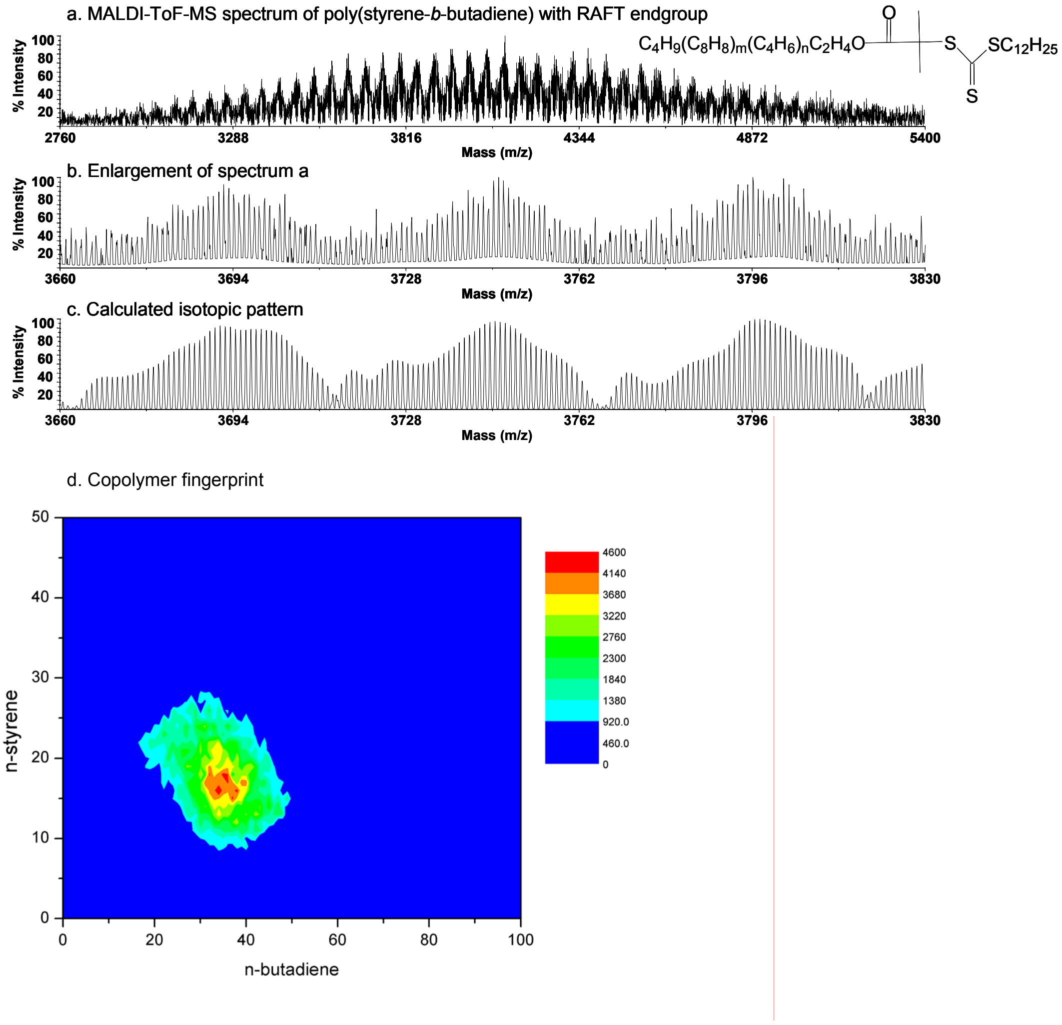


Figure 5.9.

a. MALDI-ToF-MS mass spectrum of *s*-butyllithium initiated poly(styrene-*b*-butadiene) after ethylene oxide endcapping and esterification with DIBTC

b. an enlargement of the spectrum between 3660 and 3830 g/mol

c. calculated isotopic patterns and

d. the copolymer fingerprint for poly(styrene-*b*-butadiene) after ethylene oxide endcapping and esterification with DIBTC

Gradient polymer elution chromatography (GPEC) analysis supports the results obtained from MALDI-ToF-MS. Comparison of the chromatograms of the starting material (pSB-OH) with the chromatograms of the products of the esterification with DIBTC (Figure 5.10) demonstrates that UV-active polymer with a different endgroup was formed. However, also some residual pSB-OH was detected, which was estimated to be approximately 20%. This seems to be a plausible percentage, since it is comparable to the percentages obtained for pEB-RAFT and pB-RAFT. The fact that similar conversions were obtained for all model systems, allows the conclusion that the ester formation does not proceed to full conversion.

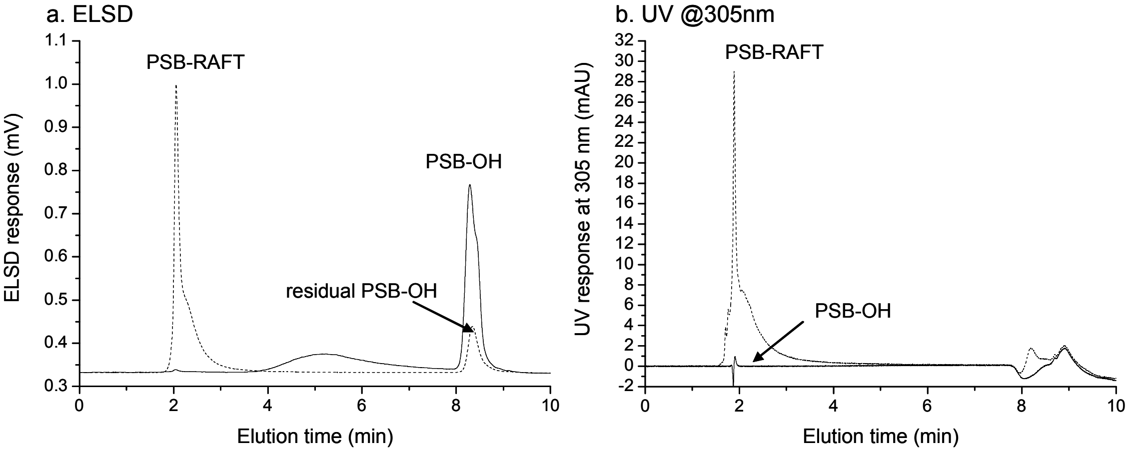


Figure 5.10. GPEC chromatograms for hydroxyl-functional poly(styrene-*b*-butadiene) (pSB-OH, —) and of the product of the esterification of hydroxyl-functional poly(styrene-*b*-butadiene) with DIBTC (pSB-RAFT and residual pSB-OH, ----)

a. ELSD response

b. UV response at a wavelength of 305 nm

5.3.2 Polymerizations

The intermediate molecular weight RAFT-agents described in Section 5.3.1 were chain extended with styrene and maleic anhydride. The reaction conditions are listed in Table 5.2

Table 5.2. Reaction conditions for chain extensions of intermediate molecular weight RAFT-agents[a]

Entry	RAFT-agent	M_n RAFT (g/mol)	PDI RAFT	[R]/[I]	[M] (mol/L)	Time (h)	M_n target (g/mol)
SMA-3	pEB	4100	1.03	5	0.8	24	18700
SMA-4	pB	4100	1.03	5	0.9	24	34000
SMA-5	pSB	4100	1.07	8	0.5	5	45000

[a]solvent: methyl ethyl ketone:toluene (1:2), reaction temperature = 85 °C

For SMA-5, the reaction was stopped after 5 hours because the reaction mixture became very viscous.

The main results of the three different chain extensions are collected in Table 5.3

Table 5.3. Results for chain extensions of intermediate molecular weight RAFT-agents

Entry	Conversion (%)	M_n calc (g/mol)	M_n SEC (g/mol)	PDI	Conversion of macro-RAFT (%)
SMA-3	93	17123	14404	1.4	70
SMA-4	94	33000	57500	2.5	75
SMA-5	70	33300	40500	2.3	70

Styrene conversions were calculated using gas chromatography (GC) to measure the amount of residual monomer. Assuming that styrene and maleic anhydride copolymerize in an alternating fashion,[12-15] the total monomer conversion is equal to the styrene conversion.

For all three polymerization systems bimodal molecular weight distributions were obtained. M_n SEC and the polydispersity index (PDI) are determined for the entire distribution.

The residual starting polymer was determined by calculating the relative areas under the SEC-signal corresponding to the (residual) starting polymer after the necessary deconvolution procedures.

For SMA-3, which was the chain extension of pEB-RAFT, the SEC-chromatograms and the M_n vs conversion plot are shown in Figure 5.11

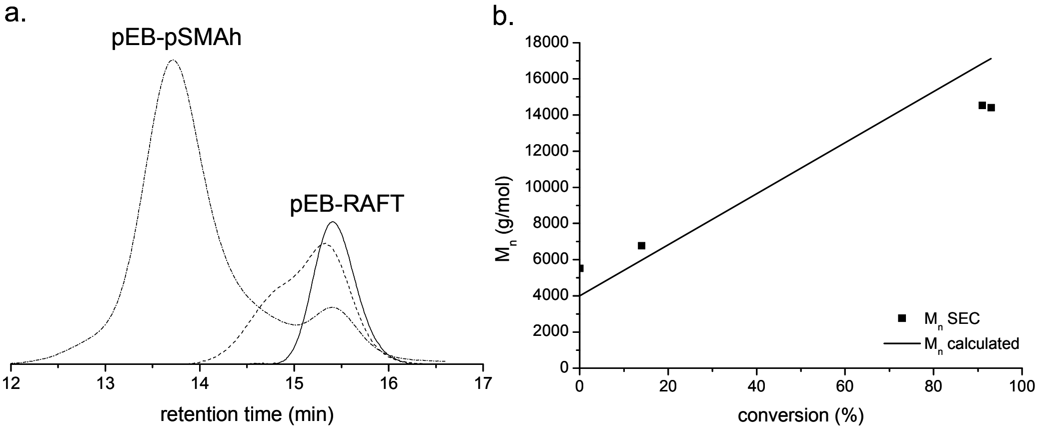


Figure 5.11. SEC-chromatograms (a) and M_n as a function of conversion (b) for reaction SMA-3 (Table 5.2 and 5.3)

When looking at the SEC-chromatograms it can be seen that the signal corresponding to the starting pEB decreases and block copolymer is formed. After deconvolution it was calculated that approximately 70% of the starting polymer was chain extended. The remaining 30% is most probably pEB-OH which was not converted into the RAFT-agent. The SEC-results correspond with the ^{1}H-NMR analysis of the pEB-RAFT that showed that only 75% of pEB-OH was converted into pEB-RAFT. The number averaged molecular weights (M_n) determined with SEC agree with the calculated values for M_n (see Chapter 2, Equation 2.3).

Figure 5.12 displays the results for SMA-4, the chain extension of pB-RAFT.
This reaction proceeded in a similar way as SMA-3, until a certain amount of monomer was consumed. Running the reaction for longer times resulted in a very broad molecular weight distribution and in the formation of (partly insoluble) high molecular weight polymer, indicating branching and crosslinking through the double bonds present in polybutadiene. This can also be seen from M_n as a function of conversion (Figure 5.12b), which starts to deviate strongly from the expected evolution of M_n for a RAFT-polymerization at conversions higher than 70%.

However, until approximately 70% of monomer conversion is reached, monomer addition is preferred over crosslinking and polymerization proceeds in a controlled way. The amount of chain extended pB was found to be close to 75%, which corresponds well with the result obtained for pEB.

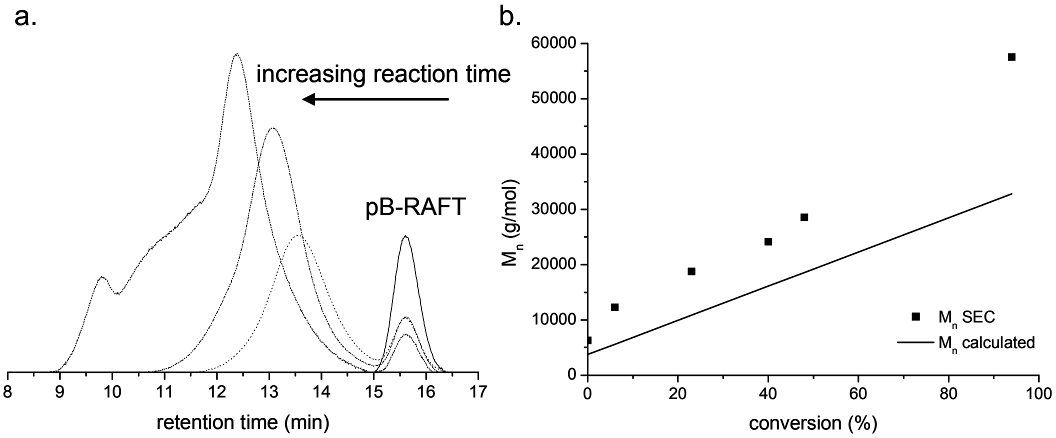


Figure 5.12. SEC-chromatograms (a) and M_n as a function of conversion (b) for reaction SMA-4 (Table 5.2 and 5.3)

Finally, the results for SMA-5, the chain extension of pSB-RAFT, are shown in Figure 5.13.

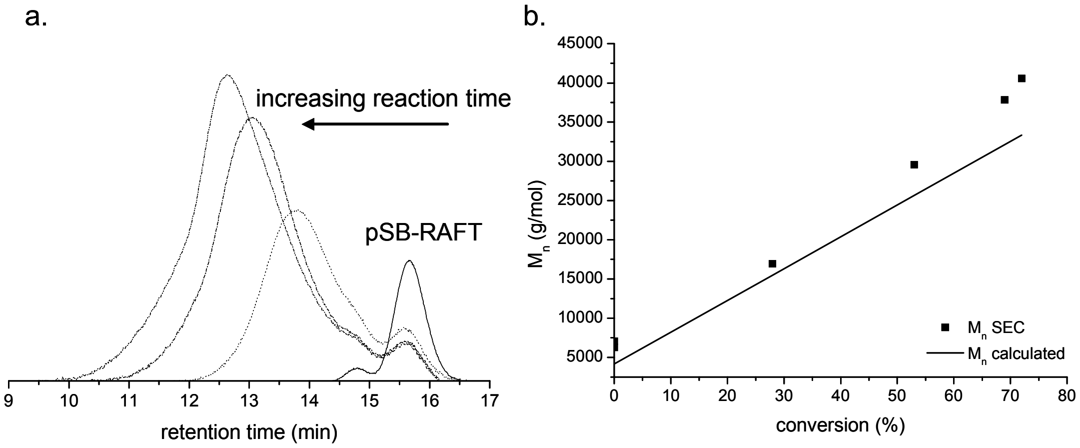


Figure 5.13. SEC-chromatograms (a) and M_n as a function of conversion (b) for reaction SMA-5 (Table 5.2 and 5.3)

The chain extension of pSB-RAFT proceeded faster than the other chain extension reactions. Furthermore, crosslinking did not occur to a significant extent in contrast to the case of pB-RAFT. This can be explained by the fact that less double bonds are present in the pSB block copolymer, since the polybutadiene block has an M_n of about 2000 g/mol compared to 3800 g/mol for pB-RAFT. At first, these two observations seemed to indicate that chain extension was rather successful. However, it should be noted that, although the amount of crosslinking seems to be not significant, a broad MWD is obtained (PDI=2.3). Taking a close look at the SEC-chromatograms in Figure 5.13, a trimodal distribution can be observed, with the third distribution appearing as a shoulder at the low molecular weight side of the triblock copolymer distribution. The broad MWD and the trimodal distribution lead to the conclusion that the control in this chain extension is poorer than for pEB-RAFT and pB-RAFT. In retrospect, we attribute this to the differences in phase separation behavior of the respective macro-RAFT-agents, which will have a more pronounced influence with increased molecular weight. The influence of molecular weight on phase separation will be discussed later in this chapter.

The results for the different intermediate molecular weight RAFT-agent syntheses and chain extension reactions justify the conclusion that chain extension of high molecular weight RAFT-agents based on polybutadiene and poly(styrene-*b*-butadiene) is feasible. However, crosslinking of the double bonds in the system may form a problem, which can be circumvented by hydrogenation of the double bonds. Furthermore, care has to be taken in choosing the experimental conditions, since considerable differences in polarity between different species present in the system can lead to loss of control over the chain extension reaction.

5.4 Macromolecular RAFT-agents: High molecular weight

5.4.1 RAFT-agent synthesis

The final block copolymers we are aiming at should exhibit elastomeric properties. Therefore, certain requirements with regard to molecular weight should be met.[16] For styrene-diene-styrene (SDS) triblock copolymers used as thermoplastic elastomers, the following rules of thumb hold:

The molecular weights of the polystyrene blocks should be in the range of 10-15 kg/mol, while the molecular weight of the polydiene block can range from 50-70 kg/mol. The lower limits are determined by incompatibility requirements and the upper limits are set by viscosity considerations.

In our case, the first polystyrene block and the polydiene block are synthesized within these boundaries; the polystyrene block is around 10 kg/mol and the polybutadiene block is 60 kg/mol. For an SDS-rubber, the last block would be polystyrene of approximately 10 kg/mol. It is our aim to replace the last block with a polar poly(styrene-*co*-maleic anhydride) block. This means that the macromolecular RAFT-agents are based on poly(styrene-*b*-diene) with molecular weights of around 70 kg/mol. For the preparation of these RAFT-agents, the same procedures were used as for the low and intermediate molecular weight RAFT-agents. The polymers were isolated via a slightly different work-up procedure which included steam-coagulation. During the work-up some preliminary crosslinking of the polymers occurred as can be seen from the SEC-chromatogram (Figure 5.14).

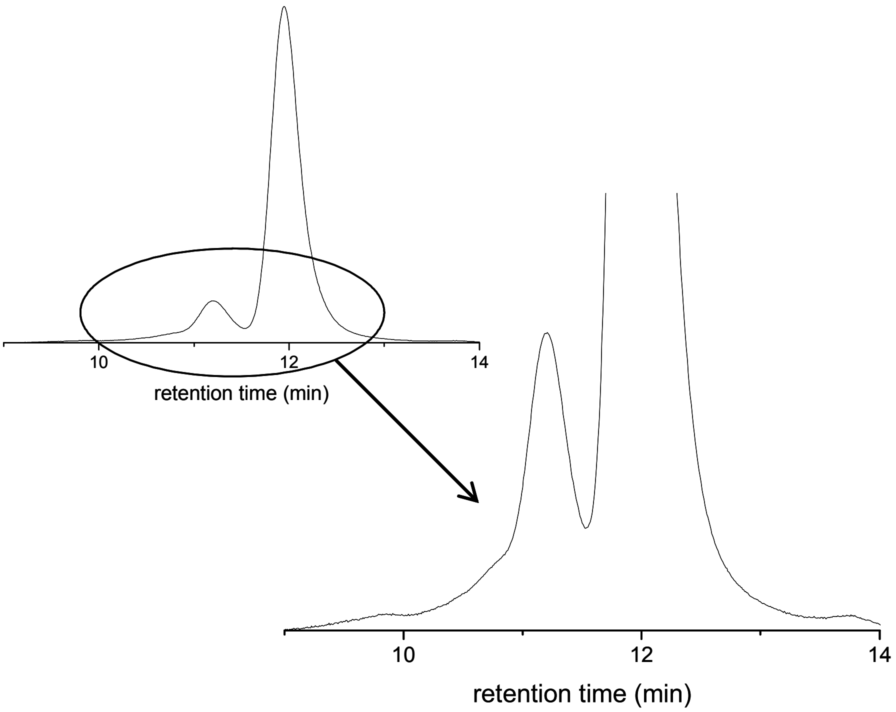


Figure 5.14. SEC-chromatogram of poly(styrene-*b*-butadiene) macro-RAFT, showing the presence of crosslinked material

Since this limited amount of crosslinked material was expected to influence subsequent polymerization, a fully saturated macromolecular RAFT-agent was prepared as well. In order to obtain that saturated macromolecular RAFT-agent, poly(styrene-*b*-isoprene) was synthesized via living anionic polymerization. The living polymer was endcapped with ethylene oxide and terminated by quenching in methanol. The double bonds of the resulting hydroxyl-functional poly(styrene-*b*-isoprene) were saturated via catalytic hydrogenation. After hydrogenation, hydroxyl-functional poly[styrene-*b*-(ethylene-*co*-propylene)] was isolated and then esterified with the acid chloride derivative of DIBTC. *In situ* esterification of the polymeric lithium alkoxide was not possible, because during hydrogenation and subsequent purification the RAFT-group would be destroyed.

Because of the high molecular weight of the RAFT-agents, characterization possibilities are limited. A comparison of the SEC-chromatograms (Figure 5.15) using a refractive index detector and a UV-detector at a wavelength of 305 nm, which corresponds to the characteristic absorbance of the C=S bond, gives an indication for the presence of the RAFT-group at the chain end. However, no conclusion can be drawn about the extent of functionalization, since the intensity of the signals cannot be compared. To make an estimate of the number of chains that bear a RAFT-group at the chain end, chain extension reactions have to be carried out in order to determine which fraction of the polymer can be chain extended. These chain extension reactions are described in detail in the next section.

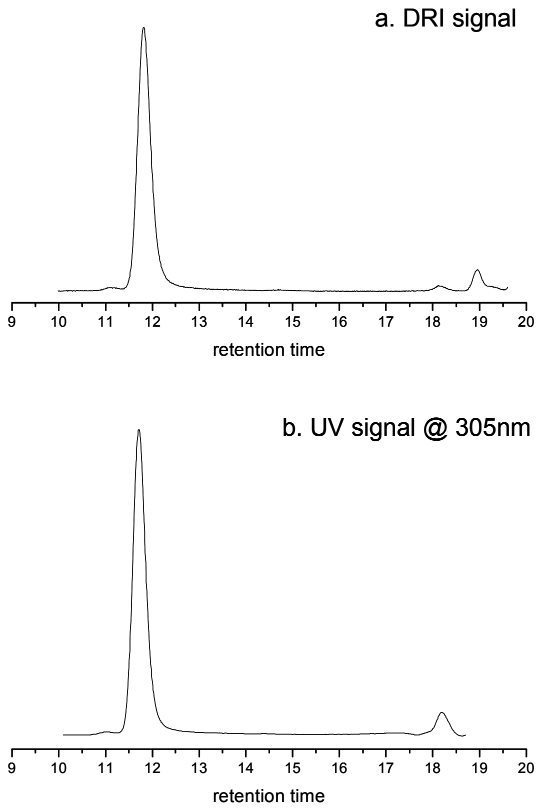


Figure 5.15. SEC-chromatograms of poly[styrene-*b*-(ethylene-*co*-propylene)] macro-RAFT

a. DRI-signal

b. UV-signal at a wavelength of 305 nm, showing the presence of high molecular weight material in both cases, at the same retention time

5.4.2 Polymerizations

The unsaturated (pSB) and saturated (pSEP) macromolecular RAFT-agents were both used to control the copolymerization of styrene and maleic anhydride. Hereby, chain extension of the RAFT-agents should take place, leading to the formation of triblock copolymers.

First, chain extension of pSB-RAFT was attempted. Running this reaction overnight at 85 °C only resulted in some crosslinking of the pSB-RAFT while no monomer conversion, and therefore no chain extension, could be observed (Figure 5.16). This was attributed to the very unfavorable ratio of double bonds to monomer, which makes crosslinking more likely to occur than propagation.

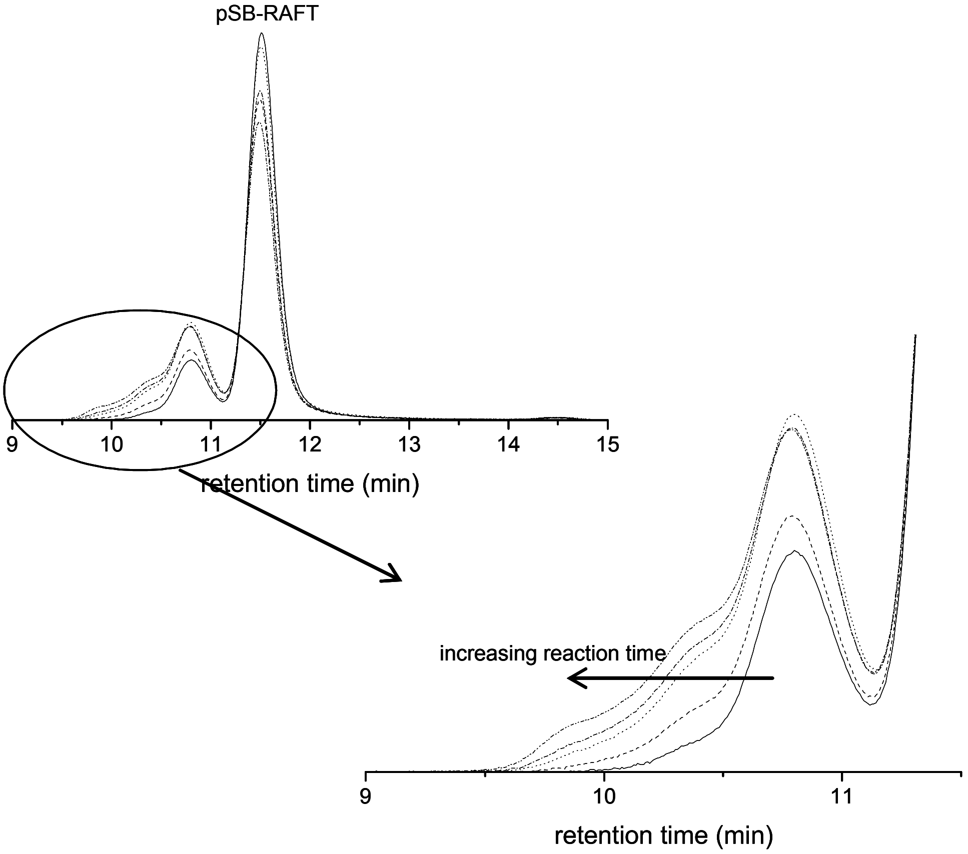


Figure 5.16. SEC-chromatograms of the chain extension reaction for poly(styrene-*b*-butadiene) macro-RAFT, showing the increasing amount of crosslinked material with reaction time, while no chain extension reaction is taking place

Since the presence of a high concentration of double bonds inhibits polymerization, further chain extension experiments were all done using pSEP-RAFT. The reaction conditions for these experiments are listed in Table 5.4. All reactions were carried out at a temperature of 85 °C, using equimolar amounts of styrene and maleic anhydride.

Table 5.4. Reaction conditions for chain extensions of poly[styrene-*b*-(ethylene-*co*-propylene)] macro-RAFT (pSEP-RAFT)

Entry	RAFT-agent[a]	[M] (mol/L)	[R]/[I]	M_n target (kg/mol)	Solvents[c]	Time (h)
SEP-SMA1	pSEP1	0.9	5	157	MEK:tol (1:1)	47[d]
SEP-SMA2	pSEP1 [b]	1	5	286	MEK:tol (1:1)	22
SEP-SMA3	pSEP2	4	10	345	MEK:tol (1:1)	2
SEP-SMA4	pSEP2	1	5	168	MEK:tol (1:1)	23
SEP-SMA5	pSEP2	1.5	2	380	Diox:tol (2:1)	4
SEP-SMA6	pSEP2	1.5	5	388	BuAc:tol (2:1)	22
SEP-SMA7	pSEP2	0.5	2	147	Diox:tol (2:1)	30[d]

[a] two different batches of pSEP-RAFT were used, pSEP1 and pSEP2 respectively

[b] DIBTC was also added to the reaction (pSEP-RAFT:DIBTC = 1:1)

[c] MEK = methyl ethyl ketone, BuAc = butyl acetate, Diox = 1,4-dioxane, tol = toluene

[d] additional initiator was added after 24 hours

The first reaction, SEP-SMA1 in Table 5.4 was carried out in a solvent mixture of methyl ethyl ketone and toluene, similar to the chain extension reactions for the intermediate molecular weight RAFT-agents. Figure 5.17 shows the SEC-results for SEP-SMA1.

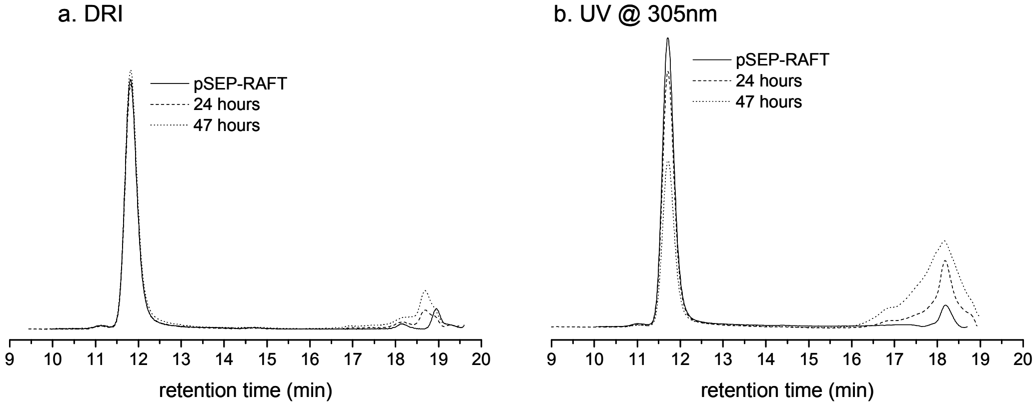


Figure 5.17. SEC-chromatograms of the chain extension reaction SEP-SMA1 in Table 5.4.

a. DRI response

b. UV-absorbance at a wavelength of 305 nm

After 24 hours no monomer conversion could be measured, so an additional amount of initiator was added, which was equal to the starting amount of initiator. The reaction was left for 23 more hours, but after that time, still no monomer consumption was measured. As can be seen from Figure 5.17a, the pSEP-RAFT remains unchanged and the only change that can be observed in the chromatogram is the appearance of low molecular weight material at high retention times. Figure 5.17b displays the material that is UV-active at a wavelength of 305 nm, *i.e.* material that contains a C=S bond, thus a RAFT-group. In this figure, a decrease of the pSEP-RAFT peak is observed while a peak corresponding with low molecular weight material containing a RAFT-group is found. These observations indicate that the polymer did act as a leaving group, thereby splitting off its RAFT-functionality, which is detected as low molecular weight compound. The polymeric radical that is formed in this process does not reinitiate polymerization, since no shift of the pSEP-peak in Figure 5.17a is observed and no monomer conversion was measured.

The observed inhibition could have been due to impurities in the pSEP-RAFT, for example residual catalyst which was not properly removed after the hydrogenation step. To exclude this possibility a model experiment was designed where a copolymerization of styrene and maleic anhydride was done in the presence of DIBTC and pSEP-OH from the same batch that was used for the pSEP-RAFT synthesis. The other reaction conditions were similar to SEP-SMA1. This reaction resulted in the controlled copolymerization of styrene and maleic anhydride, without any inhibition. Impurities in the starting material could therefore not be the cause for inhibition.

Earlier investigations on inhibition in RAFT-mediated polymerization by McLeary *et al.*[17-19] have demonstrated that in the polymerization systems which these authors studied no propagation takes place before all the initial RAFT-agent is converted into its mono-monomeric adduct. The decrease in the macro-RAFT peak as observed in Figure 5.17b indicates that a similar process is taking place in our system. Even after 47 hours of reaction time, still some pSEP-RAFT seems to be present, which could inhibit further polymerization. If this is indeed the case, we should see the same kind of inhibition behavior in a system which contains pSEP-RAFT and low molecular weight RAFT-agent (DIBTC). This system corresponds with entry SEP-SMA2 in Table 5.4. The presence of residual pSEP-RAFT should then inhibit polymerization controlled by DIBTC. The SEC-chromatograms obtained for SEP-SMA2 are shown in Figure 5.18.

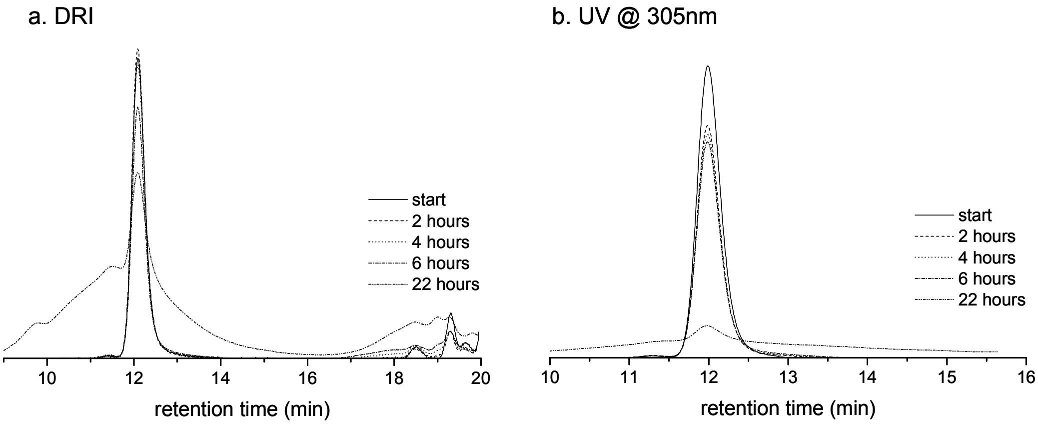


Figure 5.18. SEC-chromatograms of the chain extension reaction SEP-SMA2 in Table 5.4.

a. DRI response

b. UV-absorbance at a wavelength of 305 nm

As expected, inhibition was observed, but after the consumption of the pSEP-RAFT, as indicated by the almost complete disappearance of the response at a wavelength of 305 nm (Figure 5.18b) polymer was formed (Figure 5.18a). After 22 hours, 70% of monomer conversion was reached. However, in spite of the presence of DIBTC and pSEP-RAFT, the polymerization proceeded in an uncontrolled way according to the broad molecular weight distribution that is obtained. Presumably, the radicals that are formed at the polymer chain end upon splitting off the RAFT-moiety are not participating in the RAFT-mediated polymerization because they cannot be easily reached by monomer and low molecular weight RAFT-agent. In that case chain transfer is no longer reversible and part of the polymerization proceeds according to a free radical mechanism.

Increasing the monomer concentration leads to an increased probability of monomer reaching the polymeric radical before it is terminated. The first few monomer additions make the chain end more polar and therefore less shielded and more accessible to other monomer molecules and low molecular weight RAFT-agent.

In experiment SEP-SMA3 we increased the monomer concentration from 1 mol/L to 4 mol/L. After only two hours, the reaction was stopped because the high viscosity of the reaction mixture made stirring impossible. The SEC-results for this reaction (not shown) demonstrate the formation of extremely high molecular weight material with a broad molecular weight distribution. So this polymer was not formed by RAFT-mediated (controlled) polymerization. Furthermore, the UV-detected SEC-results demonstrate that polymer was formed while pSEP-RAFT was still present in the system.

The fact that polymerization occurs in presence of the macromolecular RAFT-agent contradicts the assumption we made earlier based on results reported in literature, that the presence of initial RAFT-agent inhibits polymerization.

In Table 5.4 it can be seen that another difference between SEP-SMA3 and SEP-SMA1/2 is that a different batch of pSEP-RAFT was used. To verify the influence of this change in RAFT-agent, SEP-SMA1 was repeated with use of the new RAFT-agent (pSEP-RAFT2 (SEP-SMA4). After 23 hours of reaction time, the reaction mixture had turned white, indicating phase separation, and some solid polymer precipitate has separated off. This observation was not made for reaction SEP-SMA1. Figure 5.19 shows the SEC-results of SEP-SMA4

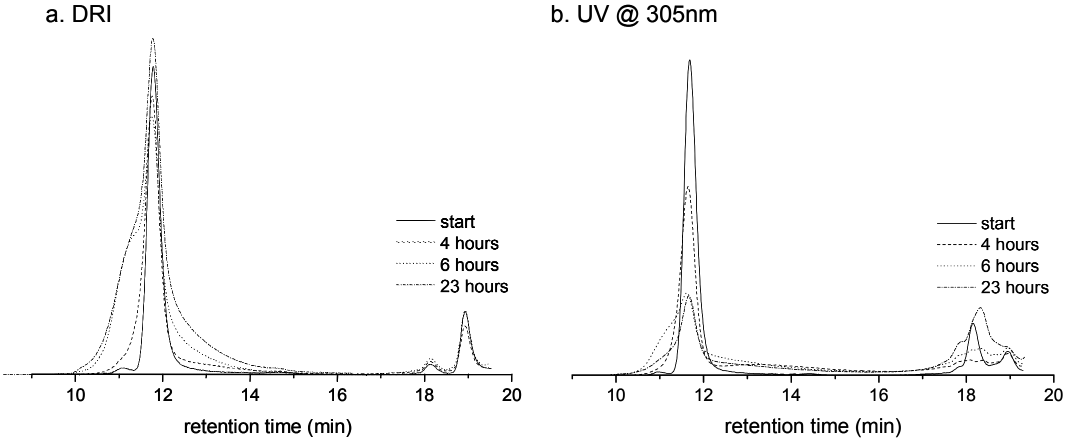


Figure 5.19. SEC-chromatograms of the chain extension reaction SEP-SMA4 in Table 5.4.

a. DRI response

b. UV-absorbance at a wavelength of 305 nm

In contrast to the results for SEP-SMA1, no inhibition has been observed for SEP-SMA4 and high molecular weight material is formed from the onset of the reaction. The difference between SEP-SMA1 and SEP-SMA4 can be attributed to the different batches of RAFT-agent, but the difference in phase behavior also indicates the poor quality of the solvent system that is used. Poor solvents can result in systems that are very sensitive to small changes in conditions.

Changing the solvent system may solve this problem. In the MEK/toluene mixture used so far, pSEP-RAFT could only be dissolved upon heating. To facilitate the dissolution we chose a less polar solvent system, namely a 1,4-dioxane/toluene mixture. Dioxane should still be capable of dissolving maleic anhydride and at the same time increase the solubility of the RAFT-agent as compared with MEK. Reaction conditions for this experiment can be found in Table 5.4, SEP-SMA5. As expected, the RAFT-agent dissolved easily at room temperature. However, after 30 minutes of reaction the mixture turned opaque and soon after that it became white. After only three hours some solid precipitate separated off. The SEC-chromatograms for SEP-SMA5 are shown in Figure 5.20.

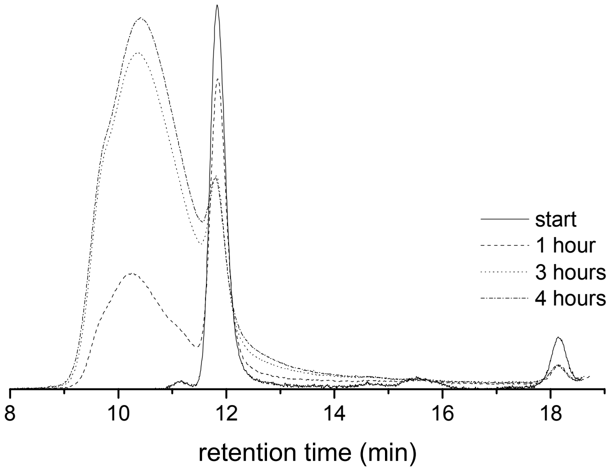


Figure 5.20. SEC-chromatograms (DRI) of the chain extension reaction SEP-SMA5 in Table 5.4

Once more, high molecular weight material was formed in an uncontrolled way. A decrease in the pSEP-RAFT peak can also be observed, indicating some chain extension. However, the phase separation problems were not solved by switching to this specific solvent mixture. The pSEP-RAFT solubility increased, but the solubility of the formed polymer decreased dramatically since rapid phase separation was observed.

One more solvent system of intermediate polarity was tested (SEP-SMA6). In the butyl acetate/toluene mixture used in this case, pSEP-RAFT could only be dissolved upon heating. The first hours of reaction, the reaction mixture remained clear, but after about 4 hours it turned white and after one night a considerable amount of polymer had precipitated and stirring was not possible anymore. SEC-results (not shown) were very similar to the results for SEP-SMA5.

Since the 1,4-dioxane/toluene system was most capable of dissolving the RAFT-agent, starting from this system, another possibility to avoid phase separation during polymerization is to decrease the monomer concentration and M_n target (SEP-SMA7). Figure 5.21 shows the result for this reaction. Even though the polymer that was produced was not as high in molecular weight as for the previously described reactions, no controlled polymerization has been observed. This can be derived from the very broad distributions depicted in Figure 5.21

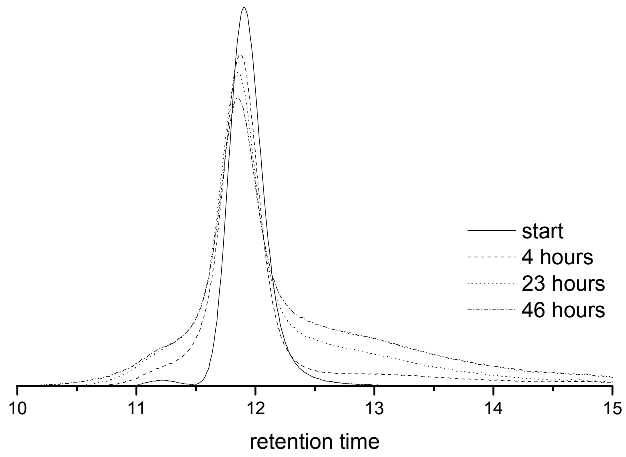
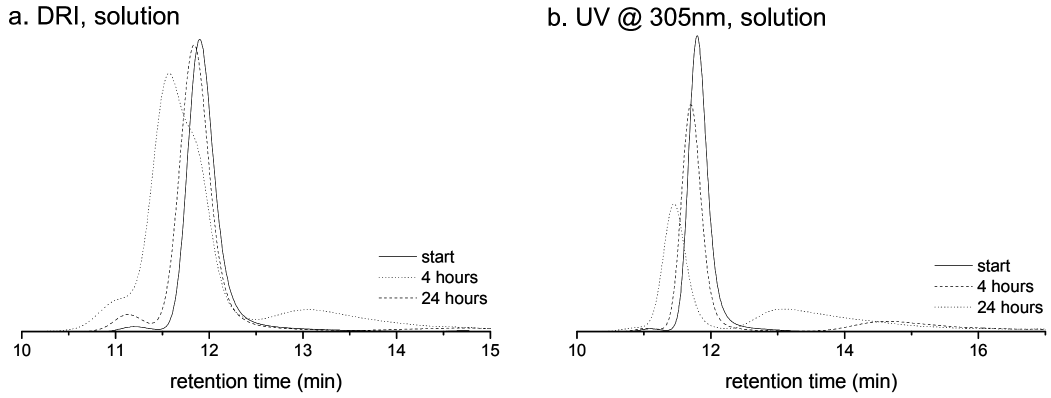
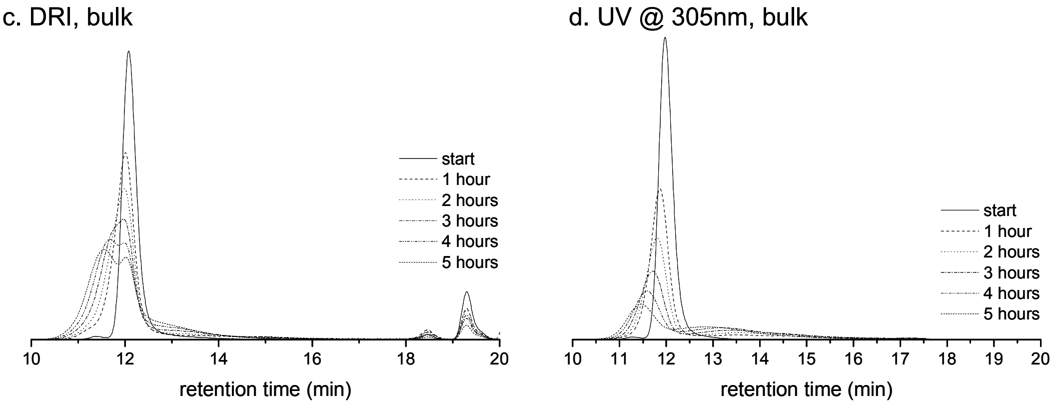


Figure 5.21. SEC-chromatograms (DRI) of the chain extension reaction SEP-SMA7 in Table 5.4

Although the macromolecular RAFT-agent seemed to dissolve well in the chosen solvent system, the radical formed at the polymer chain end still appears to be inaccessible to the monomers. Apparently, the polarity differences cannot be overcome by choosing a suitable solvent system. Most probably, a less polar solvent and a less polar monomer are required for successful chain extension of pSEP-RAFT. This was tested by means of two styrene homopolymerizations using pSEP-RAFT; one bulk polymerization and one solution polymerization in toluene. The results are shown in Figure 5.22.


a. DRI, solution

b. UV @ 305nm, solution


c. DRI, bulk

d. UV @ 305nm, bulk

Figure 5.22. SEC-chromatograms of the chain extension reactions of pSEP-RAFT with styrene: (a) and (c) show the DRI responses for solution and bulk and (b) and (d) show the UV-absorbance at a wavelength of 305 nm for solution and bulk

Both the solution polymerization and the bulk polymerization show a significant amount of chain extended polymer. Also some uncontrolled polymerization occurred as can be concluded from the presence of a broad distribution next to the pSEP-RAFT and block copolymer distributions. The SEC-chromatograms at a wavelength of 305 nm clearly show that the original distribution for the macromolcular RAFT-agent shifts to higher molecular weights, indicating that it is chain extended successfully. In the DRI-chromatograms, a considerable amount of residual material can be seen at the location of the original RAFT-agent. This compound can either be pSEP-OH that was not converted into RAFT-agent in the first place, or pSEP which cleaved off from the RAFT-group as a radical leaving group, but did not reinitiate polymerization as was the case for the chain extension reactions with styrene-maleic anhydride described earlier.

The results obtained for the styrene homopolymerizations agree with the conclusions drawn for the styrene-maleic anhydride copolymerizations. By decreasing the differences in polarity in the system, pSEP-RAFT could be chain extended successfully.

We can conclude that the molecular weight of the RAFT-agents that are used in chain extension reactions drastically influences the ability of the RAFT-agents to control polymerization. In case of an unsaturated macromolecular RAFT-agent, poly(styrene-*b*-butadiene), the high number of double bonds inhibits polymerization, because crosslinking of the double bonds is preferred over propagation. In case of a fully saturated macromolecular RAFT-agent, poly[styrene-*b*-(ethylene-*co*-propylene)], where crosslinking does not play a role, we encountered several other problems. First of all it should be noted that the reproducibility of the chain extension reactions was poor, partly due to the difficulties in characterizing the starting material, but mainly due to an inhomogeneous polymerization system. The inhomogeneities in the system have several reasons. pSEP-RAFT is poorly soluble in most common solvents unless very non-polar solvents are used. However, since a polar monomer (maleic anhydride) is present in the system and a polar polymer is being formed, a certain polarity of the solvent is required. A solvent system which is too polar leads to poor solubility of the pSEP-RAFT, which then forms phase separated domains, leading to low accessibility of the (radicals formed at the) polymer chain ends. On the other hand, a non-polar solvent system results in precipitation of the polar polymer that is formed. Despite our attempts to optimize the reaction conditions, we did not succeed in achieving controlled chain extension of pSEP-RAFT with poly(styrene-*co*-maleic anhydride). However, chain extension of the same RAFT-agent with a polystyrene block was performed in a controlled way, yielding the corresponding triblock copolymer.

5.5 Conclusions

The synthesis of different macromolecular RAFT-agents via a two-step esterification procedure and their chain extension with styrene and maleic anhydride have been described in this chapter. The esterification procedure proved to be a relatively straightforward and efficient way to obtain macromolecular RAFT-agents starting from carbanions. The route was further simplified by esterifying the lithium alkoxide directly instead of protonating and isolating the polymer first, which is the conventional route.

Chain extension reactions for three different model systems were carried out. In all three systems, the macromolecular RAFT-agents had molecular weights of approximately 4000 g/mol. A completely saturated RAFT-agent based on poly(ethylene-*co*-butylene) could be chain extended without problems. The polybutadiene-based RAFT-agent could be chain extended as well, but care has to be taken when going up to high monomer conversions. When the monomer concentration decreases too much, crosslinking of the double bonds starts to interfere with the propagation reaction.

The third model system used a RAFT-agent based on poly(styrene-*b*-butadiene). Again, we were able to chain extend the macromolecular RAFT-agent, without significant crosslinking of the double bonds.

Our work on higher molecular weight RAFT-agents ($M_n \approx 70$ kg/mol) revealed that the molecular weight has an enormous influence on the behavior of the polymerizing systems. In case of an unsaturated RAFT-agent (poly(styrene-*b*-butadiene)) the monomer to double bond ratio is unfavorable, leading to crosslinking in the initial stage of the reaction. This could be circumvented by using a fully saturated RAFT-agent (poly[styrene-*b*-(ethylene-*co*-propylene)]). However, the pronounced differences in polarity between the species present in the system caused phase separation during the polymerization and prevented chain extension (in a controlled way).

A reduction of the polarity differences by using styrene instead of styrene/maleic anhydride as monomer resulted in successful chain extensions, both in solution and in bulk.

In summary, we can conclude that the sequential approach we used to obtain block copolymers is feasible for a limited molecular weight range and also for a limited polarity difference between the different blocks.

5.6 Experimental procedures

5.6.1 Materials

Anionic polymerizations and ethylene oxide endcapping: 1,3-butadiene (Shell Chemical Europe, 99%), styrene (VWR, 99%), cyclohexane (VWR, high purity) were passed over an activated alumina column before use. *sec*-Butyllithium [*s*-BuLi, Acros, 1.3 M solution in cyclohexane/hexane (92/8)], ethylene oxide (Aldrich, >99.5%), methanol (Biosolve, AR grade) and dichloromethane (DCM, Biosolve, AR grade) were all used without further purification.

Acid chloride functional DIBTC synthesis and esterifications: S-dodecyl S'-(isobutyric acid) trithiocarbonate (DIBTC) was prepared according to a literature procedure described by Lai *et al.*[5] Pyridine (VWR, 99%) was distilled prior to use and stored over molecular sieves. Thionyl chloride (Fluka, >99%) was distilled before use. 1-Butanol (Aldrich, HPLC grade) was dried over molecular sieves. Dichloromethane (DCM, Biosolve AR grade) and tetrahydrofuran (THF, Biosolve, AR grade) were dried over an alumina column. Lithium ethoxide (Aldrich, 1 M solution in THF) and isopropanol (Biosolve, AR grade) were used as received.

RAFT-mediated polymerizations: Styrene (VWR, 99%) was passed over a basic alumina column to remove the inhibitor. Maleic anhydride (Aldrich, 99%) and 1,1-azobis(cyclohexanecarbonitrile) (VAZO88, Aldrich, 98%) were used without further purification. All solvents were purchased from Biosolve and used as received.

5.6.2 Anionic polymerizations and ethylene oxide endcapping

All reactions were carried out under nitrogen atmosphere.

Polybutadiene (M_n 3800 g/mol)

Living anionic polymerization of butadiene was carried out in a 2 L stainless steel autoclave reactor equipped with a screw stirrer. The reactor was charged with 1 kg of cyclohexane and heated to 60 °C. Butadiene (50 g, 0.99 mol) and *s*-BuLi [40 mL of a 0.33 M solution in cyclohexane, (13 mmol)] were added. The polymerization was allowed to reach full conversion (approximately 90 min of reaction time). After that, the mixture was cooled down to 50 °C and ethylene oxide [28 mL of a 0.1 g/mL solution in cyclohexane (64 mmol)] was added. The reaction was allowed to continue for 1 hour. When subsequent esterification was done *in situ* with the lithium alkoxide, the reaction mixture was cooled down to room temperature. When the alcohol had to be isolated, the reaction mixture was quenched in an excess of methanol. The solvent was evaporated and the reaction products were redissolved in dichloromethane and extracted three times with brine and three times with water. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The product was dried under vacuum.

Poly(styrene-b-butadiene) (M_n 3800 g/mol)

The procedure used for the synthesis of poly(styrene-*b*-butadiene) was the same as described for polybutadiene. The only difference is that, instead of 50 g butadiene, 25 g of styrene was used to produce a polystyrene block and after complete conversion of styrene (about 90 min) 25 g of butadiene was added.

After ethylene oxide endcapping, only the lithium alkoxide was used in the esterification reaction.

Poly(styrene-b-butadiene) (M_n 70 kg/mol)

Polymerization was carried out in a 10 L stainless steel autoclave reactor equipped with a screw stirrer. The reactor was charged with 6 L of cyclohexane and heated to 60 °C. Styrene (71 g, 0.51 mol) and *s*-BuLi [23 mL of a 0.3 M solution in cyclohexane, (6.9 mmol)] were added. Styrene polymerization was allowed to reach complete conversion (ca. 90 min). After that the reaction mixture was heated to 70 °C and butadiene (429 g, 7.9 mol) was slowly added. After the addition of butadiene the reaction was left at 70 °C for 40 min and then cooled down to 60 °C. After 15 min. the reactor was further cooled to 50 °C. At that point ethylene oxide [7 mL of a 0.1 g/mL solution in cyclohexane (15 mmol)] was added and left to react for 1 hour. The product was used directly for the esterification.

Poly[styrene-b-(ethylene-co-propylene)] (M_n 70 kg/mol)

The reaction was carried out in a 10 L stainless steel autoclave reactor equipped with a screw stirrer. The reactor was charged with 6 L of cyclohexane and heated to 60 °C. Styrene (73 g, 0.7 mol) and *s*-BuLi [25.7 mL of a 0.3 M solution in cyclohexane, (77 mmol)] were added. Polymerization was allowed to proceed to full conversion (ca. 90 min). Then the reaction mixture was heated to 70 °C and isoprene (427 g, 7.9 mol) was slowly added. 15 min. after the isoprene addition was complete, the reactor was cooled down to 60 °C and left at that temperature for 45 min. After that time, the reactor was cooled further to 50 °C and ethylene oxide [7 mL of a 0.1 g/mL solution in cyclohexane (15 mmol)] was added. The reaction was kept at 50 °C for 1 hour. After that the reaction mixture was quenched in an excess of methanol.

In order to saturate the double bonds, catalytic hydrogenation was carried out according to a confidential industrial procedure. After hydrogenation and several washing steps, further work-up consisted of steam-coagulation of the polymer and drying the product under reduced pressure.

5.6.3 Acid chloride functional DIBTC synthesis and esterifications

Acid chloride functional DIBTC (DIBTC-Cl) synthesis

The reaction was carried out under argon atmosphere.

DIBTC (1.0 g, 2.75 mmol) was dissolved in anhydrous dichloromethane (5 mL) in an oven-dried argon-purged flask. The flask was immersed in a cold isopropanol bath until the reaction mixture solidified. Thionyl chloride (1.0 mL, 13.75 mmol) was added dropwise to the cold reaction mixture.

The mixture was allowed to warm up to room temperature while stirring. During the warm-up, gas development (HCl and SO_2) was observed. After reaching room temperature the flask was put in a water bath of 30 °C for 3 hours. The solvent and excess of thionyl chloride were removed under vacuum overnight. In order to avoid unwanted side reactions, the product was used directly for further reactions without any purification or characterization.

Esterification of DIBTC-Cl with alcohols

Low molecular weight: 1-butanol

The reaction was carried out under argon atmosphere.

1-butanol (1.94 g, 2.62 mmol) and pyridine (0.21 mL, 2.62 mmol) were dissolved in dry THF (5 mL). To this solution, DIBTC-Cl (1.0 g, 2.62 mmol, in 5 mL THF) was added dropwise while stirring. The reaction mixture was left overnight at room temperature. The solvent was evaporated, the product was redissolved in dichloromethane and extracted three times with brine and three times with water. The organic layer was dried over Na_2SO_4 and the solvent was removed. The product, a dark yellow oil, was dried under vacuum.

^{1}H-NMR: δ (ppm) 4.09 [t, $CH_3(CH_2)_2\underline{CH_2}OCOC(CH_3)CS_3C_{12}H_{25}$],

3.26 [t, $CH_3(CH_2)_2CH_2OCOC(CH_3)CS_3\underline{CH_2}C_{11}H_{23}$], 1.1-1.9 [m, 30H, $(CH_2)_{10}$, $(CH_2)_2$ and $C(CH_3)_2$], 0.8-0.95 [m, 6H, CH_3]

Intermediate and high molecular weight: pEB-OH, pB-OH and pSEP-OH

Reactions were carried out under argon atmosphere.

In a typical procedure the polymeric alcohol (2.62 mmol) and pyridine (0.21 mL, 2.62 mmol) were dissolved in dry THF (30 mL). To this solution, DIBTC-Cl (1.0 g, 2.62 mmol, in 5 mL THF) was added dropwise while stirring. The reaction was allowed to proceed overnight at room temperature. THF was evaporated, the product was redissolved in dichloromethane and extracted three times with brine and three times with water. The organic layer was dried and the solvent was removed under vacuum.

Esterification of DIBTC-Cl with lithium alkoxides

Low molecular weight: lithium ethoxide

The reaction was carried out under argon atmosphere.

To a solution of lithium ethoxide in THF (3.6 mmol in 3.6 mL) DIBTC (1.0 g, 2.62 mmol, in 5 mL THF) was added while stirring. The reaction mixture was left to react overnight at room temperature. THF was evaporated, the product was redissolved in dichloromethane and extracted with brine (three times) and with water (three times). The organic layer was dried, the solvent was removed and the product was dried under vacuum and isolated as a yellow oil.

^{1}H-NMR: δ (ppm) 4.10 [t, $CH_3\underline{CH_2}OCOC(CH_3)CS_3C_{12}H_{25}$], 3.28 [t, $CH_3CH_2OCOC(CH_3)CS_3\underline{CH_2}C_{11}H_{23}$], 1.1-1.9 [m, 26H, $(CH_2)_{10}$ and $C(CH_3)_2$], 0.8-0.95 [m, 6H, CH_3]

Intermediate molecular weight: pBOLi and pSBOLi

Reactions were carried out under nitrogen atmosphere.

In a typical procedure the polymeric lithium alkoxide was used directly after endcapping with ethylene oxide in cyclohexane solution. Approximately one fifth of the reaction mixture (200g, containing 2.6 mmol of polymer) was transferred to an oven-dried and nitrogen-purged glass bottle. DIBTC-Cl (1.0 g, 2.62 mmol, in 5 mL THF) was added dropwise at room temperature while stirring. The reaction was allowed to run overnight at room temperature. The solvent was evaporated, the product was redissolved in dichloromethane and extracted with brine (three times) and water (three times). The organic layer was dried over Na_2SO_4 and the solvent was removed. The polymer was dried under vacuum.

High molecular weight: pSB-OLi

The reaction was carried out under nitrogen atmosphere.

The polymeric lithium alkoxide was used directly after ethylene oxide endcapping in cyclohexane solution. DIBTC-Cl (2.8 g, 7.2 mmol, dissolved in THF) was added to the reactor via an autoinjector and the mixture was left to stir overnight at room temperature. The polymer solution was then transferred to a steam coagulator. After coagulation, the polymer was dried under reduced pressure.

5.6.4 RAFT-mediated polymerizations

A general procedure for the RAFT-mediated polymerizations is given here.

Initiator (Vazo88), RAFT-agent and monomers (styrene and maleic anhydride) were added to a three-neck round bottom flask equipped with a stirrer and condenser and dissolved in a MEK/toluene mixture. The solution was degassed by purging with argon for 45 min. After that time the flask was kept under argon atmosphere and immersed in a preheated oil bath at 85 °C. Samples were taken at regular time intervals through a septum using a syringe.

5.6.5 Characterization techniques

^{1}H-NMR

^{1}H-NMR analyses were performed on a Varian Mercury-Vx 400 MHz spectrometer. Samples were dissolved in deuterated chloroform (Cambridge Isotope Laboratories)

MALDI-ToF-MS

MALDI-ToF-MS measurements were carried out on a Voyager-DE-STR (Applied Biosystems) equipped with a 337 nm nitrogen laser. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malonononitrile (DCTB)[20] was used as the matrix. The matrix was dissolved in THF at a concentration of approximately 40 mg/mL. Silver trifluoroacetate (Aldrich, 98%) was used as the cationization agent and was added to THF at a concentration of 1 mg/mL. The polymer sample was dissolved in THF at a concentration of 2 mg/mL. In a typical measurement, the matrix, cationization agent and sample solutions were premixed in a 10:1:5 ratio. Approximately 0.5 μL of the mixture obtained was hand spotted on the target plate and left to dry. Mass spectra were recorded in the reflector mode. For each spectrum, 5000 laser shots were accumulated. Data Explorer© software (Applied Biosystems) was used for data interpretation. Additionally, simulations for the poly(styrene-*b*-butadiene) block copolymers were carried out using in house developed software[11] written in Visual Basic 6.0.

Size Exclusion Chromatography (SEC)

Molecular weight and molecular weight distributions were determined using size exclusion chromatography. Before analysis, the polymer containing samples were dissolved in THF at a concentration of 1 mg/mL and filtered through a 13 mm × 0.2 μm PTFE-filter (Alltech)

SEC analyses were performed using a Waters Model 600 pump and a Waters Model WISP 712 autoinjector. The columns used were a PLgel guard precolumn (5 μm, 50 × 7.5 mm) and two PLgel mixed-D columns (5 μm particles, 300 × 7.5 mm, Polymer Laboratories) set at 40 °C. The injection volume was 50 μL. Stabilized THF (Biosolve) + acetic acid (5% v/v) (Aldrich) was used as eluent at a flow rate of 1.0 mL/min. A model 410 refractive index detector and a model 486 UV detector operating at wavelengths of 254 nm and 305 nm were used for detection. Calibration was done using polystyrene standards (Polymer Laboratories).

Data acquisition and processing were performed using Waters Millennium32 (v4.0) software.

Gas Chromatography (GC)

Monomer conversion was determined from the concentration of residual monomer (styrene) measured via gas chromatography. Toluene was used as the internal standard. Before injection the samples were dissolved in THF to a concentration of 10 mg/mL.

The analyses were carried out on a Hewlett Packard 5890 Series II gas chromatograph with a HP Ultra 2 crosslinked 5% Me-Ph-Si column (25 m × 0.32 mm × 0.52 μm film thickness) and equipped with a split injector and autosampler. The injection volume was 1.0 μL and helium was used as the mobile phase. Detection was done using a FID detector, which was kept at a constant temperature of 250 °C. The temperature profile that was used was as follows:

- Keep the initial temperature at 40 °C for 5 min.
- Heat to 80 °C at a rate of 5 °C/min.
- Heat to 250 °C at a rate of 25 °C/min.
- Keep at final temperature (250 °C) for 10 min.
- Cool down to 40 °C.

Gradient Polymer Elution Chromatography (GPEC)

GPEC measurements were performed on a Agilent 1100 series HPLC setup equipped with a degasser (G1322A), a Quaternary Pump (G1311A), an autosampler (G1313A), a UV diode-array detector (G1315B), a column compartment (G1316A), a Zorbax SB_CN column (4.6 × 150 mm, 25 °C) and an Alltech evaporative light scattering detector (nitrogen flow 1.6 mL/min, 60 °C). Samples were dissolved in THF at a concentration of 10 mg/mL. The injection volume was 1 μL. An eluent gradient was used, starting from a heptane/THF (95/5 v/v) mixture keeping isocratic conditions for 5 min., then applying a gradient to 100% THF in 3 min. and finally an isocratic period of 2 min.

References

1 Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* **2002**, *35*, 2912-2918.
2 Quirk, R. P.; You, F.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* **2004**, *37*, 1234-1242.
3 Quirk, R. P.; Guo, Y.; Wesdemiotis, C.; Arnould, M. A. *Polymer* **2004**, *45*, 3423-3428.
4 Quirk, R. P.; Mathers, R. T.; Ma, J. J.; Wesdemiotis, C.; Arnould, M. A. *Macromolecular Symposia* **2002**, *183*, 17-22.
5 Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754-6756.
6 Jesberger, M.; Barner, L.; Stenzel, M. H.; Malmstroem, E.; Davis, T. P.; Barner-Kowollik, C. *Journal of Polymer Science, Part A: Polymer Chemistry* **2003**, *41*, 3847-3861.
7 Stenzel, M. H.; Davis, T. P. *Journal of Polymer Science, Part A: Polymer Chemistry* **2002**, *40*, 4498-4512.
8 Liu, B.; Liu, F.; Luo, N.; Ying, S. K.; Liu, Q. *Chinese Journal of Polymer Science* **2000**, *18*, 39-43.
9 Kaiser, E. M.; Woodruff, R. A. *Journal of Organic Chemistry* **1970**, *35*, 1198-1199.
10 Hsieh, H. L.; Quirk, R. P. *Anionic polymerization: Principles and practice*; New York: Dekker: 1996.
11 This software package is based on work published in: *Characterization of (co)polymers by MALDI-TOF-MS*; B.B.P.Staal, PhD Thesis; Eindhoven; **2005**
12 Chernikova, E.; Terpugova, P.; Bui, C.; Charleux, B. *Polymer* **2003**, *44*, 4101-4107.
13 De Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 3596-3603.
14 Du, F. S.; Zhu, M. Q.; Guo, H. Q.; Li, Z. C.; Li, F. M.; Kamachi, M.; Kajiwara, A. *Macromolecules* **2002**, *35*, 6739-6741.
15 Zhu, M. Q.; Wei, L. H.; Du, F. S.; Li, Z. C.; Li, F. M.; Li, M.; Jiang, L. *Chemical Communications (Cambridge, United Kingdom)* **2001**, 365-366.
16 Holden, G.; Kricheldorf, H. R.; Quirk, R. P. *Thermoplastic elastomers*; Munich: Hanser: **2004.**
17 McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2004**, *37*, 2383-2394.
18 McLeary, J. B.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Chemical Communications (Cambridge, United Kingdom)* **2004**, 1950-1951.
19 McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2005**, *38*, 3151-3161.
20 Ulmer, L.; Mattay, J.; Torres-Garcia, H. G.; Luftmann, H. *European Journal of Mass Spectrometry* **2000**, *6*, 49-52.

6

Feasibility studies on block copolymer formation by click chemistry

6.1 Introduction

So far, we have investigated sequential living anionic polymerization and RAFT-mediated polymerization to obtain block copolymers. The sequential approach consisted of anionic polymerization of the first block(s), transformation of the anionic chains into macromolecular RAFT-agents and subsequent use of those RAFT-agents to control the radical polymerization of the last block. As was discussed in Chapter 5, the large polarity differences in our systems prevented us from obtaining high molecular weight block copolymers. The sequential approach proved to be viable only for a limited molecular weight range.

An entirely different approach to obtain high molecular weight block copolymers could consist of the separate polymerization and isolation of the different blocks. If these blocks bear suitable chain-end functionalities, they can be coupled afterwards. A major disadvantage of this method is the possibility of relatively low yields of block copolymer. Efficient and specific chain-end functionalization and coupling reactions are required to achieve successful block copolymer formation. Recently, a group of very efficient coupling reactions[1], commonly known as “Click chemistry”, has regained a lot of interest, because of its high specificity and quantitative yields.

In this chapter, the principles of click chemistry are outlined briefly. Furthermore, the results of our preliminary studies on the use of click chemistry as an alternative approach to obtain block copolymers by combination of living anionic polymerization and RAFT-mediated polymerization are evaluated.

6.2 Click chemistry

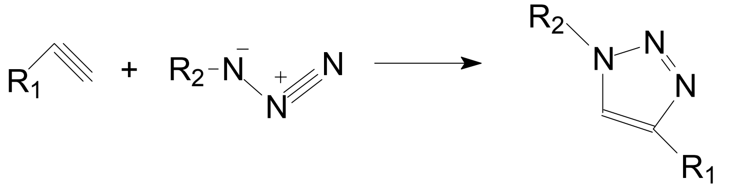
In 2001, Sharpless *et al.*[1] described a set of reactions they termed click chemistry. To define the concept, these authors set up a list of requirements for a process to be classified as click chemistry. According to their list, the reaction must be modular, wide in scope, give very high yields and generate only inoffensive byproducts that can be removed by non-chromatographic methods.

The required process characteristics include simple reaction conditions (ideally insensitive to oxygen and water), readily available starting materials, the use of no solvent or a solvent that is benign or easily removed and finally simple product isolation. It is important to recognize that click reactions achieve their characteristics by having a high thermodynamic driving force, the Gibbs energy of reaction being usually lower than -90 kJ/mol. Such processes proceed rapidly to completion and also tend to be highly selective for a single product.

Carbon-heteroatom bond forming reactions comprise the most common examples of click reactions. They include the following classes of chemical reactions:

- Cycloadditions of unsaturated species
- Nucleophilic substitution reactions
- Carbonyl chemistry of the “non-aldol” type
- Addition to carbon-carbon double bonds

Among the cycloaddition reactions, especially 1,3-dipolar cycloaddition reactions obey all the requirements for a true click reaction. Within this class of reactions, the Huisgen dipolar cycloaddition of azides and alkynes, which yields triazoles (Scheme 6.1), is probably the most useful example.



Scheme 6.1. 1,3-dipolar cycloaddition of azides and alkynes

This reaction has not been given proper attention for a long time, most likely because scientists were concerned about the safety of working with organic azides. However, azides are the most crucial group for click chemistry. What makes them unique for click chemistry purposes is their extraordinary stability towards water, oxygen and the majority of organic synthetic conditions. Therefore, they can be kept "hidden" during many synthetic steps, until a good dipolarophile is present.

Usually, the cycloaddition of azides to alkynes required elevated temperatures and proceeded relatively slowly. Recently, interest in the reaction was renewed because two groups[2;3] reported that, with the use of a Cu(I) catalyst, the cycloaddition of azides to alkynes results in the highly specific and efficient preparation of 1,4-disubstituted 1,2,3-triazole products under moderate reaction conditions. A number of Cu(I) sources can be used directly, or prepared *in situ* by the reduction of Cu(II) salts. The reaction does not require special precautions. It proceeds to completion in three to six hours at room temperature in a variety of solvents, including water.

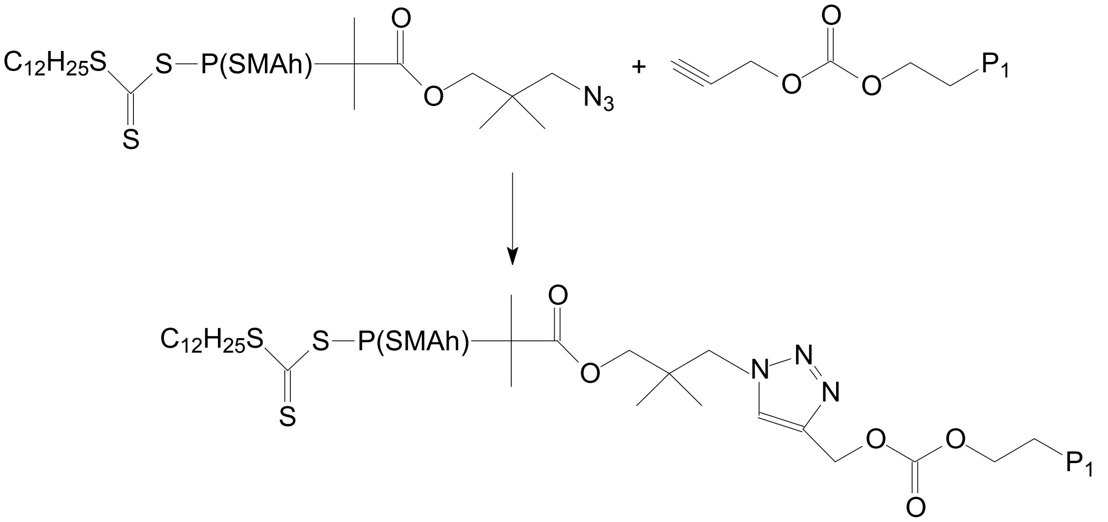
Since these reports, click chemistry has been employed extensively within the field of polymer chemistry. The use of click chemistry ranges from the preparation of dendrimers[4-7], graft[8] and block[9;10] copolymers and functionalized polymers[11-17] to crosslinked adhesives.[18]

6.3 Block copolymers by click chemistry

When click chemistry is applied to make block copolymers, the blocks are synthesized separately and each block bears either an azide or an alkyne functionality at its chain end.

Within the scope of this thesis, we aim for block copolymers containing polar and non-polar block(s). The non-polar block is prepared via living anionic polymerization and is therefore limited to polystyrene, polydiene (hydrogenated or not), or a block copolymer of the two. The polar block is an alternating copolymer of styrene and maleic anhydride made via RAFT-mediated polymerization.

For practical reasons we chose to incorporate the alkyne-functionality at the chain end of the non-polar block and the azide-functionality at the chain end of the polar block. By means of the previously described 1,3-cycloaddition reaction the two blocks can then be “clicked” together as shown in Scheme 6.2.

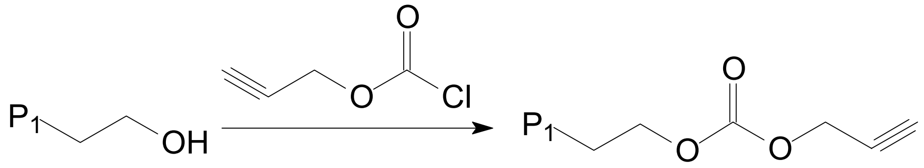


P$_1$ = poly(ethylene-*co*-butylene) or poly[styrene-*b*-(ethylene-*co*-butylene)]
S = styrene
MAh = maleic anhydride

Scheme 6.2. Click coupling of azide and alkyne functional building blocks

6.4 Non-polar block: Alkyne functionalization

Two different non-polar polymers with terminal alkyne functionality were synthesized. Both starting polymers have a hydroxyl endgroup, which can be esterified with propargyl chloroformate[19] to yield a terminal alkyne as is shown in Scheme 6.3.



P_1 = poly(ethylene-*co*-butylene) or poly[styrene-*b*-(ethylene-*co*-butylene)]

Scheme 6.3. Introduction of terminal alkyne functionality in hydroxyl-functional polymers

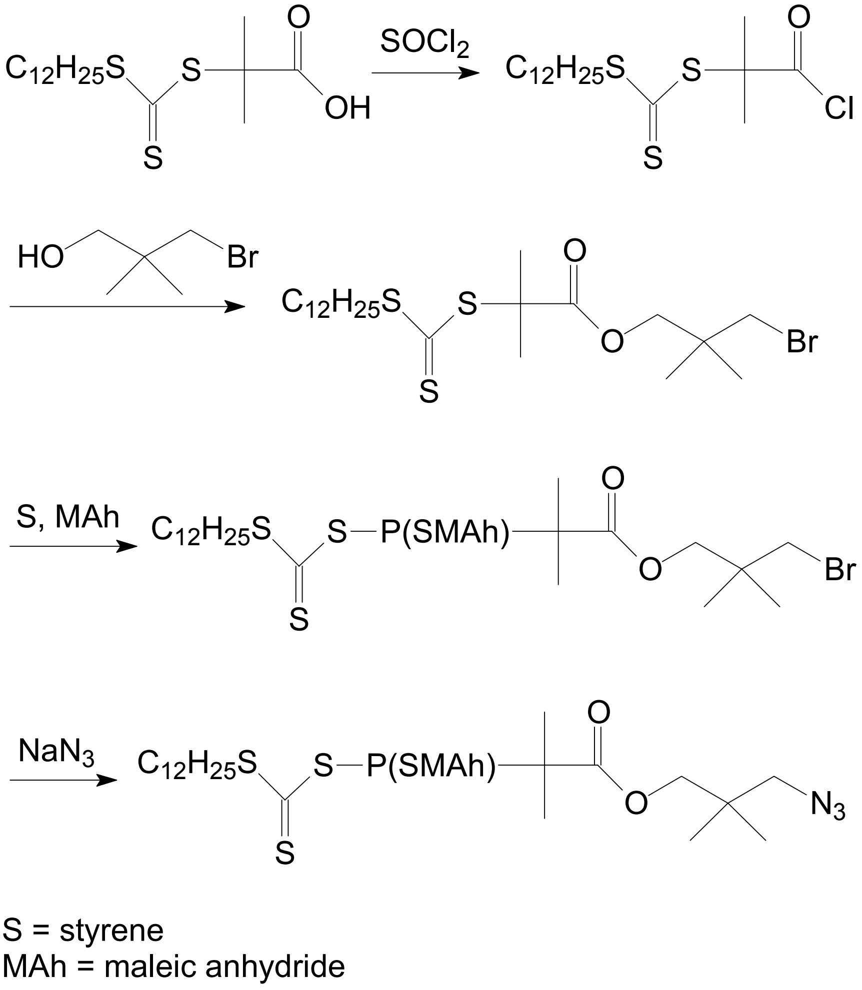
The first hydroxyl-functional polymer that was used as starting material is poly(ethylene-*co*-butylene) with a molecular weight of 3800 g/mol, which is commercially available. The second hydroxyl-functional polymer that was used is poly[styrene-*b*-(ethylene-*co*-butylene)] with a molecular weight of 80,000 g/mol. This block copolymer was prepared by living anionic polymerization of styrene and butadiene. The living poly(styrene-*b*-butadiene) that was obtained after polymerization was endcapped with ethylene oxide, terminated by quenching in methanol and subsequently hydrogenated.

The product of the esterification of poly(ethylene-*co*-butylene) with propargyl chloroformate was analyzed by ^{1}H-NMR, which showed no residual signal for the CH_2-OH protons, indicating complete formation of the ester.

For the esterification of poly[styrene-*b*-(ethylene-*co*-butylene)], which has a much higher molecular weight, ^{1}H-NMR analysis of the endgroups is not possible. Since reaction conditions were comparable with those used for the esterification of poly(ethylene-*co*-butylene), we used the polymer under the assumption that the esterification was also successful for the higher molecular weight polymer.

6.5 Polar block: Polymerization and azide functionalization

Next to the alkyne-functional non-polar block, an azide-functional polar block was prepared. In order to obtain a polymer with a well-defined molecular weight and a narrow molecular weight distribution, poly(styrene-*alt*-maleic anhydride) was prepared by RAFT-mediated polymerization. Scheme 6.4 shows the reaction steps that were followed to obtain the azide-functional polymer



Scheme 6.4. Synthesis of azide-functional poly(styrene-*alt*-maleic anhydride) via RAFT-mediated polymerization

Since the original RAFT-agent is preserved in the endgroups of the resulting polymer, the RAFT-agent has to be chosen in such a way that the leaving group can be modified into an azide group after polymerization. It is preferable to incorporate the azide group at the leaving group of the RAFT-agent rather than at the activating group, because after click coupling, the relatively unstable trithio-moiety will be located at the polymer chain end instead of at the junction between the coupled blocks.

An azide-functionality can be readily introduced by the substitution of a halide. Therefore, we synthesized a bromide-functional RAFT-agent, using S-dodecyl S'-(isobutyric acid) trithiocarbonate (DIBTC)[20] as the starting material. First, DIBTC was converted into its acid chloride derivative,[21] which was then esterified with 3-bromo-2,2-dimethyl-1-propanol. The resulting bromide-functional RAFT-agent was then used to control the copolymerization of styrene and maleic anhydride, yielding poly(styrene-*alt*-maleic anhydride) with a bromide endgroup. Reaction of this polymer with sodium azide[22] results in the desired azide functionality.

Two azide-functional polymers were prepared via this procedure. The characteristics of these polymers are displayed in Table 6.1.

Table 6.1. Azide-functional poly(styrene-*alt*-maleic anhydride) characteristics

Polymer	M_n SEC (g/mol)	PDI
SMA-1	8800	1.3
SMA-2	15600	1.3

The results of the substitution of the bromide endgroups with azide endgroups could not be determined via conventional methods such as ^{1}H-NMR and IR. However, the substitution reaction of halides by azides is known to proceed readily to completion. Therefore, also here we assumed complete conversion of the bromide endgroups into azide endgroups.

6.6 Click coupling of alkyne and azide

The first click coupling reaction was attempted with alkyne-functional poly(ethylene-*co*-butylene) (M_n = 3800) and SMA-1 (Table 6.1). Anhydride groups are present in our system, therefore we want to avoid water as a solvent. According to literature a number of other solvents are suitable for performing click chemistry.[3] In most of these solvents the copper(I) salt is not soluble. Therefore a nitrogen base is added as ligand in order to complex and solubilize copper(I).

Following a recipe from literature,[10] we employed THF as solvent, copper(I)iodide as catalyst and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as ligand. When solvent, polymers, copper(I) salt and ligand were mixed, a white precipitate formed. The solids were filtered off and the filtrate was analyzed with size exclusion chromatography (SEC). Only poly(ethylene-*co*-butylene) was detected, indicating that poly(styrene-*alt*-maleic anhydride) formed an insoluble complex with the copper(I) salt and/or the ligand.

In order to get insight in the formation of such a complex, we performed a small series of tests. Solutions of SMA-1 (Table 6.1) and commercially available poly(styrene-*co*-maleic anhydride) in THF were prepared. To these solutions copper(I)iodide and/or two different ligands, DBU and N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA), were added. The observations are listed in Table 6.2.

Table 6.2. Observations during mixing of poly(styrene-*co*-maleic anhydride) with Cu(I) and ligands

Polymer	Cu(I)	Cu(I) + DBU	DBU	PMDETA
SMA-1	no visible change	white precipitate	white precipitate	white precipitate
Commercial SMA	---	---	orange color, then white precipitate	green color, then white precipitate

--- = not tested

From the results in Table 6.2 it can be concluded that poly(styrene-*co*-maleic anhydride) with and without RAFT and azide endgroups forms a precipitate when a ligand is added. The presence of Cu(I) does not lead to precipitate formation.

The use of a ligand can be avoided by choosing a good solvent for the copper(I) salt as a medium for the click coupling reaction. To dissolve the copper(I) salt, the use of a polar solvent, such as dimethylformamide (DMF),[9] which is a non-solvent for the alkyne-functional poly(ethylene-*c*o-butylene), is required. To solve this problem, we decided to perform the click coupling reaction in a two-phase system where Cu(I) and poly(styrene-*alt*-maleic anhydride) are dissolved in DMF and poly(ethylene-*co*-

butylene) is dissolved in cyclohexane. In this system the click coupling reaction should take place at the interface between the two phases.

The SEC-results for the two-phase click coupling reaction are shown in Figure 6.1.

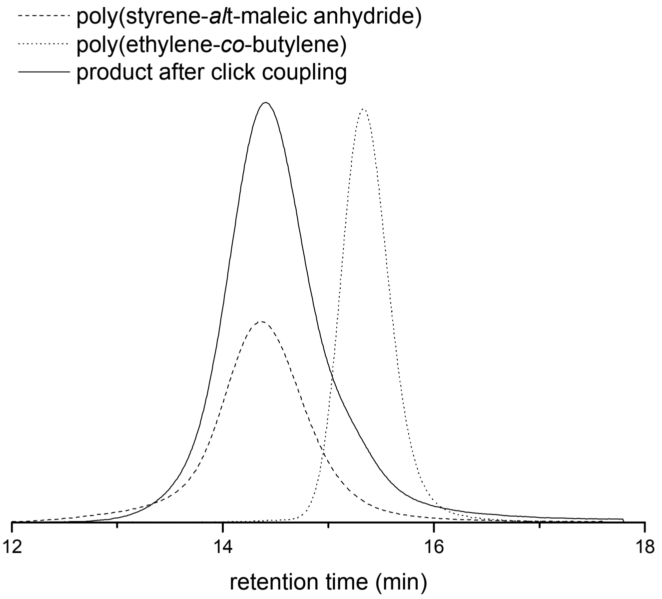


Figure 6.1. SEC-results for the click coupling reaction of poly(ethylene-*co*-butylene) and poly(styrene-*alt*-maleic anhydride)

The disappearance of the poly(ethylene-*co*-butylene) distribution indicates the formation of block copolymer. It should be noted that in the product distribution a shoulder at the low molecular weight side can be observed, which corresponds to the residual poly(ethylene-*co*-butylene). Some residual poly(ethylene-*co*-butylene) was expected because we used a 1.1-fold excess.

The small differences in molecular weights of the individual blocks and the resulting block copolymer prevent good separation of the product and the azide-functional poly(styrene-*alt*-maleic anhydride). Therefore, we can not decisively conclude that the click coupling reaction went to quantitative conversion.

The click coupling reaction was done once more with two different starting blocks, being alkyne-functional poly[styrene-*b*-(ethylene-*co*-butylene)] (M_n = 80,000 g/mol) and azide-functional poly(styrene-*alt*-maleic anhydride) (M_n = 15,600 g/mol, SMA-2, Table 6.1). The choice of these two blocks as starting materials allows a better separation in SEC because of the bigger differences in molecular weight. At the same time, the click coupling reaction of these two high molecular weight blocks would yield a block copolymer that could exhibit elastomeric properties.

Again a two-phase system was chosen as reaction medium. DMF was the polar solvent and xylene was used as solvent for poly[styrene-*b*-(ethylene-*co*-butylene)], since this polymer did not dissolve in cyclohexane. Even after prolonged reaction times, SEC analysis only showed the presence of the starting materials, so we were not able to confirm the results we obtained for the first click reaction.

There are several possible causes for the failure of the click coupling of poly[styrene-*b*-(ethylene-*co*-butylene)] and poly(styrene-*alt*-maleic anhydride). Possibly, the esterification of the hydroxyl endgroup of poly[styrene-*b*-(ethylene-*co*-butylene)] with propargyl chloroformate was not successful and therefore no terminal alkyne was introduced. The result of the esterification was not checked, because of the limitations of the conventional analytical techniques.

The failure of this click reaction can also be attributed to the reaction conditions and, more specifically, the solvent system that was used. It is known that copper(I) readily inserts into terminal alkynes in the presence of a base.[3] The polarization of the terminal triple bond by the covalently bound copper(I) catalyzes the cycloaddition reaction of azide and alkyne. Thus, the first step in the catalytic cycle is the formation of a bond between copper(I) and alkyne. In our two-phase system, the copper(I) salt is soluble in the DMF-phase, while the alkyne containing polymer is soluble in the non-polar cyclohexane or xylene phase. In the first click reaction that was done, the starting alkyne-functional poly(ethylene-*co*-butylene) was of relatively low molecular weight and therefore the alkyne endgroup was readily accessible. However, in the second click reaction alkyne-functional poly[styrene-*b*-(ethylene-*co*-butylene)] with a molecular weight of 80,000 g/mol was used. Most likely, the alkyne endgroup was not accessible to the copper(I) salt, so the bond formation between copper(I) and alkyne could not take place.

To get more insight into the different reaction steps, in particular the chain end functionalizations, a profound analysis of the different reaction products is required. To be able to analyze the endgroups of the high molecular weight polymers, a number of model reactions would have to be carried out. In these model reactions, labeled azides and alkynes, which can be easily detected, for example by UV-measurements should be used.

6.7 Conclusions

Click chemistry is a versatile and promising approach for the preparation of various macromolecular architectures. We attempted to synthesize block copolymers by click chemistry. First the blocks were prepared separately by living anionic polymerization and RAFT-mediated polymerization. After the polymerizations the blocks were functionalized with a terminal alkyne and azide unit respectively. Via the cycloaddition of alkyne and azide the blocks were then clicked together.

The alkyne endgroup was introduced via the esterification of a hydroxyl-functional polymer with propargyl chloroformate. The esterification was successful, but yields a polymer which contains a carbonate, which is not very stable. Therefore, other routes to introduce the alkyne group should be investigated. A possible way of introducing the alkyne functionality could be the addition of trimethylsilyl propargyl bromide to living anionic chains. This addition would yield a protected terminal alkyne. Deprotection of the alkyne and click coupling can be done subsequently according to a literature procedure described by Malkoch *et al.*[16]

The azide-functional polar block was prepared via RAFT-mediated copolymerization of styrene and maleic anhydride, with the use of a bromide-functional RAFT-agent. After polymerization, the bromide endgroup was replaced by an azide group. This method proved to be successful and seems applicable to many monomer systems. The use of ATRP would seem preferable to the use of RAFT, since it yields polymers with bromide endgroups in a more straightforward way than RAFT-mediated polymerization. However, via ATRP it is not possible to copolymerize styrene and maleic anhydride, so other monomer systems would have to be used.

The click coupling reaction via the "conventional" way, *i.e.* with the use of a copper(I) catalyst and a ligand, proved to be impossible for our system, since poly(styrene-*alt*-maleic anhydride) forms an insoluble precipitate in the presence of a ligand. We managed to achieve click coupling in absence of a ligand, employing a two-phase system. However, the two-phase system was not effective when high molecular weight blocks were used, probably because of poor accessibility of the endgroups.

In conclusion, if poly(styrene-*alt*-maleic anhydride) is chosen as the polar block, a smart two-phase system has to be designed, where probably the endgroups of the polymers have to be switched. That means poly(styrene-*alt*-maleic anhydride) should be functionalized with a terminal alkyne, which can form a reactive complex with copper(I) in the polar phase. Consequently, the non-polar block should be functionalized with an azide endgroup. This polar endgroup can react with the alkyne-copper complex at the interface of the two phases

If other polar monomer systems are chosen, which do not form complexes with the common ligands, the click coupling can be done via the usual methods in one solvent.

6.8 Experimental procedures

6.8.1 Materials

Non-polar block with terminal alkyne functionality: Hydroxyl-functional poly(ethylene-*co*-butylene) was obtained from Kraton Polymers and dried under vacuum before use. Pyridine (VWR, 99%) was distilled prior to use and stored over molecular sieves. Dichloromethane (DCM, Biosolve, AR grade) was dried over an alumina column. Propargyl chloroformate (Aldrich, 96%) and isopropanol (Biosolve, AR grade) were used as received

Polar block with azide functionality:
Synthesis of bromide-functional RAFT-agent: S-dodecyl S'-(isobutyric acid) trithiocarbonate (DIBTC) was prepared according to a literature procedure described by Lai *et al.*[20] Pyridine (VWR, 99%) was distilled prior to use and stored over molecular sieves. Thionyl chloride (Fluka, >99%) was distilled before use. Dichloromethane (DCM, Biosolve AR grade) was dried over an alumina column. 3-bromo-2,2-dimethyl-1-propanol (Aldrich, 96%), cyclohexane (Biosolve, AR grade), ethyl acetate (Biosolve, AR grade) and n-pentane (Biosolve, AR grade) were all used without further purification.
RAFT-mediated polymerization of styrene and maleic anhydride: Styrene (VWR, 99%) was passed over a basic alumina column to remove the inhibitor. Maleic anhydride (Aldrich, 99%) and 1,1-azobis(cyclohexanecarbonitrile) (VAZO88, Aldrich, 98%) were used without further purification. Solvents were purchased from Biosolve and used as received.
Azide functionalization: Sodium azide (Aldrich, 99%), dimethylformamide (DMF, Biosolve, extra dry) and isopropanol (Biosolve, AR grade) were all used as received.

Click coupling reactions: Copper(I)iodide (Aldrich, 99.99%), Copper(I)bromide (Aldrich, 98%), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich, 98%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), dimethylformamide (DMF, Biosolve, extra dry), cyclohexane (Biosolve, AR grade) and p-xylene (Aldrich, 99+%) were all used without further purification.

All reactions were carried out under an argon atmosphere

6.8.2 Non-polar block with terminal alkyne functionality

Poly(ethylene-co-butylene)

Hydroxyl-functional poly(ethylene-*co*-butylene) (10.104 g, 2.66 mmol) and pyridine (1.26 mL, 15.6 mmol) were dissolved in anhydrous dichloromethane (50 mL) in an oven-dried, degassed Schlenk tube. The solution was cooled down to -50 °C. Propargyl chloroformate (1.0 mL, 10.4 mmol) was added dropwise via a rubber septum.. The white mixture was kept between -30 and -50°C for 4.5 hours. The reaction mixture was allowed to warm up to room temperature overnight. During that time the color turned light brown. The mixture was washed with brine and then 3 times with water. After that, the organic layer was dried with Na_2SO_4 and dichloromethane was evaporated. The product was purified by column chromatography using dichloromethane as the eluent.

^{1}H NMR: δ (ppm) 4.72 [s, $C{\equiv}C\text{-}\underline{CH_2}\text{-}O$], 4.19 [t, $CH_2\text{-}\underline{CH_2}\text{-}O$], 2.51 [s, $\underline{HC}{\equiv}C\text{-}CH_2$], 1.5 [m, $\underline{CH_2}\text{-}CH_2\text{-}O$], 1.0-1.3 [m, CH_2, polymer chain], 0.8 [t, CH_3, polymer chain]

Poly[styrene-b-(ethylene-co-butylene)]

The reaction procedure was similar to the procedure described before for poly(ethylene-*co*-butylene). The work-up procedure consisted of precipitation of the product from a THF solution into isopropanol.

6.8.3 Polar block with terminal azide functionality

Synthesis of bromide-functional RAFT-agent

Acid chloride functional DIBTC (DIBTC-Cl) synthesis

DIBTC (1.0 g, 2.75 mmol) was dissolved in anhydrous dichloromethane (5 mL) in an oven-dried argon-purged flask. The flask was immersed in a cold isopropanol bath until the reaction mixture solidified. Thionyl chloride (1.0 mL, 13.75 mmol) was added dropwise to the cold reaction mixture. The mixture was allowed to warm up to room temperature while stirring. During the warm-up, gas development (HCl and SO_2) was observed. After reaching room temperature the flask was put in a water bath of 30 °C for 3 hours. The solvent and excess of thionyl chloride were removed under vacuum overnight. In order to avoid unwanted side reactions, the product was used directly for further reactions without any purification or characterization.

Esterification of DIBTC-Cl with 3-bromo-2,2-dimethyl-1-propanol

3-bromo-2,2-dimethyl-1-propanol (0.45 g, 2.7 mmol) and pyridine (0.22 mL, 2.8 mmol) were dissolved in dry dichloromethane (10 mL). The solution was cooled down with an ice bath. To the solution, DIBTC-Cl (1.0 g, 2.62 mmol, in 5 mL DCM) was added dropwise while stirring. The reaction mixture allowed to warm up and left at room temperature overnight. After that, the reaction mixture was extracted three times with brine and three times with water. The organic layer was dried over Na_2SO_4 and the solvent was removed. The product was purified by column chromatography using a mixture of cyclohexane:n-pentane:ethyl acetate (68:23:9 v/v%) as the eluent

^{1}H NMR: δ (ppm) 3.90 [s, $Br\text{-}CH_2C(CH_3)_2\underline{CH_2}OCOC(CH_3)CS_3C_{12}H_{25}$],
3.32 [s, $Br\text{-}\underline{CH_2}C(CH_3)_2CH_2OCOC(CH_3)CS_3C_{12}H_{25}$],
3.26 [t, $Br\text{-}CH_2C(CH_3)_2CH_2OCOC(CH_3)CS_3\underline{CH_2}C_{11}H_{23}$], 1.1-1.9 [m, 32H, $(CH_2)_{10}$, $Br\text{-}CH_2\text{-}C\underline{(CH_3)_2}$ and $S\text{-}C(CH_3)_2$], 0.9 [t, $C_{11}H_{22}\underline{CH_3}$]

RAFT-mediated polymerization of styrene and maleic anhydride

A general procedure for the RAFT-mediated polymerizations is given here.

Initiator (Vazo88), bromide-functional RAFT-agent, styrene and maleic anhydride were added to a three-neck round bottom flask equipped with a stirrer and condenser and dissolved in a MEK/toluene mixture. The solution was degassed by purging with argon for 45 min. After that time the flask was kept under argon atmosphere and immersed in a preheated oil bath at 85 °C. Polymerization was allowed to proceed for 24 hours. The product was isolated by precipitation from the MEK/toluene solution into isopropanol and dried under vacuum.

Azide functionalization

In a typical procedure to introduce the azide-group poly(styrene-*alt*-maleic anhydride) (1.5 g , 0.18 mmol) was dissolved in dimethylformamide (30 mL). Sodium azide (NaN_3, 0.015 g , 0.24 mmol) was added. The color of the reaction mixture gradually changed from light yellow to dark yellow. The reaction mixture was left for 20 hours at room temperature. The resulting azide-functional polymer was precipitated from the DMF solution into isopropanol.

6.8.4 Click coupling reactions

Click coupling in the presence of ligand (DBU)

Alkyne-functional poly(ethylene-*co*-butylene) (102 mg, 0.027 mmol), azide-functional poly(styrene-*alt*-maleic anhydride) (213 mg, 0.024 mmol) and copper(I)iodide (1.0 mg, 0.0053 mmol) were added to an oven-dried, degassed Schlenk tube. Dry THF was added (5 mL) and the reaction mixture was heated to 35 °C. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 79 mg, 0.52 mmol) was added. Almost instantaneously, a white precipitate formed.

Click coupling without ligand

Alkyne-functional poly(ethylene-*co*-butylene) (37 mg, 0.01 mmol), azide-functional poly(styrene-*alt*-maleic anhydride) (64 mg, 0.008 mmol) and copper(I)bromide (0.8 mg , 0.006 mmol) were added to an oven-dried, degassed Schlenk tube. Dimethylformamide (1 mL) and cyclohexane (0.5 mL) were added. The mixture was heated to 35 °C and left to react for 24 hours. When the reaction was stopped the mixture appeared clear.

6.8.5 Characterization techniques

^{1}H-NMR

^{1}H-NMR analyses were performed on a Varian Mercury-Vx 400 MHz spectrometer. Samples were dissolved in deuterated chloroform (Cambridge Isotope Laboratories)

Size Exclusion Chromatography (SEC)

Molecular weight and molecular weight distributions were determined using size exclusion chromatography. Before analysis, the polymer containing samples were dissolved in THF at a concentration of 1 mg/mL and filtered through a 13 mm × 0.2 μm PTFE-filter (Alltech)

SEC analyses were performed using a Waters Model 600 pump and a Waters Model WISP 712 autoinjector. The columns used were a PLgel guard precolumn (5 μm, 50 × 7.5 mm) and two PLgel mixed-D columns (5 μm particles, 300 × 7.5 mm, Polymer Laboratories) set at 40 °C. The injection volume was 50 μL. Stabilized THF (Biosolve) + acetic acid (5% v/v) (Aldrich) was used as eluent at a flow rate of 1.0 mL/min. A model 410 refractive index detector and a model 486 UV detector operating at wavelengths of 254 nm and 305 nm were used for detection. Calibration was done using polystyrene standards (Polymer Laboratories).

Data acquisition and processing were performed using Waters Millennium32 (v4.0) software.

References

1 Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angewandte Chemie, International Edition* **2001**, *40*, 2004-2021.

2 Tornoe, C. W.; Christensen, C.; Meldal, M. *Journal of Organic Chemistry* **2002**, *67*, 3057-3064.

3 Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angewandte Chemie, International Edition* **2002**, *41*, 2596-2599.

4 Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin, V. V. *Macromolecules* **2005**, *38*, 3663-3678.

5 Joralemon, M. J.; O'Reilly, R. K.; Matson, J. B.; Nugent, A. K.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **2005**, *38*, 5436-5443.

6 Wu, P.; Malkoch, M.; Hunt, J. N.; Vestberg, R.; Kaltgrad, E.; Finn, M. G.; Fokin, V. V.; Sharpless, K. B.; Hawker, C. J. *Chemical Communications (Cambridge, United Kingdom)* **2005**, 5775-5777.

7 Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Frechet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angewandte Chemie, International Edition* **2004**, *43*, 3928-3932.

8 Parrish, B.; Breitenkamp, R. B.; Emrick, T. *Journal of the American Chemical Society* **2005**, *127*, 7404-7410.

9 Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3558-3561.

10 Opsteen, J. A.; van Hest, J. C. M. *Chemical Communications (Cambridge, United Kingdom)* **2005**, 57-59.

11 Tsarevsky, N. V.; Bernaerts, K. V.; Dufour, B.; Du Prez, F. E.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9308-9313.

12 Englert, B. C.; Bakbak, S.; Bunz, U. H. F. *Macromolecules* **2005**, *38*, 5868-5877.

13 Lutz, J. F.; Boerner, H. G.; Weichenhan, K. *Macromolecular Rapid Communications* **2005** , *26*, 514-518.

14 Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 7540-7545.

15 Gao, H.; Louche, G.; Sumerlin, B. S.; Jahed, N.; Golas, P.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8979-8982.

16 Malkoch, M.; Thibault, R. J.; Drockenmuller, E.; Messerschmidt, M.; Voit, B.; Russell, T. P.; Hawker, C. J. *Journal of the American Chemical Society* **2005**, *127*, 14942-14949.

17 Riva, R.; Schmeits, S.; Stoffelbach, F.; Jerome, C.; Jerome, R.; Lecomte, P. *Chemical Communications (Cambridge, United Kingdom)* **2005**, 5334-5336.

18 Diaz, D. D.; Punna, S.; Holzer, P.; McPherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *Journal of Polymer Science, Part A: Polymer Chemistry* **2004**, *42*, 4392-4403.

19 Ramesh, R.; Bhat, R. G.; Chandrasekaran, S. *Journal of Organic Chemistry* **2005**, *70*, 837-840.

20 Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754-6756.

21 Jesberger, M.; Barner, L.; Stenzel, M. H.; Malmstroem, E.; Davis, T. P.; Barner-Kowollik, C. *Journal of Polymer Science, Part A: Polymer Chemistry* **2003**, *41*, 3847-3861.

22 Yebassa, D.; Balakrishnan, S.; Feresenbet, E.; Raghavan, D.; Start, P. R.; Hudson, S. D. *Journal of Polymer Science, Part A: Polymer Chemistry* **2004**, *42*, 1310-1321.

Epilogue

The main objective of the research described in this thesis was to develop routes for the synthesis of block copolymers by combination of living anionic polymerization and living radical polymerization. These block copolymers should contain polar and non-polar blocks and exhibit the properties of thermoplastic elastomers.

The living radical polymerization technique that was used is RAFT (reversible addition-fragmentation chain transfer) mediated polymerization, since that is considered to be the most versatile living radical polymerization technique. A sequential approach was used in which the first non-polar block(s) were synthesized via living anionic polymerization. After subsequent modification of the chain end, the resulting macromolecular chain transfer agent was used in the RAFT-mediated copolymerization of styrene and maleic anhydride. The key step in this sequential approach is the transition from one mechanism to the other via conversion of a living anionic polymer into a macromolecular RAFT-agent with a polymeric leaving group. Two different pathways for the conversion of anion into RAFT-agent were investigated:

- Functionalization reactions performed directly at the carbanionic chain end to obtain the RAFT-agent.
- Attenuation of chain-end reactivity by endcapping of the carbanionic chain end with ethylene oxide prior to functionalization reactions.

When functionalization reactions are performed directly at the carbanionic chain end, the high reactivity of the carbanion is used to achieve efficient conversion of the chain end, which leads to a high yield of block copolymer in the end. A smart choice of reactants could even result in a one-pot procedure for the entire block copolymer synthesis. Therefore, reactions at the carbanion would be preferable, and this method was investigated first.

As a first step, a suitable leaving group had to be added to living polybutadiene. Three different capping agents were investigated for that purpose. A very short polystyrene block with a well-defined molecular weight (distribution) was found to be the most suitable leaving group.

Subsequent modification reactions consisted of the transformation of carbanionic chain ends into bromide or thiol functionalities. The most promising of all chain-end modification reactions was the functionalization with a cyclic disulfide (1,4-dihydro-2,3-benzodithiin), which yields a suitable leaving group and a sulfide at the chain end in one step.

However, in spite of partial successes, all reactions at the carbanion suffered from poor selectivity, leading to side product formation and incomplete functionalization. Finally, we concluded that direct conversion of anionic chain ends into thiol or bromide functionality is not possible in a selective way to the best of our knowledge. Therefore, the synthesis of a RAFT-agent via this method is also highly unlikely. Most probably, attenuation of the chain-end reactivity is required for selective chain-end functionalization.

The attenuation of the chain-end reactivity by endcapping with ethylene oxide was already mentioned as an alternative route towards macromolecular RAFT-agents. Esterification of the resulting lithium alkoxide with an acid chloride functional RAFT-agent proved to be a relatively straightforward and efficient way to obtain the desired macromolecular chain transfer agent. Subsequent chain extension of the macromolecular RAFT-agents with poly(styrene-*alt*-maleic anhydride) was successful for three model compounds ($M_n \approx 4000$ g/mol). Block copolymers with controlled molecular weight (distribution) were obtained in good yield. However, in order to obtain materials that exhibit elastomeric properties, higher molecular weights are required. Our investigations on high molecular weight RAFT-agents ($M_n \approx 70$ kg/mol) revealed that the molecular weight of the RAFT-agent had an enormous influence on the behavior of the polymerizing system. The pronounced polarity differences in the system cause phase separation and poor accessibility of the chain-end radicals thereby preventing (controlled) chain extension.

In order to circumvent the problems that were encountered for high molecular weight systems, less polar monomers could be used to form the polar block. Chain extension with styrene was successful, so monomers with intermediate polarity, such as acrylates, may be used. Hydrolysis of the acrylates after polymerization would yield a poly(acrylic acid) as the polar block in the end.

The use of a semi-continuous system could be another way of avoiding phase separation problems. A solvent gradient could be applied during the RAFT-mediated polymerization, where the solvent polarity is increased with the growth of the polar block. Monomer could also be added during the RAFT-mediated polymerization.

Furthermore, an increase of the polarity of the RAFT-group at the chain end of the non-polar block(s) might lead to a macromolecular RAFT-agent that behaves as a surfactant. The RAFT-mediated polymerization of the polar block can then be done in a heterogeneous (two-phase) system, since the polar chain end will be accessible to the polar monomers.

In Chapter 6 an alternative for the sequential approach was investigated: “Click chemistry”. In the click chemistry approach an alkyne-functional polymer is coupled to an azide-functional polymer via copper(I) catalyzed cycloaddition of the alkyne and the azide groups. By synthesizing the polar and non-polar blocks independently, we hoped to avoid the previously encountered phase-separation problems.

The use of conventional systems for click chemistry, which consist of a copper(I) salt and a ligand, proved to be impossible because an insoluble precipitate of the ligand with poly(styrene-*alt*-maleic anhydride) was formed. We managed to achieve click coupling in absence of a ligand, employing a two-phase system. However, the two-phase system was not effective for high molecular weight blocks, probably because of poor accessibility of the alkyne and azide endgroups.

It should be noted that the studies on click chemistry reported in this thesis, are only preliminary. Therefore, our systems are far from optimized. Click chemistry, or a similar method in which the polar and non-polar blocks are synthesized separately and coupled afterwards, is definitely worth further investigations.

First of all, reversal of the endgroups may be advantageous when working in a two-phase system. Locating the polar azide group at the chain end of the non-polar polymer and the relatively non-polar alkyne group at the chain end of the polar polymer would increase the driving force for the endgroups to go to the interface. Furthermore, the choice of the solvents can probably be optimized to force the endgroups to the interface.

Click chemistry is a very rapidly developing field. In the near future novel catalytic systems or reactions similar to the cycloaddition of azides and alkynes, which could be of use for our system, may be explored.

In general, from the research described in this thesis, we can conclude that the most important step in the synthesis of block copolymers via sequential living anionic polymerization and RAFT-mediated polymerization seems to be the transition from one mechanism to another. However, when the transition is accomplished, other factors, such as polarity differences and molecular weight play a decisive role in the efficiency of the RAFT-mediated polymerization. We showed that in principle it is possible to synthesize block copolymers with polar and non-polar blocks by combination of living anionic polymerization and RAFT-mediated polymerization. However, going one step further towards the production of high molecular weight block copolymers which exhibit the properties of thermoplastic elastomers requires further investigations to optimize the reaction conditions. Furthermore, alternatives to the sequential approach, such as click chemistry, seem promising and should be investigated in more detail.

Summary

Styrenic block copolymers (SBCs) are the largest-volume category of thermoplastic elastomers. SBCs are produced via living anionic polymerization, resulting in polymers with a well-defined molecular weight and microstructure, and a narrow molecular weight distribution. Via living anionic polymerization only a limited range of monomers can be polymerized in a controlled way. These monomers are mainly non-polar. However, one or more polar blocks are desirable to enhance compatibility of the block copolymers with polar materials. The use of recently developed living radical polymerization techniques in combination with living anionic polymerization offers the possibility to extend the monomer range considerably.

The aim of the work reported in this dissertation was to develop synthetic routes to obtain block copolymers containing polar and non-polar block(s) by combination of living anionic polymerization and living radical polymerization. The block copolymers that are aimed for should exhibit elastomeric properties.

We decided to combine living anionic polymerization with RAFT (reversible addition-fragmentation chain transfer) mediated polymerization, because RAFT-mediated polymerization is considered to be the most versatile living radical polymerization technique. The approach used to synthesize the desired block copolymers was sequential living anionic and RAFT-mediated polymerization.

The key step in the combination of two polymerization mechanisms is the transition from one mechanism to the other. In our case, this implied the conversion of a living anionic chain into a macromolecular RAFT-agent with a polymeric leaving group. Several steps were needed to obtain the desired chain-end functionality. First a suitable leaving group was added to living anionic polybutadiene by endcapping with various styrenic compounds. After the attachment of a suitable leaving group, the chain end had to be converted into a RAFT-agent. Based on the relative ease of synthesis, we chose a trithiocarbonate as the RAFT-agent.

Generally, trithiocarbonates are prepared by deprotonation of a mercaptan, followed by the addition of carbon disulfide and finally coupling with an alkyl halide. This means that a halide or mercapto functionality is required at the polymer chain-end.
Attempts were made to obtain one of the two functionalities by halogen-lithium exchange reactions and by endcapping reactions with different sulfur-compounds, including elemental sulfur and (cyclic) disulfides. Although most of these reactions were partially successful, in all cases unwanted side reactions occurred to a significant extent. These side reactions were a direct consequence of the high reactivity of the carbanions and prevented the high yield formation of the desired functional polymers.

We also used a slightly more conventional approach to obtain macromolecular RAFT-agents. That approach consisted of a two-step esterification procedure. First the living anionic chain end reactivity was attenuated by endcapping the chains with ethylene oxide, to obtain a lithium alkoxide. This lithium alkoxide was then esterified with an acid chloride functional RAFT-agent.

The macromolecular RAFT-agents obtained via the esterification procedure were then chain extended with poly(styrene-*alt*-maleic anhydride) in order to obtain the desired block copolymers with non-polar and polar blocks. We were able to produce these block copolymers in a controlled way for a limited molecular weight range. Using high molecular weight RAFT-agents (>10,000 g/mol) caused phase separation during reaction because of the incompatibility between the different components present in the system. Therefore we only produced high molecular weight poly(styrene-*co*-maleic anhydride) in an uncontrolled way.

To provide an alternative for the sequential approach described before, some feasibility studies on “click chemistry” were performed. Click chemistry is based on the very efficient 1,3-dipolar cycloaddition reaction between azides and alkynes. We synthesized a non-polar polymer with an alkyne endgroup and coupled it to a polar polymer with an azide endgroup.
The click coupling reaction worked well for a low molecular weight model system. In a high molecular weight system however, we did not obtain block copolymers. Further investigations are required in order to optimize the reaction conditions for click chemistry.

In conclusion, we showed that in principle it is possible to produce block copolymers with polar and non-polar blocks by combination of living anionic polymerization and RAFT-mediated polymerization.

Since we used a sequential approach, at first the most important step seemed to be the transition from living anionic polymerization to RAFT-mediated polymerization. However, we found that the final result of the block copolymer synthesis largely depends on the efficiency of the RAFT-mediated polymerization. Factors such as polarity differences and molecular weight proved to have a decisive influence on this efficiency. Therefore, the production of high molecular weight block copolymers which exhibit elastomeric properties turned out to be very complicated and requires further research to optimize the reaction conditions.

Furthermore, the development of the “click chemistry” approach, which seems to be a promising alternative to the sequential approach, deserves attention.

Samenvatting

Blokcopolymeren gebaseerd op styreen (SBCs) vormen de grootste categorie thermoplastische elastomeren op basis van productievolume. SBCs worden geproduceerd door middel van levende anionische polymerisatie. Deze polymerisatietechniek leidt tot polymeren met een goed gedefinieerd molgewicht en microstructuur en een smalle molgewichtsverdeling. Met behulp van levende anionische polymerisatie kan slechts een beperkt aantal monomeren gecontroleerd gepolymeriseerd worden. Deze monomeren zijn vrijwel allemaal apolair.

Het is echter wenselijk om één of meer polaire blokken in te bouwen in SBCs om de compatibiliteit met polaire materialen te verbeteren. Het gebruik van recentelijk ontwikkelde technieken voor levende radicaalpolymerisatie in combinatie met levende anionische polymerisatie biedt de mogelijkheid het aantal monomeren aanzienlijk uit te breiden.

Het doel van het onderzoek dat wordt beschreven in dit proefschrift was het ontwikkelen van syntheseroutes voor blokcopolymeren met polaire en apolaire blok(ken) door middel van de combinatie van levende anionische polymerisatie en levende radicaalpolymerisatie. De blokcopolymeren dienen zich te gedragen als thermoplastische elastomeren.

Wij hebben levende anionische polymerisatie gecombineerd met RAFT (reversibele additie-fragmentatie ketenoverdrachts) polymerisatie, omdat RAFT-polymerisatie beschouwd wordt als de meest veelzijdige techniek voor levende radicaalpolymerisatie. Om tot de gewenste blokcopolymeren te komen is gekozen voor opeenvolgende levende anionische polymerisatie en RAFT-polymerisatie.

De belangrijkste stap in de combinatie van twee polymerisatiemechanismen is de overgang van het ene mechanisme naar het andere. In dit geval bestaat deze overgang uit de omzetting van een levende anionische polymeerketen naar een macromoleculaire *RAFT-agent* met een polymere *leaving group*. Verschillende

stappen waren nodig om de uiteindelijke functionaliteit op het ketenuiteinde te verkrijgen.

Als eerste werd een goede *leaving group* aan het ketenuiteinde van het eerste blok, polybutadieen, gezet door middel van *endcappen* met verschillende styreen-afgeleide verbindingen. Nadat een goede *leaving group* op het ketenuiteinde was verkregen, moest het ketenuiteinde omgezet worden in een *RAFT-agent*. Wij hebben gekozen voor een trithiocarbonaat als *RAFT-agent*, omdat trithiocarbonaten relatief gemakkelijk te synthetiseren zijn. In het algemeen worden trithiocarbonaten gemaakt door het deprotoneren van een mercaptaan, gevolgd door de additie van koolstofdisulfide en tenslotte door koppeling met een alkylhalide. Dit betekent dat het ketenuiteinde van het polymeer voorzien moet worden van een halogeen- of zwavelfunctionaliteit.

Pogingen om één van deze twee functionaliteiten te introduceren zijn gedaan met behulp van lithium-halogeen uitwisseling en functionalisatie van het ketenuiteinde met verschillende zwavelverbindingen waaronder elementair zwavel en (cyclische) disulfides. Hoewel de meeste van deze reacties gedeeltelijk succesvol waren, traden in alle gevallen nevenreacties op. Deze nevenreacties zijn een direct gevolg van de hoge reactiviteit van de carbanionen en zorgden ervoor dat de gewenste functionele polymeren niet selectief gemaakt konden worden.

Een meer conventionele benadering om macromoleculaire *RAFT-agents* te maken bestaat uit een tweestaps veresteringsprocedure. Eerst werd de reactiviteit van het anionische ketenuiteinde verlaagd door *endcappen* met ethyleenoxide. Deze reactie levert een lithiumalkoxide op. Dit alkoxide werd vervolgens veresterd met een *RAFT-agent* met zuurchloride functionaliteit.

Ketenverlenging van de macromoleculaire *RAFT-agents* die waren verkregen na de verestering, met poly(styreen-*alt*-maleïnezuur anhydride) zou leiden tot de gewenste blokcopolymeren. Deze blokcopolymeren zijn op gecontroleerde wijze geproduceerd voor een beperkt bereik van molecuulgewichten. Wanneer hoogmoleculaire (> 10.000 g/mol) *RAFT-agents* gebruikt werden trad fasenscheiding op tijdens de ketenverlenging vanwege de incompatibiliteit tussen de verschillende componenten van het systeem. Hierdoor werd alleen zeer hoog moleculair poly(styreen-*co*-maleïnezuur anhydride) gevormd op ongecontroleerde wijze.

Om een alternatief te bieden voor de opeenvolgende levende anionische polymerisatie en RAFT-polymerisatie is een haalbaarheidsonderzoek uitgevoerd betreffende het gebruik van “klikchemie”. Klikchemie is gebaseerd op de zeer efficiënte 1,3-dipolaire cycloadditie van azides en alkynen. Een apolair polymeer met alkyn eindgroep is gekoppeld aan een polair polymeer met azide eindgroep. De koppeling door middel van klikchemie was succesvol voor een modelsysteem met relatief lage molecuulgewichten. Voor een systeem met hogere molecuulgewichten waren we echter niet in staat blokcopolymeer te produceren.

Verder onderzoek is vereist om de reactiecondities voor klikchemie te optimaliseren.

Concluderend hebben we aangetoond dat het in principe mogelijk is blokcopolymeren met polaire en apolaire blokken te maken door combinatie van levende anionische polymerisatie en RAFT-polymerisatie.

Vanwege het gebruik van opeenvolgende levende anionische polymerisatie en RAFT-polymerisatie leek de overgang van het ene naar het andere mechanisme op het eerste gezicht de belangrijkste stap. Het eindresultaat van de blokcopolymeersynthese is echter in grote mate afhankelijk van de efficiëntie van de RAFT-polymerisatie. Deze efficiëntie wordt voor een belangrijk deel bepaald door factoren als polariteitsverschillen en molecuulgewicht. Hierdoor bleek de productie van hoogmoleculaire blokcopolymeren met de eigenschappen van thermoplastische elastomeren gecompliceerd. Verder onderzoek is dan ook vereist om de reactiecondities te optimaliseren.

Klikchemie tenslotte, lijkt een veelbelovend alternatief voor opeenvolgende levende anionische polymerisatie en RAFT-polymerisatie. Verder onderzoek naar deze methode is aanbevelenswaardig.

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Ellen

Curriculum Vitae

Ellen Donkers werd geboren op 24 juli 1978 te Eindhoven. In 1996 behaalde zij haar vwo-diploma aan het Stedelijk College Eindhoven te Eindhoven. In datzelfde jaar begon zij aan de opleiding Scheikundige Technologie aan de Technische Universiteit Eindhoven. Op 31 augustus 2001 legde ze met succes het doctoraalexamen af. Na het voltooien van de Technisch Universitaire Lerarenopleiding, startte zij in februari 2002 haar werkzaamheden als promovendus aan de Technische Universiteit Eindhoven onder begeleiding van Prof. Dr. C.E. Koning en Dr. Ir. L. Klumperman. Het promotieonderzoek werd gedeeltelijk uitgevoerd bij Kraton Polymers te Amsterdam onder begeleiding van Dr. M. van Dijk en Dr. A van der Huizen.