> ***» Chosen are those artists who penetrate the region***
> ***of that secret place, where primeval power nurtures all evolution...***
> ***Who is the artist that would not dwell there?***
> ***In the womb of nature at the source of creation,***
> ***where the secret key to all lies guarded. «***[1]

# 4. Living Radical Copolymerization of Styrene and Maleic Anhydride and the Synthesis of Novel Polyolefin-based Block Copolymers via RAFT Polymerization.[2]

*Synopsis: This chapter describes the application of RAFT polymerization in the copolymerization of styrene and maleic anhydride. Novel well-defined polyolefin-based block copolymers are prepared using a macromolecular RAFT agent derived from a commercially available polyolefin (Kraton L-1203). The second block consisted of either polystyrene or poly(styrene-co-maleic anhydride). The product has a low polydispersity and is of predetermined molar mass. Furthermore, it is demonstrated that the colored labile dithioester moiety in the product of RAFT polymerizations can be removed from the polymer chain by UV photolysis.*

## 4.1. Polyolefin-based Architectures

Polyolefins find application in a large number of areas ranging from cheap bulk commodity plastic to high added value engineering materials. One can think of packaging materials (plastic bags & bottles), rubbers and thermoplastic elastomers like EPDM and EPM (copolymers of ethylene, propylene, butadiene), superstrong fibres and coatings. The inert character of polyolefins is an advantageous property in many cases, *e.g.* contact with foods, tacking of dirt, resistance to solvents and other chemicals, but complicates efficient application as the adhesion of polyolefin coatings on substrates and the miscibility with other polymer materials is poor. The pure hydrocarbon polymer backbone with its low interfacial tension lacks the ability to form interactions with other materials by the formation of primary (covalent) or secondary bonds (acid–base or polar interactions). An established technique for improving the interfacial tension between polymers and other materials is the use of block and graft copolymers as compatibilizers.[3,4,5] Small amounts of functional groups, concentrated in a few short segments dramatically increase the interaction between polyolefins and a broad range of materials containing polar groups with most of the original properties of the polyolefin retained. In principle, there are two ways to obtain functionalized polyolefins: ① chemical modification or free-radical grafting of preformed polyolefins; ② block copolymerizations and random copolymerizations of olefins with suitable polar monomers.[6]

The latter method gives direct access to the desired materials under mild and controlled conditions but suffers from the serious drawback of the limited compatibility between Ziegler-Natta and metallocene catalysts – both widely used to prepare polyolefins – and polar monomers. The first method is widely used, but requires aggressive reaction conditions. The polymer is activated by either exposure to high energy radiation or heating in the presence of a suitable free-radical initiator and followed by initiation of the second monomer.

In this chapter it will be shown how living radical polymerization techniques can be used to prepare macromolecular structures containing polyolefinic elements. Chapter 2 (*e.g.* Figure 2.2, page 32) showed that living radical polymerization is well suited for the preparation of block copolymers. This approach required the monomers for both blocks to be polymerized in a sequential manner, something which is bound to fail for olefins as free-radical techniques – living or not – are unable to polymerize these monomers. Several methods have been reported to overcome this problem allowing these techniques to be used for the preparation of polyolefin-based polymer architectures (block and graft copolymers).

It was shown that an alkene functionalized with an alkoxyamine moiety could be copolymerized with olefins like propene and 4-methylpentene using a cationic metallocene catalyst.[7] The resulting polyolefin with alkoxyamine groups scattered along its backbone was used as a macro-initiator in the nitroxide mediated polymerization of styrene to form polyolefin-*graft*-polystyrene with low polydispersity polystyrene grafts (pd$<$1.15).

An alternative approach is the transformation of a ready-made polyolefin into a suitable dormant species by organic procedures. This requires a polyolefin starting material with some sort of functional group in the polymer chain that can be converted into the desired starting material for living radical polymerization.

Kraton L-1203, for example, is a commercial product prepared from butadiene. Low molar mass polybutadienes are end-capped and hydrogenated to form semi-random copolymers of ethylene and butylene with a terminal hydroxyl group. The hydroxyl group may be esterified with *e.g.* 2-bromo-2-methyl propionyl bromide to form a mono-bromide functionalized polyolefin which can be converted to a block copolymer by atom transfer radical polymerization (ATRP).[8,9,10]

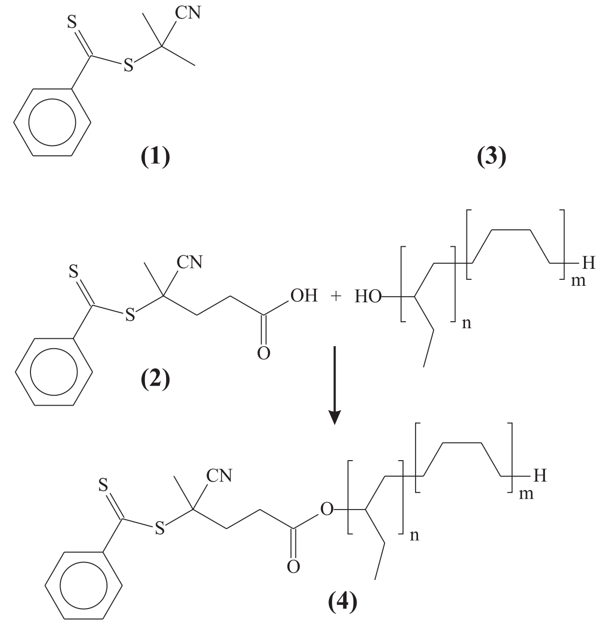
Waterson and Haddleton[10] showed that this material could be used to prepare poly[(ethylene-*co*-butylene)-*block*-methyl methacrylate] and poly[(ethylene-*co*-butylene)-*block*-trimethylsilyl methacrylate] which in turn could be hydrolyzed to poly[(ethylene-*co*-butylene)-*block*-methacrylic acid]. Jancova *et al.*[9] used a similar Kraton derivative to prepare poly[(ethylene-*co*-butylene)-*block*-styrene] and poly[(ethylene-*co*-butylene)-*block*-(4-acetoxy styrene)]. Again this polymer was hydrolyzed forming poly[(ethylene-*co*-butylene)-*block*-(4-hydroxy styrene)]. Matyjaszewski *et al.*[11] transformed a commercial copolymer of ethylene and glycidyl methacrylate into a suitable initiator for ATRP, allowing the preparation of poly(ethylene-*graft*-styrene) and poly(ethylene-*graft*-methyl methacrylate).

The examples above show that an additional hydrolysis step is required to come to truly functional block copolymers. Although advances have been made in this field, the combination of ATRP and highly polar or functional monomers was found to be problematic. Direct polymerization of acidic monomers is not possible with the current generation of catalysts as the metals rapidly react with the acids to form metal carboxylates that are ineffective as deactivator and often insoluble in the reaction medium[12]. Polymerization of the sodium salts of methacrylic acid[13] and of 4-vinyl benzoic acid[14] has been reported but the required aqueous polymerization medium prevents the incorporation of these monomers in more complex polymer architectures together with most other (water insoluble) monomers.

For compatibilization purposes, maleic anhydride is often used as the grafting monomer as it introduces a highly polar group in the polyolefin, while the incorporation is regulated by its inability to form a homopolymer, restricting the addition to a single monomer unit per site.[15] Maleic anhydride has proved elusive so far in terms of controlled polymerization by living radical techniques. All attempts at the controlled copolymerization of styrene and maleic anhydride using ATRP, both in literature[16,17] and in our own laboratory, remained fruitless. Either polymerization did not take place at all because of some deleterious interaction between the monomer and the ATRP catalyst,[17] or the molar mass developed in an unpredictable way.[16]

It has been shown that the copolymerization of styrene and maleic anhydride *can* proceed in a controlled fashion using nitroxide-mediated polymerization.[16] This required 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide to be used at high temperatures (120 °C). Although this specially designed nitroxide is able to polymerize many different types of monomer,[18] its complicated synthesis[19] renders it unattractive. The more commonly applied and readily available 2,2,6,6-tetramethylpiperidinine-*N*-oxyl (TEMPO) was unable to control the polymerization.[16,20]

Reversible addition–fragmentation chain transfer (RAFT) polymerization is known to be compatible with acid- and amine-functional monomers,[21,22,23] and therefore appears to be the best choice for this type of work. It does not require more stringent polymerization conditions than conventional free-radical polymerization, and thereby allows the robustness of radical chemistry to be combined with a more sophisticated design of the polymer chain architecture. Especially in the context of block copolymers, the need for control on the polymer design cannot be overemphasized. The strong correlation between block lengths and block composition on the one hand and material properties on the other, requires careful tailoring of the polymer microstructure to arrive at materials with unique properties that are not solely of academic significance but are of commercial interest as well.[24,25,26] While random or statistical copolymers, in general, possess properties that appear to be an average of the properties found in the homopolymers of the constituent monomers, block copolymers retain many of the macroscopic characteristics of their homopolymers. Diblock copolymers can be used to prevent phase-compatibility problems in a variety of situations. Gaillard *et al.*[27] used poly(styrene-*b*-butadiene) as a compatibilizer for blends of polystyrene and polybutadiene. Duivenvoorde *et al.*[28] used block copolymers of ε-caprolactone and 2-vinyl pyridine as dispersants in powder coatings to stabilize pigment particles in polyester matrix materials. Amphiphilic diblock copolymers of styrene and styrene sulfonate have been used as surfactants in the emulsion polymerization of styrene.[29]



**Scheme 4.1.** Both 2-cyanoprop-2-yl dithiobenzoate (**1**) and macromolecular RAFT agent (**4**) were applied in the polymerization of this chapter. The latter was synthesized from a commercial hydroxyl terminated ethylene butylene copolymer (**3**, Kraton L-1203) and an acid functional dithioester (**2**). The syntheses are described in chapter 2. Note that **3** consists of a more or less random sequence of ethylene and butylene units and that it is *not* a block copolymer as might be suggested by this simplified representation.

The aim of the work in this chapter is the preparation of low polidispersity block copolymers of predetermined molar mass, containing both a polyolefin block and a poly(styrene-*co*-maleic anhydride) block. This type of polymer may prove useful as blend compatibilizer or as adhesion promoter for polyolefin coatings on more polar substrates like metals.[30,31]

## 4.2. Results and Discussion

### 4.2.1. The Macromolecular RAFT Agent

The polyolefin block was introduced into the polymerization in the form of a macromolecular transfer agent. This was achieved by the modification of Kraton L-1203, a commercially available copolymer of ethylene and butylene (PEB) containing one hydroxyl end group and having a low polydispersity (≈1.04). The hydroxyl group was esterified with an acid-functional dithioester (Scheme 4.1) to yield a polyolefin-based RAFT agent (**4**). Addition of this RAFT agent to a radical polymerization allows the PEB chain to be activated (reversibly), upon which it can incorporate monomer units and form a block copolymer. This course

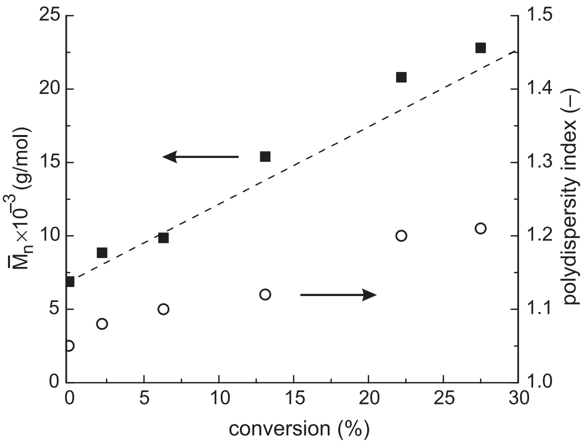


**Figure 4.1.** Experimentally determined number average molar mass (■, *left axis*) compared with theoretically expected values (---, *left axis*) and polydispersity indices (○, *right axis*) for several samples taken from experiment 2.

of reaction is studied first in several styrene polymerizations to develop and facilitate the analyses of the more complex anhydride containing block copolymers that will be prepared later (section 4.2.4).

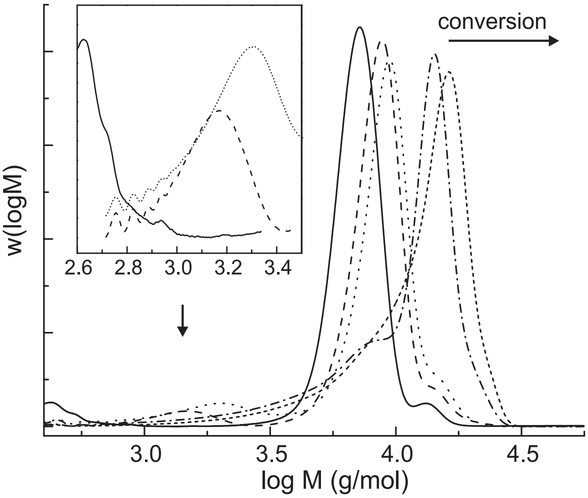
## 4.2.2. Styrene Polymerizations

The polymerizations involving styrene and the macromolecular RAFT agent (**4**) (Table 4.1, page 99; experiments 1 and 2) allowed verification of the living character of the polymerization and confirmed that the polystyrene is indeed attached to the PEB chain. The number average molar mass is plotted against conversion in Figure 4.1. A linear relationship is found that corresponds closely to the theoretical values, which can be obtained using formula 4-1.

$$\overline{M}_{n,\,th} = \overline{M}_{n,\,raft} + \frac{FW_M \cdot x \cdot [M]_0}{[RAFT]_0} \tag{4-1}$$

where $[M]_0$ and $[RAFT]_0$ are the starting concentrations of the monomer and the RAFT agent, respectively. $x$ is the fractional conversion and $FW_M$ is the molar mass of the monomer. $\overline{M}_{n,\,raft}$ is the number average molar mass of the RAFT agent as determined by GPC (in this case $6.5 \cdot 10^3 \mathrm{g \cdot mol^{-1}}$). All molar masses are in polystyrene equivalents, as correction for the difference in hydrodynamic volume is inherently difficult when dealing with block copolymers of gradually changing composition. The molar mass distributions of samples taken at different conversions (Figure 4.2) clearly show the growth of the PS-*block*-PEB chains. In addition to these block copolymer chains, a small number of chains exist being derived from

**Figure 4.2.** Normalized logarithmic molar mass distributions of samples taken from experiment 2. A gradually growing block copolymer can be observed while the inset shows the development of PS homopolymer (derived from initiator radicals) in the low molar mass region.



the azo initiator, rather than from the polymeric RAFT agent. These chains do not contain a PEB chain and are clearly visible in the first three samples as low molar mass polystyrene homopolymer (inset Figure 4.2). During the later stages of polymerization these homopolymer chains are no longer separated from the main peak, but remain visible as a low molar mass tail. All molar mass distributions have a shoulder at the high molar mass side, which is due to bimolecular termination. In this case, the block copolymer radicals recombine to form triblock copolymers, the middle block being polystyrene (reaction **b**, Scheme 4.2).

Both the high molar mass shoulder and the low molar mass homopolymer broaden the molar mass distribution and reduce the living character and the purity of the block copolymer. Although the effect on the polydispersity is not dramatic (table 4.1 & Figure 4.1), it should be noted that narrower molar mass distributions can be obtained with a careful choice of reaction conditions. Lowering the initiator concentration will reduce the amount of termination events relative to propagation. In addition, a reduction of the termination-derived shoulder will also eliminate most of the low molar mass tail of PS homopolymer. However, the trade-off in this case is a reduction of the polymerization rate as discussed in Chapter 2.

HPLC analyses of the same samples, using a triple detection setup, confirmed the GPC observations. This analysis allows the various components of the polymerizing system to be traced separately. The evaporative light scattering (ELSD) detector detects all polymeric compounds, while the diode array UV detector selectively observes the dithiobenzoate moiety at a wavelength of 320 nm and detects both the dithiobenzoate group and polystyrene at 254 nm.

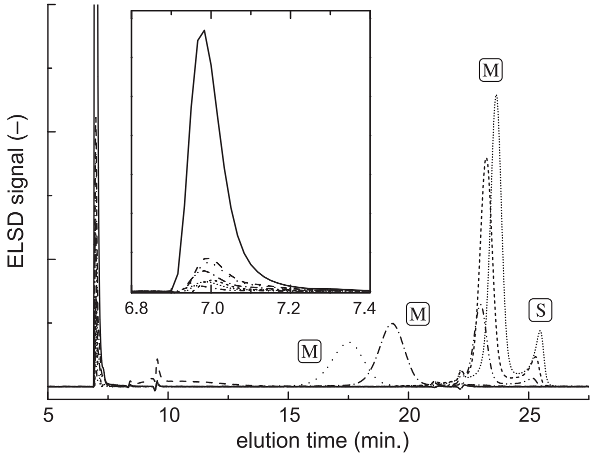


**Figure 4.3.** HPLC chromatograms of samples taken from experiment 2. The signal of the RAFT agent eluting at 7 min quickly disappears. The main peak (M) is the growing block copolymer. While the second peak (S) at higher elution volumes is expected to be the polystyrene homopolymer.

The signal of the macromolecular transfer agent, eluting at 7 minutes (Figure 4.3) diminishes rapidly during the initial phase of the polymerization. Although it disappears completely in the UV detection, a small ELSD signal, corresponding to a few percent of the starting material remains visible during the entire polymerization (The ELSD signal does not scale linearly with the amount of material.[32,33] This treatment indicates the *approximate* level of remaining material.). The signal is caused by unmodified PEB that is not coupled to the UV absorbing dithioester. This can be attributed to the fact that the starting material does not consist of purely monofunctional material. HPLC analyses of the original material (not shown) revealed that 2–3 % of the chains is unfuctionalized. During these analyses no other irregularities (*e.g.* multifunctional material) were found. The disappearance of the corresponding UV signal indicates that the transformation of the RAFT agent into growing block copolymers is quantitative and rapid on the polymerization timescale. The main peak (**M**) which corresponds to the growing PS-*block*-PEB copolymer shifts towards longer elution times as the PS block increases in size. This peak precedes a secondary peak (**S**) that corresponds to the PS homopolymer material.

Figure 4.4 shows the ratio of the UV signal ($\lambda$=320nm) over the ELSD signal for both the main peak and the secondary peak. An increase in chain length is confirmed by the decrease in the end-group sensitive UV signal at 320nm relative to the two other signals. Furthermore, the signal ratio for the secondary peak is consistently higher, indicating the lower molar mass for the PS homopolymer. Again, no calibration was performed for the ELSD detector response to these materials, but the trends can be unmistakably observed.

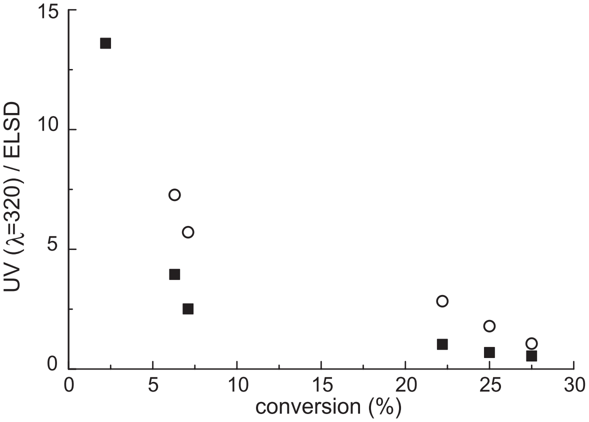


**Figure 4.4.** Evolution of the ratio of the end-group sensitive UV signal at a wavelength of 320nm and the ELSD signal for both the block copolymer (■) and the homopolymer (**O**).

The final product combined properties not found in the individual homopolymers that constitute the blocks. Upon precipitation in methanol a pink colored solid was isolated, whereas low molar mass ethylene–butylene copolymers have a sticky viscous liquid appearance. The polymer was fully soluble in heptane in contrast to polystyrene homopolymer of similar molar mass.

### 4.2.3. UV Irradiation

Low conversion samples of experiment 2, essentially block copolymers with a short PS block-length were dissolved in heptane and subjected to UV broadband irradiation for 5 hours. A part of the resulting product was passed through a short silica column using a mixture of heptane and dichloromethane (9:1) as the eluent. Both the crude product and the purified material were analyzed using GPC and their molar mass distributions were compared with those of the sample before irradiation. Although the UV irradiated product still had the same red color as the polymer before irradiation, the compound responsible for this color was no longer attached to the polymer chain. The polymer collected after passing through the column was colorless and the red color from the product had turned into a brown component with a very low $R_f$ value. This color change is also observed when *e.g.* dithiobenzoic acid and its dimer, bis(thiobenzyl)disulfide, come into contact with silica and the brown color corresponds to that of dithiobenzoate salts. This led us to conclude that the dithioester group has been cleaved from the polymer chain and transformed into a more labile species. Examination of the molar mass distributions indicates that some of the material has been transformed into higher molar mass species of precisely twice and three times the original molar mass (as clearly visible in the second derivative in Figure 4.5). This is expected to be attributed to the reactions

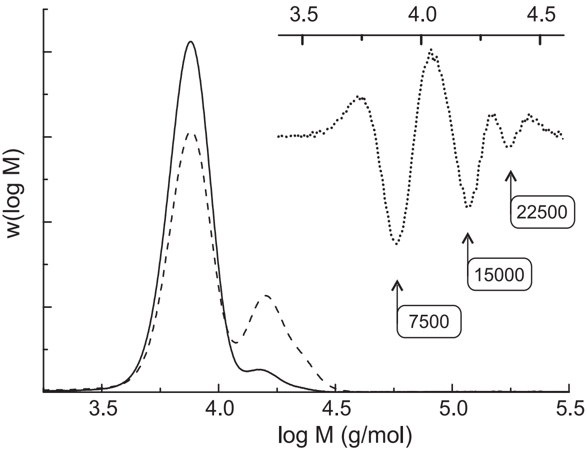
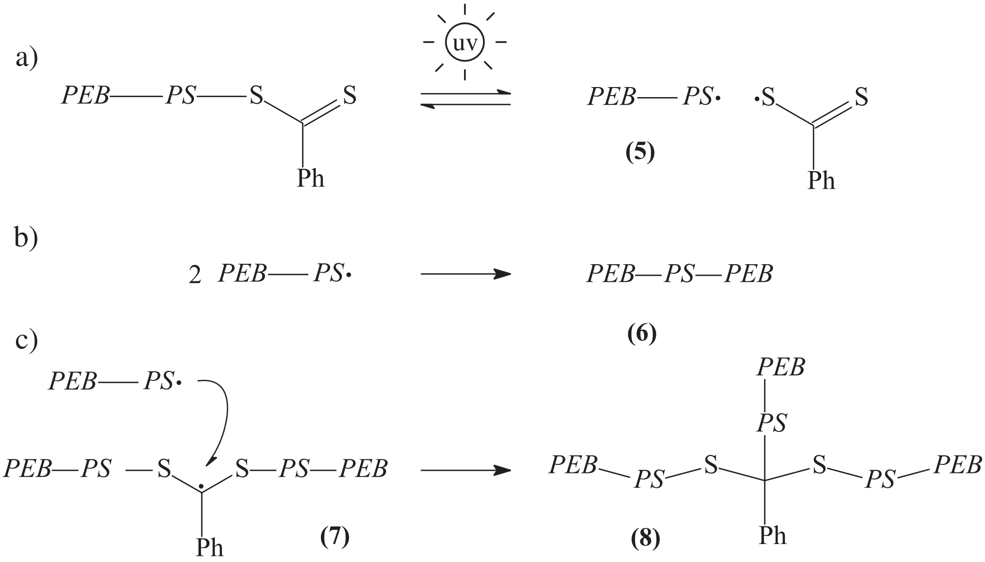


**Figure 4.5.** Normalized molar mass distributions of PEB-*block*-PS copolymers before (—) and after (- - -) UV irradiation. The second derivative of the distribution (····, *inset*) clearly shows the signal at twice and three times the original mass.

depicted in Scheme 4.2, which would mean that part of the diblock copolymer has been transformed into triblock material **(6)** free of the labile dithiogroup. The triple molar mass shoulder can be explained by combination of a block copolymer radical **(5)** with intermediate species **(7)** to yield a star shaped block copolymer with three arms **(8)**. Both termination reactions (**b** & **c**) take place during a common RAFT polymerization process as well. The occurrence of the additional termination reaction (**c**) forms the first experimental evidence for the postulate in section 2.3, explaining the retardation that is usually observed in RAFT homopolymerizations. Whereas this material will be difficult to detect under normal polymerization circumstances due to the minor fraction in which it is present combined with its relatively broad molar mass distribution (see section 2.3, page 43), the conditions in this experiment were such that the formation of the presumably star-shaped species yielded a material of a unique molar mass which could be identified by GPC analysis.

Although the colored dithiobenzoate group could be removed from the product by passing it over a short silica column, this process did not change the molar mass distribution. The process not only shows the facile removal of the labile colored end group, but also reveals the relative ease with which radicals are generated using UV irradiation. Such generation of radicals in a (post-)application phase forms an interesting potential for *e.g.* crosslinking reactions. In this respect one will have to solve the destination of the cleaved sulfur-containing moiety.



**Scheme 4.2.** Proposed reaction scheme. **a**) Under the influence of UV light the polymer dissociates and forms a dithiobenzoate radical and a block copolymer radical (**5**). **b**) The polymer radicals can recombine to form triblock copolymers (**6**) or react with intact polymeric RAFT agent to form a intermediate radical (**7**) which can be terminated by a second block copolymer radical (**5**) to form a three-armed star (**8**).

### 4.2.4. Styrene – Maleic Anhydride Copolymerizations

The free-radical copolymerization of styrene and maleic anhydride exhibits some interesting features. Maleic anhydride itself does not homopolymerize and its copolymerization with styrene has a strong tendency towards alternation, indicated by the reported reactivity ratios.[30] Convincing evidence was published a few years ago indicating that the STY/MAh copolymerization obeys the penultimate unit model.[34] On the basis of the copolymerization parameters it can easily be estimated that the vast majority of propagating radicals carries a terminal styrene unit. As the reaction between styrene-ended radicals and the RAFT agent proceeds rapidly, also the copolymerization of styrene with MAh is expected to proceed in a controlled fashion.

As can be seen in table 4.1 (experiments 3 to 5, page 99), three STY/MAh copolymerizations were carried out under similar conditions, but different with respect to the RAFT agent that was employed and the monomer concentrations used. The blank experiment without RAFT agent (experiment 3) became turbid after a few percent conversion. The heterogeneity was caused by precipitation due

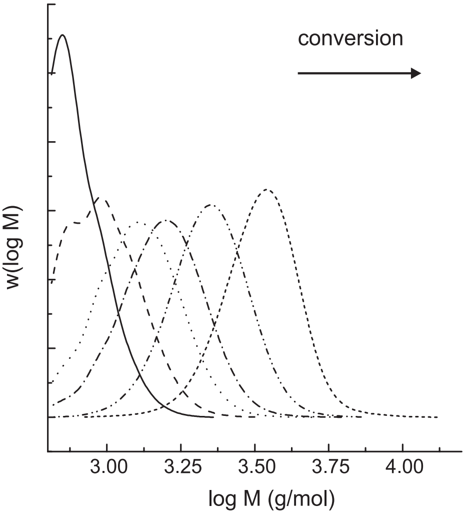


**Figure 4.6.** Normalized logarithmic molar mass distributions for samples taken during experiment 4, the controlled copolymerization of STY and MAh.

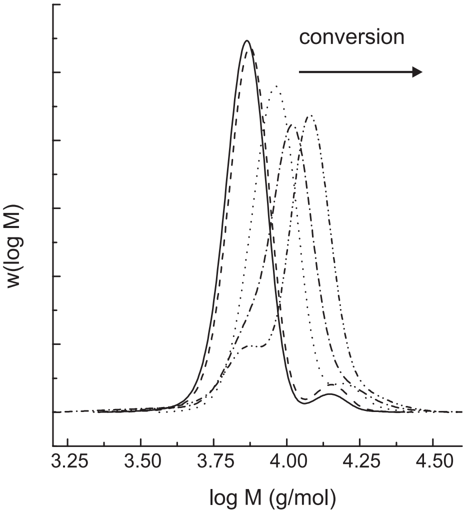


**Figure 4.7.** Normalized logarithmic molar mass distributions for samples taken during experiment 5, growing a STY/MAh block onto the PEB chain.

to the poor solvent properties of butyl acetate for high molar mass STY/MAh copolymer. The molar mass of the resulting polymer exceeded the exclusion limit of the applied columns ($M > 2 \cdot 10^6 g \cdot mol^{-1}$).

The experiment with RAFT agent **1** (experiment 4) remained homogeneous during the entire polymerization and GPC analysis of samples that were periodically drawn from the reaction mixture revealed a controlled growth (Figure 4.6). Due to the nonvolatile character of the MAh monomer, gravimetric conversion measurements are rather inaccurate but the molar mass of the final sample ($\overline{M}_n = 4.1 \cdot 10^3 g \cdot mol^{-1}$) is close to the expected theoretical value of $4.4 \cdot 10^3 g \cdot mol^{-1}$, obtained from equation 4-1. The polydispersity of the final product is 1.06.

Application of the macromolecular RAFT agent (**4**, experiment 5) allowed the preparation of low polydispersity poly[(ethylene-*co*-butylene)-*block*-(styrene-*co*-maleic anhydride)] polymers. Although the reaction mixture is heterogeneous at room temperature, it forms a clear, single-phase solution at the reaction temperature of 60°C. The first few samples at low conversion, phase separate when cooled to room temperature into a red PEB-rich phase and a colorless monomer rich phase. As conversion increases the STY/MAh block grows and solubilizes the PEB block to form a homogeneous solution at room temperature.

**Table 4.1: Experimental Details of the RAFT Polymerizations**

| Exp. | Styrene concentration (mol·dm$^{-3}$) | MAh concentration (mol·dm$^{-3}$) | RAFT Agent [conc. ×10$^2$ (mol·dm$^{-3}$)] | Solvent | $\overline{M}_n \times 10^{-3}$ (g·mol$^{-1}$) | $\overline{M}_w/\overline{M}_n$ | Conversion (%) | Theoretical $\overline{M}_n$ [a] ×10$^{-3}$ (g·mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.0 | — | **4** [1.0] | Xylene | 10 | 1.18 | 21 | 10 |
| 2 | 4.8 | — | **4** [1.0] | Xylene | 23 | 1.20 | 28 | 20 |
| 3 | 1.0 | 1.0 | None | BuAc | >2000 | — [b] | — [b] | — [b] |
| 4 | 1.0 | 1.0 | **1** [2.6] | BuAc | 4.1 | 1.06 | 57 | 4.4 |
| 5 | 0.50 | 0.50 | **4** [1.3] | BuAc | 11 | 1.12 | 62 | 12 |

a) calculated from formula 4-1.
b) polymerization turned heterogeneous at low conversion.

Low conversion samples exhibited a bimodal molar mass distribution (Figure 4.7). The first and large peak is the starting polyolefin-based RAFT agent (**4**), and the second is the block copolymer, which is of somewhat higher molar mass. The usual explanation for this type of behavior is a low transfer constant to the RAFT agent. It seems unlikely in this case, as this behavior was not observed in experiment 4 with RAFT agent (**1**), since the electronic structure close to the reactive dithioester moiety of both RAFT agents is similar. A second reason to discount this explanation is the gradual growth of the remaining PEB somewhat later in the polymerization. This would be highly unlikely, for if the rate of the transfer reaction could not compete with the fast propagation, the polydispersity should increase further. It is therefore assumed that local inhomogeneities in the reaction mixture – aggregation of PEB molecules – cause propagating radicals to grow in a microenvironment that has a considerably lower concentration of dithioester groups than expected based on macroscopic calculations. As conversion increases, the production of more block copolymer acts as compatibilizer and makes the reaction mixture more homogeneous. The low molar mass found at higher conversion is presumably the starting polyolefin RAFT agent, suggesting that some of the transfer agent was not consumed.

The final product, a pink powder, has a molar mass close to the predicted value of $1.1 \cdot 10^4$ g·mol$^{-1}$ and a polydispersity index of 1.12; only marginally increased from the starting value of the Kraton polymer (1.04).

## 4.3. Conclusions

It has been demonstrated that well-defined and low polydispersity polyolefin block copolymers can be prepared using a macromolecular RAFT agent. In addition to this it has been shown that the copolymerization of styrene and maleic anhydride can be performed under living conditions, something considered imposible until now. The combination of both achievements allowed the preparation of poly[(ethylene-*co*-butylene)-*block*-(styrene-*co*-maleic anhydride)], a polymer that is expected to be useful in coating applications. Furthermore, it was found that the highly colored and labile dithiobenzoate group could be removed from the polymer chain by UV irradiation facilitating a more extended range of polymer architectures, and perhaps future practical applications such as post grafting or crosslinking. Besides, experimental evidence was obtained of intermediate radical termination in support of the postulate describing retardation in section 2.3.

## 4.4. Experimental

**General:** The synthesis of 2-cyanoprop-2-yl dithiobenzoate (**1**) and 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (**2**) are described in sections 3.4.4 (page 80) and 3.4.5 (page 82), respectively. The experimental conditions of the coupling of the latter to Kraton L-1203 (PEB, **3**), forming macromolecular transfer agent (**4**) are outlined in section 3.4.6 on page 83.

**Polymerizations:** The RAFT agent, monomer and solvent were added together with initiator (AIBN) in a 100 ml three-necked round bottom flask equipped with a magnetic stirrer. Copolymerizations contained an equal molar ratio of styrene and maleic anhydride. The initiator concentration was always one fifth of the RAFT agent concentration. The mixture was degassed using three freeze-evacuate-thaw cycles and polymerized under argon at 60 °C. Periodically samples were taken for analysis.

**GPC analyses:** GPC analyses of the styrene polymerizations were performed on a Waters system equipped with two PLgel Mixed-C columns, a UV and an RI detector. The analyses of the STY/MAh copolymers were carried out on a HP1090M1 with both UV-DAD and Viscotec RI/DV200 detectors. All molar masses reported in this chapter are polystyrene equivalents, except where stated otherwise.

**HPLC analyses:** The HPLC analyses were performed using an Alliance Waters 2690 Separation Module. Detection was done using a PL-EMD 960 ELSD detector (Polymer Laboratories) and using a 2487 Waters dual UV detector at wavelengths of 254 and 320nm. All samples were analyzed by injecting 10µl of a dichloromethane (DCM) solution of the dried polymer with a concentration of 5mg/ml. Columns were thermostated at 35°C. The PEB-*block*-PS copolymers were analyzed on a NovaPak® Silica column (Waters, 3.9×150mm) using a gradient going from pure heptane to pure THF in 50min. The system was step by step reset to initial conditions via MeOH, THF and then DCM, after which the column was re-equilibrated in 30 minutes with heptane. PEB-*block*-PS/MAh and PS/MAh copolymers were analyzed on a NovaPak® CN column (Waters, 3.9×150mm) by the application of the following gradient: (heptane:THF+5%v/v acetic acid:MeOH) (100:0:0) to (0:100:0) in 25 minutes, then to (0:0:100) from 25 to 35 minutes. After each run the system was stepwise reset to initial conditions via THF and then DCM, after which the column was re-equilibrated in 30 minutes with heptane. Data were acquired by Millennium 32 3.05 software.

**UV irradiation:** For UV irradiation of the concentrated block-copolymer solutions (in heptane), a broadband high pressure mercury lamp (Philips) was used with a maximum intensity at a wavelength of 360nm. The spectrum of the emitted light had a significant intensity as low as 290nm. These experiments were carried out at 25°C.

## 4.5. References

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