Controlled Radical Copolymerization of Styrene and Maleic Anhydride and the Synthesis of Novel Polyolefin-Based Block Copolymers by Reversible Addition–Fragmentation Chain-Transfer (RAFT) Polymerization

HANS DE BROUWER, MIKE A. J. SCHELLEKENS, BERT KLUMPERMAN, MICHAEL J. MONTEIRO, ANTON L. GERMAN

Department of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

Received 8 May 2000; accepted 10 July 2000

ABSTRACT: Reversible addition–fragmentation chain transfer (RAFT) was applied to the copolymerization of styrene and maleic anhydride. The product had a low polydispersity and a predetermined molar mass. Novel, well-defined polyolefin-based block copolymers were prepared with a macromolecular RAFT agent prepared from a commercially available polyolefin (Kraton L-1203). The second block consisted of either polystyrene or poly(styrene-co-maleic anhydride). Furthermore, the colored, labile di-thioester moiety in the product of the RAFT polymerizations could be removed from the polymer chain by UV irradiation.© 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 3596–3603, 2000

Keywords: controlled radical polymerization; RAFT; block copolymers; polyolefin; styrene; maleic anhydride; addition–fragmentation; degenerative transfer

INTRODUCTION

Several controlled radical polymerization techniques that have emerged in the past decade have put free-radical polymerization in a new perspective.1–6 The robustness of radical chemistry can now be combined with a more sophisticated design of the polymer chain architecture. Block copolymers are an example of such a class of materials for which careful tailoring of the block lengths and monomer composition yields materials with unique properties that are not solely of academic significance but are of commercial interest as well (e.g., surfactants, blend compatibilizers, surface modifiers, and pigment stabilizers).

The aim of this work is the preparation of block copolymers containing both a polyolefin block and a poly(styrene-co-maleic anhydride) block. This type of polymer may prove useful as a blend compatibilizer or as an adhesion promoter for polyolefin coatings on more polar substrates such as metals.7,8

Although controlled radical polymerizations are unable to polymerize olefins, several methods have been reported to overcome this problem in the preparation of polyolefins containing block and graft copolymers. It has been shown that an alkene functionalized with an alkoxyamine moiety could be copolymerized with propene to yield a polyolefin, which could be used as a macroinitiator in nitroxide-mediated polymerizations.9 An alternative approach is the transformation of a ready-made polyolefin into a suitable dormant species by organic procedures. This approach has been reported to be successful in atom transfer radical polymerization (ATRP).10–12

The application of the ATRP technique to reactive monomers, however, is not straightforward.
Some functional monomers cause problems because of their interaction with the applied copper complex. Block copolymers containing para-hydroxy styrene and methacrylic acid could be obtained exclusively in an indirect way with protecting groups (or the deprotonated form of the acid). All attempts to obtain a controlled copolymerization of styrene (STY) and maleic anhydride (MAH), both in the literature and in our own laboratory, have been fruitless.

Although the copolymerization of STY and MAH can proceed in a controlled fashion with nitroxide-mediated polymerization, it requires a specially designed alkoxamine to be used at high temperatures (120 °C).

Reversible addition–fragmentation chain-transfer (RAFT) polymerization appears to be the best choice for this type of work because it does not require more stringent polymerization conditions than conventional free-radical polymerization. In addition, its application allows the controlled polymerization of monomers containing a variety of functional groups. In this process, effective transitions between growing free-radical chains and dormant end-capped chains are ensured with an efficient degenerative transfer reaction to a dithioester moiety (Scheme 1). If the exchange reaction (Scheme 1(b)) is fast compared with propagation and the equilibrium of the transformation reaction (Scheme 1(a)) is shifted toward the right by an appropriate choice of the R group, the application of a dithioester compound will result in a pseudoliving system.

This work utilized a synthetically modified polyolefin RAFT agent (synthesized from Kraton L-1203; PEB) to prepare block copolymers in which the second block consists of either polystyrene (PS) or poly(styrene-co-maleic anhydride). Furthermore, the labile dithioester moiety (attached to the dormant chains) could be removed by UV photolysis. The prepared PEB–PS block copolymers were irradiated to produce triblock and unusual star-shaped polymers.

**EXPERIMENTAL**

**General**

Kraton L-1203 (PEB; 3) was obtained from Shell Chemicals (number-average molecular weight ≈ 3.8 · 10^3 Da; weight-average molecular weight/number-average molecular weight ≈ 1.04) and was dried under reduced pressure for several days before use. 4-Cyano-4-[(thiobenzoyl)sulfonyl]pentanoic acid (2) and 2-cyanoprop-2-yl dithiobenzoate (1) were prepared according to the literature. Anhydrous dichloromethane (DCM) was prepared by distillation over lithium aluminum hydride and was stored over molecular sieves. All other chemicals were obtained from Aldrich Chemical Co. and used without further purification.

**Synthesis of the Kraton Macromolecular Transfer Agent (4)**

Kraton L-1203 (29.5 g, 8 mmol), p-toluenesulfonic acid (0.30 g, 1.6 mmol), 4-(dimethylamino)pyridine (0.29 g, 2.4 mmol), and 1,3-dicyclohexylcar-
bodiimide (3.9 g, 19 mmol) were dissolved in anhydrous DCM in a 1-L, three-necked, round-bottom flask equipped with a magnetic stirrer. 4-Cyano-4-[(thiobenzoyl)sulfanyl]pentanoic acid (2.5 g, 9 mmol) was dissolved in anhydrous DCM and added dropwise to the reaction mixture at room temperature. Upon completion, the reaction mixture was heated to 30 °C and allowed to stir for 48 h. The mixture was then filtered and washed with water. The solution was dried with anhydrous magnesium sulfate and filtered, and DCM was removed under reduced pressure. The crude product was purified by column chromatography (silica; 9/1 hexane/ethyl acetate) to give a purplish-red, viscous liquid (29.4 g, 92% yield, based on Kraton; see Scheme 2). The 1H NMR spectrum indicated a quantitative yield based on the number of hydroxyl groups. The chemical shift of the set of protons in the Kraton situated next to the hydroxyl group changed from 3.6 to 4.2 ppm upon esterification.

**Polymerizations**

The RAFT agent, monomer, and solvent were added together with an initiator [2,2’-azobisobutyronitrile (AIBN)] in a 100-mL, three-necked, round-bottom flask equipped with a magnetic stirrer. Copolymerizations contained an equal molar ratio of STY and MAh. The initiator concentration was always one-fifth of the RAFT-agent concentration. The mixture was degassed with three freeze–evacuate–thaw cycles and polymerized under argon at 60 °C. Periodically, samples were taken for analysis.

**Gel Permeation Chromatography (GPC) Analyses**

GPC analyses of the STY polymerizations were performed on a Waters system equipped with two PL-gel mixed-C columns, a UV detector, and a refractive index (RI) detector. The analyses of the STY/MAh copolymers were carried out on an HP1090M1 with both UV-DAD and Visotec RI/DV 200 detectors. All molecular weights reported in this article are PS equivalents, unless otherwise stated.

**High Pressure Liquid Chromatography (HPLC) Analyses**

The HPLC analyses were performed with an Alliance Waters 2690 separation module. Detection was done with a PL-EMD 960 evaporative light scattering detector (ELSD) detector (Polymer Laboratories) and with a 2487 Waters dual UV detector at wavelengths of 254 and 320 nm. All samples were analyzed by the injection of 10 μL of a DCM solution of the dried polymer with a concentration of 5 mg/mL. Columns were thermostated at 35 °C. The PEB-block-PS copolymers were analyzed on a NovaPak® silica column (Waters; 3.9 × 150 mm) with a gradient going from pure heptane to pure tetrahydrofuran (THF) in 50 min. The system was stepwise reset to initial conditions via MeOH, THF, and then DCM, after which the column was re-equilibrated in 30 min with heptane. PEB-block-PS/MAh and PS/MAh copolymers were analyzed on a NovaPak® CN column (Waters; 3.9 × 150 mm) by the application of the following gradient (heptane/THF + 5% v/v acetic acid/MeOH): 100/0/0 to 0/100/0 in 25 min and then 0/0/100 from 25 to 35 min. 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 min with heptane. Data were acquired by Millennium 32 3.05 software.
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 360 nm. The spectrum of the emitted light had a significant intensity as low as 290 nm. These experiments were carried out at 25 °C.

RESULTS AND DISCUSSION

The polyolefin block was introduced in 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. The hydroxyl group was esterified with an acid-functional dithioester (Scheme 2) to yield a polyolefinic RAFT agent (4).

The addition of this RAFT agent to a radical polymerization allows the PEB chain to be activated (reversibly), after which it can incorporate monomer units to form a block copolymer. This course of reaction was first studied in several STY polymerizations to aid and facilitate the analyses of the more complex blocks prepared.

STY Polymerizations

The polymerizations involving STY and the macromolecular RAFT agent (4; Table I, experiments 1 and 2) allowed verification of the living character of the polymerization and confirmed that the PS is attached to the PEB chain. The number-average molar mass is plotted against conversion in Figure 1. A linear relationship was found that corresponds closely to the theoretical values, which can be obtained with the following formula:

\[ \tilde{M}_n = M_{n,\text{raft}} + \frac{[m]_0 \cdot M_0 \cdot x}{[\text{RAFT}]_0} \]  

where \([m]_0\) and \([\text{RAFT}]_0\) are the starting concentrations of the monomer and the RAFT agent, \(x\) is the fractional conversion, and \(M_0\) is the molar mass of the monomer. \(M_{n,\text{raft}}\) is the number-average molar mass of the RAFT agent as determined by GPC (in this case, 6.5 \(\times\) 10^3 Da). All molar masses are in PS equivalents, as the correction for the difference in hydrodynamic volume is inherently difficult with block copolymers of gradually changing compositions. The molar mass distributions of samples at different conversions (Fig. 2) clearly show the growth of the PS-block-PEB chains. Besides the growth of these chains derived from the RAFT agent, a small number of chains exist that originate from initiation by the azo initiator. These chains do not contain a PEB chain and are clearly visible in the first three samples as low molecular weight PS homopolymer (inset of Fig. 2). During the later stages of polymerization, these homopolymer...
chains are no longer separated from the main peak but remain visible as a low molecular weight tail. All of the molecular weight distributions have a shoulder at the high molar mass side that is due to bimolecular termination. In this case, the block copolymer radicals recombine to form triblock copolymers, the middle block being PS.

Both the high molar mass shoulder and the low molar mass homopolymer broaden the molar mass distribution and reduce the living character and purity of the block copolymer. Although the effect on the polydispersity is not dramatic (Table I and Fig. 1), 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 tradeoff in this case is a reduction in the polymerization rate.

HPLC analyses of the same samples, with a triple detection setup, confirmed the GPC observations. This allows the various components of the polymerizing system to be followed separately. The ELSD detects all polymeric compounds, whereas the UV detector selectively observes the dithiobenzoate moiety at a wavelength of 320 nm and detects both the dithiobenzoate group and PS at 254 nm. The signal of the macromolecular transfer agent, eluting at 7 min (Fig. 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. This signal is caused by unmodified PEB that is not coupled to the UV-absorbing di-thioester. This can be attributed to the fact that the starting material does not consist of purely monofunctional material. HPLC analyses of the original material revealed that 2–3% of the chains is unfunctionalized. During these analyses, no other irregularities (e.g., multifunctional materials) were found. The disappearance of the corresponding UV signals indicates that the transformation of the RAFT agent into growing block copolymers is both rapid and quantitative. The main peak that corresponds to the growing PS-block-PEB block copolymer shifts toward longer elution times as the PS block becomes longer. This peak is followed by a secondary peak that corresponds to the PS homopolymer material.

Figure 4 shows the ratio of the UV signal at 320 nm over the ELSD signal for both the main peak and the secondary peak. An increase in...
chain length is confirmed by the decrease of the end-group-sensitive UV signal at 320 nm 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.

The final product was precipitated in methanol to yield a pink solid. This indicates the formation of block copolymers because the starting material was originally a viscous liquid. The polymer was, however, fully soluble in heptane, in contrast to PS homopolymer of similar molar mass.

**UV Irradiation**

Low-conversion samples of experiment 2, essentially block copolymers with a small PS block length, were dissolved in heptane and subjected to UV irradiation for 5 h. A part of the resulting product was passed through a short silica column with 9/1 heptane/DCM as an eluent. Both the crude product and the columned material were analyzed with GPC, and their molar mass distributions were compared with those of the samples 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 columnning was colorless, and the red color from the product had turned into a brown component with a very low retention factor ($R_f$). This color change is also observed when, for example, dithiobenzoic acid or its dimer, bis(thiobenzyl)disulfide, comes 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. An examination of the molar mass distributions indicates that some of the material has been transformed to higher molecular weight species of precisely twice and three times the original molar mass (as clearly shown in the second derivative in Fig. 5). We expect this to be attributed to the reactions depicted in Scheme 3, which would mean that the diblock copolymer has been transformed into triblock material (6) free of the labile dithiogroup. The triple molar mass shoulder may be explained by the 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 (c and d) take place during the RAFT polymerization process as well. The occurrence of the additional termination reaction (d) is a possible explanation for the retardation that is usually observed in RAFT homopolymerizations. This will be elucidated further in a future publication.

Although columnning of the product removed the colored dithiobenzoate group, it did not change the molar mass distribution. The nature of the end groups after irradiation is currently under investigation.

**STY/MAh Copolymerization**

The copolymerization of STY with MAh copolymers exhibits some interesting features. MAh itself does not homopolymerize, and its copolymerization with STY has a strong tendency toward alternation, indicated by the reported reactivity ratios. Convincing evidence was published a few years ago indicating that the STY/MAh copolymerization obeys the penultimate unit model. On the basis of the copolymerization parameters, it can easily be estimated that the vast majority of propagating radicals carry a terminal STY unit. For this reason, the copolymerization of STY with MAh was expected to proceed in a controlled fashion similar to the STY homopolymerization.

As can be seen in Table I (experiments 3–5), three STY/MAh copolymerizations were carried out under similar conditions but were different with respect to the RAFT agent that was employed and the monomer concentrations used. The blank experiment without the RAFT agent became turbid after a conversion of a few percent.
The heterogeneity was caused by precipitation due 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 ($M > 2 \cdot 10^6$ Da).

The experiment with the RAFT agent (1; experiment 4) remained homogeneous during the entire polymerization, and a GPC analysis of samples that were periodically drawn from the reaction mixture revealed a controlled growth (Fig. 6). Because of the nonvolatile character of the MAh monomer, gravimetric conversion measurements are rather inaccurate, but the molar mass of the final sample (number-average molecular weight $= 4.1 \cdot 10^3$ Da) is close to the expected theoretical value of $4.4 \cdot 10^3$ Da obtained from eq 1. The polydispersity of the final product is 1.06.

The 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.

Low-conversion samples exhibited a bimodal molar mass distribution (Fig. 7). The first and

**Scheme 3.** Proposed reaction scheme. Under the influence of UV light, the polymer dissociates and forms a dithiobenzoate radical and a block copolymer radical. The polymer radicals can recombine to form triblock copolymers or react with intact polymeric RAFT species to form an intermediate radical that can be terminated by a second block copolymer radical.

**Figure 6.** Normalized logarithmic molar mass distributions for samples taken during experiment 4, the controlled copolymerization of STY and MAh.

**Figure 7.** Normalized logarithmic molar mass distributions for samples taken during experiment 5, the growth of an STY/MAh block onto the PEB chain.
large peak is the starting polyolefin RAFT agent, and the second is the block copolymer, which is off a very high molecular weight. 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 the RAFT agent (1), because for both RAFT agents the electronic structure close to the reactive dithioester moiety are 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 if a RAFT agent with a low transfer constant was used. It is, therefore, assumed that local inhomogeneities in the reaction mixture, the aggregation of PEB molecules, cause propagating radicals to grow in a microenvironment that has a considerably lower concentration of dithioester groups than expected on the basis of macroscopic calculations. As conversion increases, the production of more block copolymer makes the reaction mixture more homogeneous, so the local environment becomes similar to the global environment. The low molar mass found at a higher conversion is presumably the starting polyolefin RAFT agent, suggesting that some of the transfer agent is not consumed.

The final product, a pink powder, has a molar mass close to the predicted value of 1.1 \( \cdot 10^4 \) Da and a polydispersity of 1.12. Its material properties and applicability as an adhesion-promoting additive are currently under investigation and form the basis of a future publication.

CONCLUSIONS

It has been demonstrated that well-defined and low-polydispersity polyolefin block copolymers can be prepared with a macromolecular RAFT agent. In addition, the copolymerization of STY and MAh can be performed under living conditions, something that has proven to be very difficult 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 prove useful in coating applications. Furthermore, the highly colored and labile dithiobenzoate group could be removed from the polymer chain by UV irradiation facilitating a greater range of polymer architectures and perhaps future practical applications such as postgrafting or crosslinking.

The authors thank the Foundation for Emulsion Polymerization (SEP) for funding and Shell Chemicals for providing the Kraton L-1203. They are very grateful to Mr. Meijerink and Mrs. Frijns-Bruls from DSM Research, Geleen, The Netherlands for their GPC analyses of the STY/MAh copolymers.

REFERENCES AND NOTES