Synthesis of Segmented (PB(PS-*block*-PB)$_n$) and (PB(SAN-*block*-PB)$_n$) Block Copolymers via Polymeric Thermal Iniferters

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ABSTRACT: A technique is described for the synthesis of segmented poly(butadiene-*block*-styrene) block copolymers and segmented poly(butadiene-*block*-(styrene-*co*-acrylonitrile)) block copolymers through polybutadiene-based thermal iniferters. Dihydroxy- and dicarboxy-terminated polybutadienes were transformed into secondary amine-terminated compounds, which were subsequently reacted with CS_2 and iodine to obtain the corresponding polymeric iniferters containing approximately three polybutadiene units. By using these as an initiator for the thermal polymerization of styrene, multiblock copolymers of polybutadiene and polystyrene could be prepared. In the same way multiblock copolymers of polybutadiene and poly(styrene-*co*-acrylonitrile) could be prepared by thermal copolymerization of styrene and acrylonitrile, using the polymeric iniferter as an initiator. By varying polymerization time and iniferter concentration, the composition and vinyl sequence length of the segmented block copolymers could be regulated. The polymeric iniferters and block copolymers were characterized by GPC, elemental analysis, TGA, ^{1}H NMR, DMTA, and transmission electron microscopy.

Introduction

In the past decades, a lot of research has been done on the synthesis of block copolymers for use as compatibilizing agents for immiscible blends of different homopolymers. So far, it is still not totally understood what architecture a copolymer should have to ensure optimal compatibilization. Gradually, results are becoming available indicating that copolymers with a more complex architecture, like random copolymers,[6] graft copolymers,[7] or tapered diblock copolymers,[5] can be more effective compatibilizers than simple diblock copolymers. Also, low molecular weight (hydrogenated) (PB(PS-*block*-PB)$_n$) triblock copolymers turned out to be more effective in compatibilizing PE/PS or PP/PS blends than low or high molecular weight diblock copolymers.[5] Theoretically,[8] on the other hand, diblock copolymers are predicted to be the most effective compatibilizers. This unsettled situation prompted us to synthesize block copolymers of various architectures and subsequently investigate their compatibilizing properties.

Segmented (PB(PS-*block*-PB)$_n$) Block Copolymers. Block copolymers of polybutadiene (PB) and polystyrene (PS) have drawn considerable interest in view of their microstructure and structure–property relationships.[1,2] Furthermore, they are applied for compatibilization of polyethylene/polystyrene (PE/PS) blends[3,4] (after hydrogenation of the polybutadiene blocks) and polypropylene/polystyrene (PP/PS) blends.[5] In the present paper the synthesis of segmented (PB(PS-*block*-PB)$_n$) block copolymers through polybutadiene-based thermal iniferters will be discussed.

In most cases, block copolymers of polybutadiene and polystyrene are prepared by anionic techniques. These processes have several disadvantages in the sense that rigorous polymerization conditions are needed like ultrapure monomers, absolute moisture/oxygen-free atmosphere, and cryogenic temperatures, which are often difficult to realize on an industrial scale. Furthermore, it is relatively difficult to prepare multiblock copolymers anionically.

Hence, we present a free radical method for the synthesis of segmented (PB(PS-*block*-PB)$_n$) block copolymers by use of an iniferter technique. The term "iniferter" was given to certain free radical initiators with simultaneous chain transfer and polymer radical termination properties by way of a primary radical. The term was coined by Otsu,[9,10] who found tetraalkylthiuram disulfides to exhibit these properties. He showed that when these initiators are used in thermal or photoinitiated polymerization, the polymer chains are end-capped with the iniferter fragments due to their triple function. Polymerization can be restarted by irradiating the dithiocarbamate-terminated polymer in the presence of a new monomer[11–13] whereby propagation proceeds by a "living" radical polymerization, forming a triblock copolymer. Recently, Turner[14,15] observed however that the counter radical is not really inactive but is also capable of initiation, leading to a mixture of block copolymer and homopolymer.

Another way to prepare tri- or multiblock copolymers was developed by Nair and Clouet.[16–19] They synthesized polymeric iniferters (leading to segmented block copolymers) and macroiniferters (leading to triblock copolymers), which were used to initiate polymerization of another monomer. We applied this method to prepare polymeric iniferters (PIn) based on polybutadiene by end-group reactions on dihydroxy- and dicarboxy-terminated polybutadienes. The synthesized polymeric iniferters were used to prepare segmented (PB(PS-*block*-PB)$_n$) block copolymers of various compositions by polymerization of styrene with the polybutadiene iniferters.

Segmented (PB(SAN-*block*-PB)$_n$) Block Copolymers. The used polymeric iniferter technique also allowed us to prepare block copolymers containing blocks which consist of a random copolymer (unlike anionic polymerization techniques). This is a new type of block copolymer which could provide a new class of compatibilizing agents. Previously, Otsu et al. described the synthesis of AB and ABA block copolymers contain-

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ing random and alternating copolymer sequences by the iniferter technique.[13]

In this paper we present the synthesis of block copolymers of polybutadiene (PB) and poly(styrene-*co*-acrylonitrile) (SAN) by copolymerization of styrene and acrylonitrile with the synthesized polybutadiene iniferter. SAN is known to be miscible with homopolymers like poly(methyl methacrylate),[20-23] polycarbonate,[24,25] poly(vinyl chloride), and poly(ϵ-caprolactone)[26] (within a certain composition range of the random copolymer). Therefore, block copolymers of (hydrogenated) polybutadiene and SAN could have great potential as (multifunctional) compatibilizers for polyolefins with the above mentioned polymers. So far, random copolymer blocks have only been incorporated in a copolymer by grafting them on a polymer chain. These graft copolymers have proved themselves to be efficient compatibilizing agents for many different incompatible polymer mixtures.[27]

Experimental Section

Materials. Styrene and acrylonitrile were purified by vacuum distillation from finely powdered CaH_2. Toluene was distilled from sodium/benzophenone before use. Phosphorus pentachloride, CS_2, I_2, triethylamine, hydroxy-terminated polybutadiene (Aldrich), and carboxy-terminated polybutadiene (Scientific Polymer Products, Inc.) were used as received. Piperazine was recrystallized twice from ethanol.

Synthesis of a Polymeric Iniferter Based on Dihydroxypolybutadiene (M_n = 3300). Dihydroxy-terminated polybutadiene (PB) (25.3 g, 7.6 mmol) was dissolved in 250 mL of toluene and dried by azeotropic distillation. After cooling to room temperature, 3.35 g of PCl_5 (16.1 mmol) was added to the solution. The system was stirred overnight. Toluene was removed by evaporation in vacuum. The polymer was dissolved in chloroform and washed twice with water. The solution was dried on anhydrous $MgSO_4$. After filtration and evaporation of the solvent the polymer was dried in vacuum.

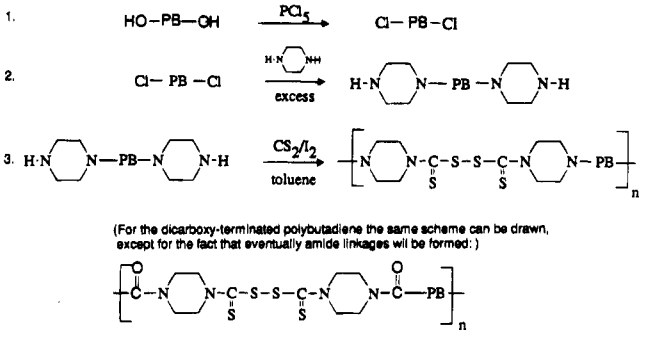
A 20 g quantity of the obtained chloro-terminated polybutadiene was dissolved in 50 mL of toluene under a N_2 atmosphere in a three-necked flask. After adding 5.04 g of piperazine (58.5 mmol) to the solution, the system was heated to reflux and kept reacting at that temperature overnight. The solution was cooled, filtered, and extracted with methanol. The polymer was dried in vacuum.

The amine-terminated PB (20.3 g, 5.9 mmol) was dissolved in 200 mL of toluene under a N_2 atmosphere. Triethylamine (1 mL, 7.2 mmol) and CS_2 (1 mL, 16.6 mmol) were added, followed by a solution of I_2 in toluene until iodine was no longer consumed. The mixture was filtered. The resulting polymer was precipitated twice into a large excess of methanol from toluene at room temperature. Characterizations were done by elemental analysis, ^{1}H NMR, differential scanning calorimetry, and GPC.

Synthesis of a Polymeric Iniferter Based on Dicarboxypolybutadiene (M_n = 10 200). The chlorination of the dicarboxy-terminated compound was carried out as described above. After chlorination the polymer was not purified but was allowed to react further with excess piperazine at −10 to −20 °C. The amine-terminated polybutadiene was precipitated in cooled methanol (−50 °C). The synthesis of the polymeric iniferter with CS_2 was carried out in the same manner as for the dihydroxy-terminated polybutadiene. Characterization was done by elemental analysis, ^{1}H NMR, differential scanning calorimetry, and GPC.

Synthesis of Segmented Block Copolymers. In a small ampule under a nitrogen atmosphere the required amount of polymeric iniferter was dissolved in toluene for (co)polymerizations in solution, or in the monomer for bulk (co)polymerizations. Styrene was added (or styrene and acrylonitrile for copolymerizations) and the ampule was placed in a thermostated oil bath. After the required polymerization time the mixture was precipitated directly into methanol. After a second precipitation from toluene into methanol the obtained block copolymers were filtered, washed with methanol, and dried in vacuum.

Scheme 1. Synthesis of a Polymeric Iniferter Based on a Dihydroxy- and Dicarboxy-Terminated Polybutadiene



Analyses. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer. Molecular weights of the polymers were determined by GPC with a refractive index detector using THF as eluent and PS standards for calibration. Dynamic mechanical thermal analyses were done using a Rheometrics RSA II analyzer at a frequency of 1 Hz. The scanning speed was 2 °C/min. TGA analyses were performed on a TGA7 thermogravimetric analyzer at a scanning speed of 10 °C/min.

Samples for transmission electron microscopy were first compression molded at 130 °C and subsequently annealed at 130 °C for 5 h under a nitrogen atmosphere, after which they were quenched in liquid nitrogen. Coupes of ~70 nm were cut of these samples using a microtome. Sections were picked up on copper grids and then stained in the vapor of an aqueous osmium tetroxide solution for approximately 3 h (this selectively stains the polybutadiene phase).

Results and Discussion

Synthesis and Characterization of Polybutadiene-Based PIn's. In this study two different polymeric iniferters (PIn) were synthesized from a dihydroxy-terminated polybutadiene (M_n = 3300, D = 1.90) and a dicarboxy-terminated polybutadiene (M_n = 10 200, D = 1.65). They were first transformed into dichloro-terminated polymers using phosphorus pentachloride (see Scheme 1). These were reacted with piperazine, providing secondary amine end groups. Finally, the polymeric iniferters were prepared by coupling the piperazine end groups with carbon disulfide, causing an increase in molecular weight.

The dihydroxy-terminated polybutadiene (a viscous liquid) used as starting materials has a very low molecular weight and T_g. Because of this it could not be easily purified by precipitation. Therefore the intermediate compounds could not be characterized to determine the efficiency of the first two reaction steps. Purification of the product after chlorination was performed by extraction of excess of PCl_5 and byproducts with water. After reaction with an excess of piperazine the polymer solution was washed with methanol.

For the dicarboxy-terminated polybutadiene no purification procedure was used after the first (chlorination) step because of the high reactivity of the acyl chloride-terminated product toward water or methanol. For this reason the chlorinated product could not be characterized in terms of chlorine content. The reaction step with piperazine was carried out at low temperatures (−10 to −20 °C) because of the high reactivity of acyl chlorides toward amines. Elemental analysis and GPC of the intermediate amine-terminated polymer indicated that some coupling between the PB chains had

Table 1. Characteristics of the Prepared Polymeric Iniferters

				elemental analysis of the PB iniferter			
				N (%)		S (%)	
prepolymer	M_n of prepol	M_n of PB iniferter	no. of PB blocks	calc[a]	found	calc[a]	found
$PB(OH)_2$	3 300	10 400	2.9	1.56	1.71	2.33	3.20
$PB\text{-}(COOH)_2$	10 200	26 500	2.5	0.53	0.70	0.73	0.90

[a] Based on the molecular weight of the iniferter, determined by GPC.

occurred during the reaction with piperazine. The amount of coupling was only on the order of a few percent (determined by GPC).

The secondary amine-terminated polybutadienes were then transformed into their thiuram disulfides by reaction with CS_2 and iodine (see Scheme 1). The resulting polymeric iniferters were precipitated in methanol.

The synthesized polymeric iniferters were characterized by elemental analysis, GPC, ^1H NMR, and dynamical mechanical thermal analysis. GPC showed no clear traces of nonreacted polybutadiene. However, this cannot be regarded as an evidence for the absence of nonreacted polybutadiene, because the peaks of the amino-terminated polybutadiene and the polymeric iniferter overlap partially. NMR could not provide information about end groups, because the piperazine hydrogen peaks overlapped with polybutadiene CH_2 peaks and had a too low intensity. FTIR showed no presence of −SH end groups, which could have been formed (in a small quantitity) from a side reaction during the thiocarbamylation step.

Table 1 shows the characteristics of the synthesized polymeric iniferters. The average number of PB blocks in the polymeric iniferter was calculated by dividing the molecular weight of the polymeric iniferter by that of the repeating unit (PB + iniferter group). PIn-3300 (polymeric iniferter from prepolymer with $M_n = 3300$) contains an average of 2.9 PB units per chain, while for PIn-10200 there are 2.5 PB units per chain. The slight discrepancy in the ratio of N and S content for the polymeric iniferters is probably caused by the above mentioned coupling of amine-terminated polymers. Furthermore, the chlorine content of both polymeric iniferters was checked to be sure that no polybutadiene double bond was chlorinated by formed HCl during the fist reaction step. In both polybutadiene iniferters no chlorine was detected.

In this work we used both synthesized polymeric iniferters as an initiator for the thermal polymerization of styrene. PIn-10200 was also used to initiate the copolymerization of styrene with acrylonitrile.

Synthesis and Characterization of Segmented (PB(PS-*block*-PB)$_n$) Block Copolymers. By using the two PB iniferters of different molecular weights as initiators for the free radical polymerization of styrene, segmented block copolymers with two different PB sequence lengths could be obtained. The polymerization of styrene, initiated by the polymeric iniferter, occurs via an insertion mechanism between the disulfide linkages in the prepared polybutadiene iniferter. The GPC traces of the prepolymer, PIn-10200 and a synthesized multiblock copolymer are shown in Figure 1. As in any "normal" free radical polymerization, the length of the styryl blocks is a function of iniferter concentration in the system. The styryl block length decreases with increasing iniferter concentration. So by varying the PB iniferter concentration in the system, block copolymers with different styryl block lengths could be synthesized. Another way to regulate the block

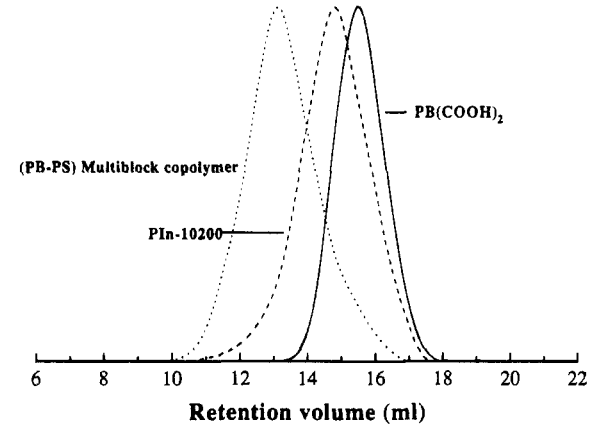


Figure 1. GPC traces of carboxy-terminated polybutadiene, the prepared polymeric iniferter PIn-10200, and a multiblock copolymer of polybutadiene and polystyrene prepared with PIn-10200.

copolymer composition is by varying the polymeriziation time at fixed PIn concentration in the system.

Characteristics of the polymerizations of styrene with PIn-3300 and PIn-10200 and the obtained segmented (PB(PS-*block*-PB)$_n$) block copolymers are given in Tables 2 and 3. Because of the limited solubility of the polybutadiene iniferters in the monomer, toluene was added as a solvent for high PIn containing systems. Table 2 shows that, although the polymerization time for the diluted systems is almost 7 times longer than for the bulk polymerizations, the monomer conversion is only slightly higher. This indicates that the dilution of the system has a detrimental effect on the conversion, because of a reduction in the rate of polymerization. This makes the polymerization system less appropriate for synthesis of segmented block copolymers of high butadiene content.

The average number of alternating blocks in the block copolymers was calculated as follows:

$$N_{PB} = M_n(\text{block copolymer})\, x_{PB}/M_n(\text{prepolymer}) \quad (1)$$

$$N_{PS} = N_{PB} - 1 \quad (2)$$

$$N_{alt} = N_{PB} + N_{PS} = 2N_{PB} - 1 \quad (3)$$

where x_{PB} represents the polybutadiene content of the block copolymer and N_{PB}, N_{PS}, and N_{alt} represent the average number of polybutadiene blocks, polystyrene blocks, and alternating blocks in the block copolymer, respectively. For relationship 2 we assumed that no −SH end groups are present in the polymeric iniferter, which is reasonable, because no −SH peak was detected with FTIR. So no active end groups are present and chain transfer only proceeds via the iniferter groups in the chain. In this way, there will always be polybutadiene blocks on both ends of every block copolymer chain and relationship 2 is valid, no matter what transfer reactions take place. Using eq 3, from the number of polybutadiene blocks in PIn-3300, block copolymers with

Table 2. Characteristics of Polymerization of Styrene with PIn-3300

[M]/[PIn]$_{eff}^{1/2}$ [a]	[PIn]$_{eff}$[a] (mmol/L of styrene)	vol % toluene[b]	T (pol) (°C)	t (pol) (h)	consumption of PIn (%)[c]	styrene conversion (%)[c]	10^{-4} M_n of block copolymer	av no. of alt blocks	styryl block length × 10^{-4}	wt % PS in copol[d]
100.6	7.5	0	80	18	66.4	10.5	3.9	4.2	1.9	77.7
64.4	18.5	0	80	18	46.8	8.1	1.4	2.4	1.2	61.0
46.1	36.0	0	80	18	15.2	5.2	2.0	4.8	0.9	61.3
139.4	3.3	20	80	119	82.1	19.6	15.4	7.4	4.4	91.0
18.5	37.3	500	80	115	61.6	15.7	2.3	5.5	0.5	53.2
16.0	50.1	500	80	115	86.6	9.8	1.6	5.6	0.3	31.7
13.5	38.0	1000	80	115	45.3	3.1	1.5	6.0	0.2	23.0

[a] Effective concentration of iniferter groups in PIn-3300. [b] Compared to monomer. [c] Calculated from copolymer composition and block copolymer yield. [d] Determined by ^{1}H NMR.

Table 3. Characteristics of Polymerization of Styrene with PIn-10200

[M]/[PIn]$_{eff}^{1/2}$ [a]	[PIn]$_{eff}$[a] (mmol/L of styrene)	vol % toluene[b]	T (pol) (°C)	t (pol) (h)	consumption of PIn (%)[c]	styrene conversion (%)[c]	10^{-4} M_n of block copolymer	av no. of alt blocks	styryl block length × 10^{-4}	wt % PS in copol[d]
208.0	1.8	0	80	91	98.0	20.3	15.0	3.2	11.7	85.6
137.9	4.0	0	80	91	97.3	28.2	12.4	4.2	6.1	79.0
116.2	5.7	0	80	91	95.0	15.2	6.6	4.3	2.4	59.3
88.0	8.9	0	80	93	98.1	12.3	5.5	5.2	1.1	41.9
74.3	13.8	0	80	91	82.0	6.4	3.7	4.6	0.5	22.6
16.5	55.9	400	80	91	76.0	3.6	3.3	5.3	0.1	4.2

[a] Effective concentration of iniferter groups in PIn-10200. [b] Compared to monomer. [c] Calculated from copolymer composition and block copolymer yield. [d] Determined by ^{1}H NMR.

4.8 alternating blocks would be expected after polymerization of styrene, and 4.0 alternating blocks for block copolymers prepared with PIn-10200. However, the calculated average numbers of alternating blocks are larger than expected for most of the block copolymers (Tables 2 and 3). We think this is due to intermolecular chain transfer and primary radical termination reactions between growing polystyrene radical sites and −S−C(=S)− sites of neighboring block copolymer chains during polymerization, comparable to transesterifications,[28] causing a change in the average number of blocks. In that case, one would expect an increase in the number of blocks for higher concentrations of PIn, because of a greater probability of intermolecular chain transfer reactions. Indeed, this effect can be seen for polymerizations with PIn-10200 (Table 3). However, the average number of blocks remains smaller than for the copolymers prepared with PIn-3300. It should be noted that for the polymerizations during 18 h with PIn-3300 (Table 2), the number of blocks may not be very accurate because these block copolymers might still contain active iniferter groups which have not initiated polymerization yet.

Comparison of Table 3 with Table 2 shows that polymerization with the higher molecular weight polybutadiene iniferter PIn-10200 provides higher conversions and styryl block lengths. In Figure 2 the styryl sequence length is plotted as a function of the ratio [M]/[PIn]$_{eff}^{1/2}$, which should give a straight line. Here [PIn]$_{eff}$ is the effective concentration (mol/L) of iniferter groups in the polymeric iniferter. From this figure it can be concluded that a higher molecular weight PIn causes an increase in styryl sequence length for the same [M]/[PIn]$_{eff}^{1/2}$. Probably, the initiating, chain transfer, and terminating capacities of the thiuram disulfide groups in the chain are influenced by the rigidity of the polymer chain.

Synthesis and Characterization of Segmented (PB(SAN-*block*-PB)$_n$) Block Copolymers. As for the polymerization of styrene, block copolymers with different SAN block lengths and compositions could be synthesized by varying the PB iniferter concentration in the system (see Table 4).

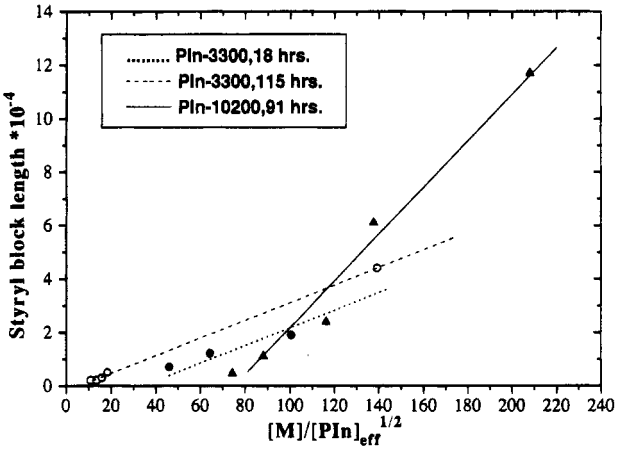


Figure 2. Variation of styryl block length with effective polymeric iniferter concentration for PIn-3300 and PIn-10200.

The content of acrylonitrile was calculated from the nitrogen content determined with elemental analysis. The found nitrogen contents were corrected for the nitrogen originating from the iniferter groups present. Table 4 shows that the acrylonitrile content in the SAN blocks of the block copolymer is higher than that in the monomer mixture. This is a result of the higher reactivity of acrylonitrile in the radical copolymerization with styrene. Because it was impossible to determine the composition of the block copolymers by NMR we assumed that the polymeric iniferter was totally consumed. This is a reasonable assumption considering the fact that the consumptions we found for polymerizations of styrene with the same polymeric iniferter were practically complete for these iniferter concentrations (see Table 2). The number of blocks in the multiblock copolymers were calculated as described for the segmented (PB(PS-*block*-PB)$_n$) block copolymers.

From the average number of polybutadiene units in the polymeric iniferter (N_{PB} = 2.5) an average number of 4 alternating blocks would be expected in the resulting block copolymers. As observed for the (PB(PS-*block*-PB)$_n$) block copolymers, the calculated number of blocks in the block copolymers is much higher.

Table 4. Characteristics of (PB(SAN-*block*-PB)$_n$) Multiblock Copolymers after Copolymerization of Styrene/Acrylonitrile with PIn-10200

[M]/[PIn]$_{eff}^{1/2}$	[PIn]$_{eff}$[a] (mmol/l)	f_{AN} in monomer feed(mol%)[b]	F_{AN} in SAN (mol %)[b]	F_{AN} in SAN (wt %)[b]	SAN conversion (%)[c]	10^{-4} M_n of block copol	no. of alt blocks in copol	% SAN in block copol	SAN-block length[c] $\times 10^{-4}$
186.1	2.4	12.1	9.4	5.0	21.6	17.7	4.8	82	6.6
161.7	2.4	24.3	33.3	20.3	29.1	21.1	7.2	80	5.5
155.4	2.5	20.9	28.5	16.9	25.4	15.9	6.1	77	4.8
147.9	3.8	10.0	19.5	11.0	20.6	15.5	7.0	74	3.8
131.1	5.0	14.6	23.6	13.7	15.8	7.6	5.4	62	2.5
100.6	7.9	9.7	26.3	15.4	8.7	6.0	6.6	36	0.8

[a] Effective concentration of iniferter groups in PIn-10200. [b] From % N in block copolymer determined by elemental analysis, corrected for % N from iniferter groups. [c] Assuming complete consumption of PIn.

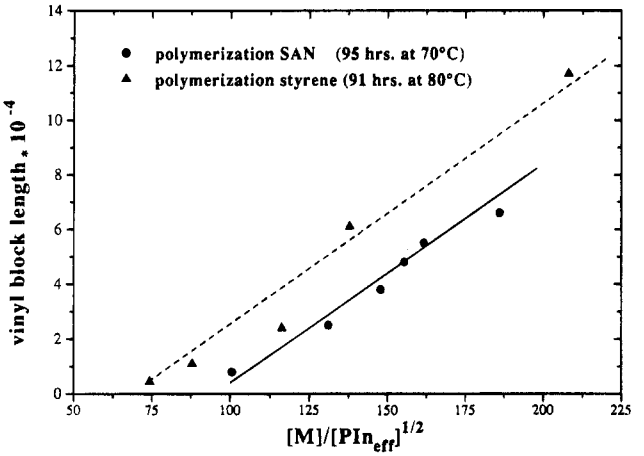


Figure 3. Variation of SAN block length with effective polymeric iniferter concentration.

In Figure 3 the vinyl block length is plotted as a function of the monomer concentration over the square root of the effective polymeric iniferter concentration (concentration of iniferter groups) for polymerizations of both SAN and styrene (under the same polymerization conditions). The straight lines in Figure 3 show the linear dependency. So by choosing the right monomer/iniferter ratio, one can prepare block copolymers with the required SAN block lengths. It is obvious from this figure that the copolymerizations of styrene with acrylonitrile with PIn-10200 produce somewhat lower molecular weights than homopolymerizations of styrene. However, this could also be due to the difference in polymerization temperature.

Figure 4 shows the TGA scans of a (PB(PS-*block*-PB)$_n$) block copolymer and a (PB(SAN-*block*-PB)$_n$) block copolymer, both prepared with PIn-10200. It is obvious that there is not much difference between the thermal stability of both block copolymers. Apparently, the iniferter groups are stable enough to avoid degradation at lower temperatures. This is consistent with a previous report from Clouet et al.,[29] who found that the thermal degradation of dithiocarbamate end groups starts only at temperatures at which the vinyl polymers themselves degrade. This is an important issue, because in order to be usable as compatibilizing agents, the block copolymers should be stable at the required processing temperatures.

Phase Behavior of the Segmented Block Copolymers. Thermal Properties. The thermal properties of the synthesized block copolymers were studied using dynamic mechanical thermal analysis. The prepared segmented (PB(PS-*block*-PB)$_n$) block copolymers show two distinct T_g's, one of the polybutadiene block at −75 °C and one of the polystyrene block at 95−100 °C, depending on block length. In Figure 5 DMTA plots for

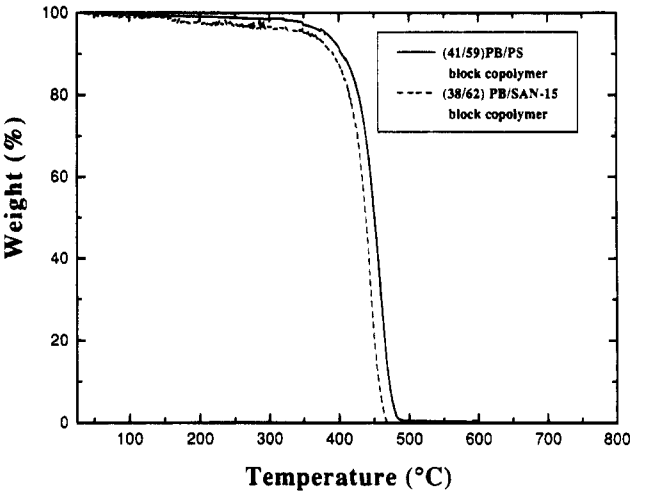


Figure 4. Thermal stability of a segmented (PB(PS-*block*-PB)$_n$) block copolymer and a segmented (PB(SAN-*block*-PB)$_n$) block copolymer, both prepared with PIn-10200.

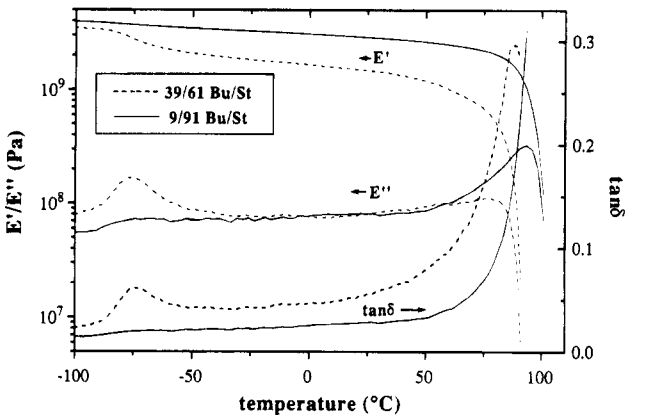


Figure 5. DMTA scan of two (PB(PS-*block*-PB)$_n$) multiblock copolymers, containing 61 and 91 wt % styrene, both based on PIn-3300.

two different segmented (PB(PS-*block*-PB)$_n$) block copolymers, both prepared with PIn-3300, are presented. The influence of styryl block length of the block copolymer on the T_g can clearly be seen. The T_g of the polystyrene block of the block copolymer with 91% styrene (M_n of the styryl blocks 4.4×10^4) is almost 10 deg higher than that of the block copolymer with 61% styrene (M_n of the styryl blocks 1.2×10^4). No mixing T_g could be detected for any of the measured samples. These results strongly indicate complete phase separation within the multiblock copolymers.

TEM Studies. To study the nature of the microstructures present in the segmented block copolymers, transmission electron micrographs were taken. The samples were prepared by compression molding at 130 °C and subsequent annealing under nitrogen atmo-

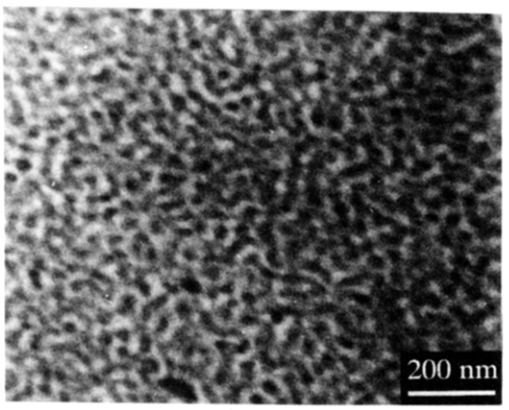


Figure 6. Electron micrograph of an OsO_4-stained sample of a segmented (PB(PS-*block*-PB)$_n$) block copolymer containing 61 wt % styrene (57 vol %), after compression molding at 130 °C and additional annealing for 5 h at 140 °C. (The dark areas correspond to polybutadiene blocks.)

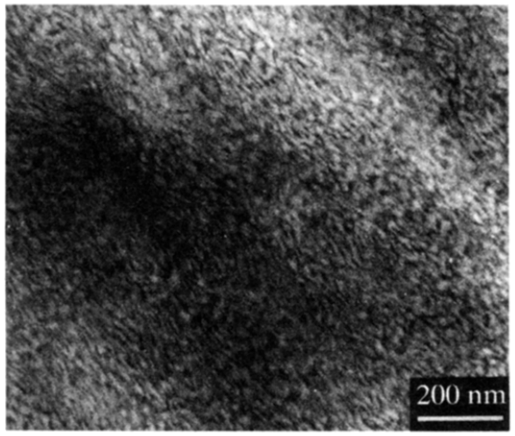


Figure 7. Electron micrograph of an OsO_4-stained sample of a segmented (41/59) (PB(PS-*block*-PB)$_n$) block copolymer, prepared with PIn-10200, after compression molding at 130 °C and annealing at 140 °C.

sphere during 5 h. Figure 6 shows a micrograph of a segmented (PB(PS-*block*-PB)$_n$) block copolymer containing 61 wt % PS (57 vol %), prepared with PIn-3300. For this composition, a lamellar structure would be expected for di- or triblock copolymers of this type.[30,31] However, in our system, no such structure is found. Instead, a very fine microstrucure is formed, which is, from our point of view, in the disordered state. The compression-molded block copolymer was still completely soluble, which proves that no cross-links had been formed during the molding process. Still, the undefined structure could be a result of the method of casting of the TEM sample. Therefore we compared the structure, obtained after compression molding of a segmented (41/59) (PB(PS-*block*-PB)$_n$) block copolymer (see Figure 7), prepared with PIn-10200, to that of a toluene-cast film of the same block copolymer (see Figure 8). Toluene is a good solvent for both blocks. Both micrographs show the same undefined lamellar-like microstructure. Probably, the method of casting is not the cause of the lack of ordening in the block copolymers. Nevertheless the structure of this block copolymer is closer to the expected lamellar structure than that of the block copolymer, prepared with PIn-3300. Possibly, the length of the polybutadiene blocks is the determining factor here for the capacity of the block copolymers to form a well-defined structure. We hope to report on this subject in a forthcoming paper.

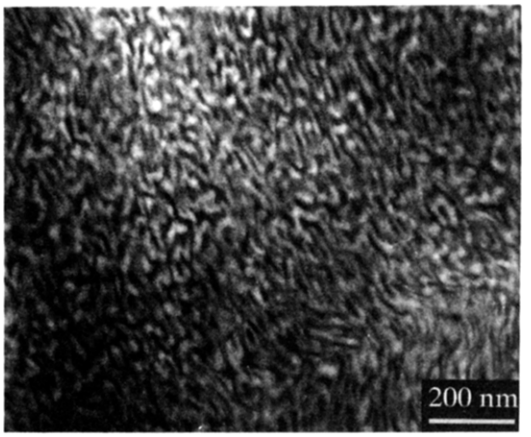


Figure 8. Electron micrograph of an OsO_4-stained sample of a toluene-cast film of the same block copolymer as in Figure 7.

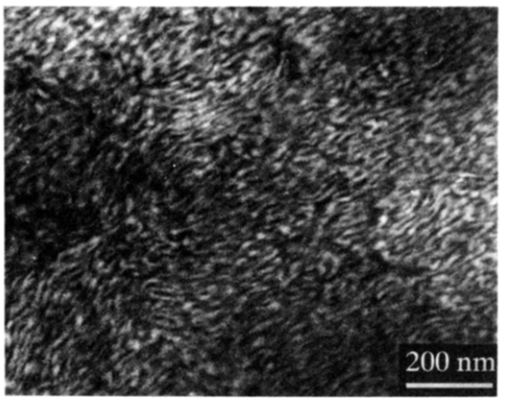


Figure 9. Electron micrograph of an OsO_4-stained sample of a (38/62) (PB–SAN-15) multiblock copolymer, after compression molding at 130 °C and annealing at 140 °C.

The same phenomenon was observed for the segmented (PB(SAN-*block*-PB)$_n$) block copolymers (which were all prepared using PIn-10200). Figure 9 shows a micrograph of an OsO_4-stained (PB(SAN-*block*-PB)$_n$) multiblock copolymer containing 62 wt % SAN-15 (SAN containing 15 wt % acrylonitrile). The micrograph shows the same lamellar-like structure as seen in Figures 7 and 8.

Electron micrographs of prepared multiblock copolymers of other compositions and molecular weights also showed no clearly defined structures.

Conclusions

The synthesis of polymeric iniferters based on polybutadiene is proven successful. These polymeric iniferters were used to prepare segmented block copolymers of polybutadiene and polystyrene, as well as segmented block copolymers of polybutadiene and poly(styrene-*co*-acrylonitrile). Compositions and polystyrene or poly(styrene-*co*-acrylonitrile) block lengths, respectively, in the block copolymer could be regulated by varying the polymeric iniferter concentration or by varying polymerization time at fixed iniferter concentration. The system is less appropriate for high PB content block copolymers. DMTA and transmission electron micrographs of the multiblock copolymers clearly show microphase separation in the multiblock copolymers. However, the nature of the microphases is not completely understood yet and is currently being studied.

The compatibilizing capacities of the synthesized (hydrogenated) multiblock copolymers will be reported in the near future.

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