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Difunctional Anionic Initiator Based on 1,3-Diisopropenylbenzene. 5. Effect of Polar Additives and Initiator Seeding on the Synthesis of Poly(styrene-*b*-butadiene-*b*-styrene) Copolymers

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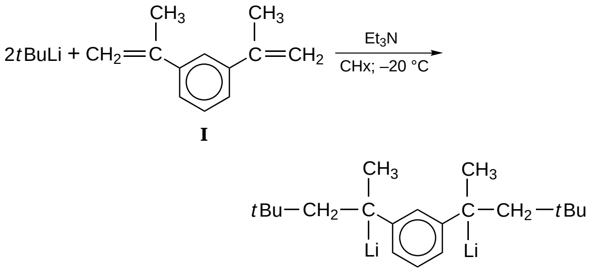
ABSTRACT: The initiation of butadiene and styrene polymerization by a pure hydrocarbon soluble difunctional organolithium, 1,3-bis(1-lithio-1,3,3′-trimethylbutyl)benzene, has been studied in a hydrocarbon solvent. The initiation occurs in such a way that part of the diadduct remains unreacted. When a second monomer feed along with tetrahydrofuran (THF) is added to the living chains, the residual diadduct is activated to the point where novel chains are formed. Weakly polar additives such as lithium alkoxides and aromatic ether can prevent part of the initiator from being inactive, although these additives are not effective enough to initiate the controlled synthesis of poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymers. The seeding of the initiator which consists of butadiene oligomerization in the presence of anisole and *t*BuOLi in cyclohexane, has proved to be very efficient in providing SBS containing 85% 1,4-microstructure polybutadiene (PBD) and with high mechanical properties, e.g., ultimate tensile strength higher than 30 MPa and elongation at a break of 1000%.

Introduction

The synthesis of a pure hydrocarbon soluble difunctional organolithium initiator, 1,3-bis(1-lithio-1,3,3′-trimethylbutyl)benzene (**II**), has been reported in a previous paper.[1] This dilithium initiator was prepared by the stoichiometric reaction of *tert*-butyllithium (*t*BuLi) with 1,3-diisopropenylbenzene (1,3-DIB) in cyclohexane (CHx), in the presence of 1 equiv of triethylamine (Et_3N), at low temperature (eq 1). A pure diadduct (**II**) was formed without concomitant oligomerization of 1,3-DIB.



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Poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymers and poly(methyl methacrylate-*b*-styrene-*b*-butadiene-*b*-styrene-*b*-methyl methacrylate) (MMA-S-B-S-MMA) five-block copolymers with good tensile properties were prepared by using this difunctional organolithium initiator in the presence of diethyl ether as a polar additive.[1,2] These block copolymers had predictable molecular weight and composition, and narrow molecular weight distribution. $\bar{M}_w/\bar{M}_n$ for triblock or five-block copolymers were usually between 1.05 and 1.1, indicating a selective initiation by the difunctional initiator so that initiation by monofunctional and/or multifunctional species could be disregarded. The polybutadiene (PBD) midblock contained ca. 55% 1,4-units. When the diadduct **II** was used to initiate the sequential polymerization of butadiene and styrene in the absence of any polar additive, the molecular weight distribution remained quite narrow, although the mechanical properties of the final SBS were very poor. Actually, the diadduct **II** did behave as a monofunctional initiator in apolar solvents so that a polar additive was required to provide compound **II** with two reactive sites.[2] Furthermore, solvent polarity also has an effect on the microstructure of the polydiene formed. In apolar solvents, the 1,4-addition mode dominates, in contrast to the 1,2-addition in tetrahydrofuran (THF). Nevertheless, a small amount of a weakly polar additive has been reported to alter the association of organolithium compounds in hydrocarbons without drastically changing the polydiene microstructure. For instance, Fetters and Morton[3] used anisole in the preparation of 1,4-dilithio-1,1,4,4- tetraphenylbutane as a dilithium initiator and found that the diene polymerization was essentially a 1,4-addition even in the presence of small amounts of this polar compound. Recently, the beneficial effect of polar additives on the diene polymerization initiated by two hydrocarbon soluble dilithium initiators, [1,3-phenylenebis(3-methyl-1-phenylpentylidene)]dilithium and [1,3-phenylenebis[3-methyl-1-(methylphenyl)-pentylidene]-dilithium, has been reported.[4] In order to confirm the performances of the diadduct **II** as a dilithium initiator, the sequential anionic polymerization of butadiene and styrene has been studied in hydrocarbon solvents, in the presence of polar additives and by use of a previously

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seeded initiator.

Experimental Section

Materials. Butadiene was purchased from Air Liquid Co. and was purified by being passed through a column filled with freshly crushed CaH_2 and then distilled over *n*-butyllithium just before use. Styrene (Janssen) was dried over CaH_2 for 2 days and then added with fluorenyllithium and distilled just prior to use. 1,3-Diisopropenylbenzene (Aldrich) was dried over CaH_2 for 1 day, distilled from fluorenyllithium, and then diluted with dry cyclohexane. Tetrahydrofuran (THF) was purified by refluxing over a sodium−benzophenone complex. Cyclohexane and toluene were refluxed over CaH_2 for several days. All solvents were added with living lithium polystyryl oligomers, and distilled just before use. Anisole (Aldrich) was purchased as reagent-grade compound, dried over CaH_2, and distilled in the presence of living lithium polystyryl oligomers prior to use. Lithium *tert*-butoxide and lithium 2-(2-methoxyethoxy)ethoxide were prepared by reaction of *tert*-butyl alcohol and polyether alcohol, respectively, with a stoichiometric amount of *sec*-butyllithium in toluene. Commercially available *sec*-butyllithium and *tert*-butyllithium (Janssen) were analyzed by the double titration method with 1,2-dibromobutane.[5]

Polymerization. The diadduct **II** was prepared just prior to use according to the synthetic pathway described elsewhere.[1] All polymerization experiments were carried out under inert atmosphere in a previously flamed 1 L glass reactor equipped with rubber septa connected through tight stopcocks. Syringes and stainless steel capillaries were used to transfer solvents, monomers, and initiator. The reaction was carried out in a thermostated water bath, and the reaction mixture was mixed with a magnetic stirrer. Solvent, additive, initiator, and monomers were sequentially added into the reactor. The concentration of butadiene was ca. 20−30 g/L, depending on the expected molecular weight. The polymerization time was 15 h for butadiene and 4 h for styrene. The polymerization temperature was dependent on the polymerization medium, i.e., 40 °C for both butadiene and styrene in apolar solvents added or not with small amounts of weakly polar additives and 25 °C in the case of strong polar additives. Polymerization was terminated by addition of a methanol/HCl mixture (previously flushed with nitrogen), and the copolymer was precipitated into methanol.

Analysis. Size exclusion chromatography (SEC) was carried out at 40 °C with a Hewlett-Packard 1090 liquid chromatograph equipped with four columns (10^5, 10^3, 500, and 100 Å) and a HP 1037 A refractive index detector. Polystyrene standards were used for calibration, and THF was the elution solvent. A conversion factor of 0.55 was found to be appropriate for the calculation of the PBD molecular weight. The composition of block copolymers was analyzed by ^1H NMR spectroscopy (Bruker AM-400 spectrometer). The tensile strength and elongation at the break were measured with a Adamel Lhomargy tensile tester. Samples were cyclohexane cast and cut into a DIN 53448 specimen. The cross-head speed was 200 mm/min. The PBD central block of SBS triblocks was selectively degraded by reaction with H_2O_2 in the presence of osmium tetroxide as described in a previous paper.[6] Crude copolymers were fractionated by using the benzene/acetone solvent pair.[7] A 1 g sample of copolymer was dissolved into 20 mL of benzene, and then 80 mL of acetone was added. The precipitated fraction was filtered off, and the filtrate was poured into a large volume of methanol in order to precipitate the soluble fraction, i.e., homo-PS or PS-rich (PS = polystyrene) copolymer.

Results and Discussion

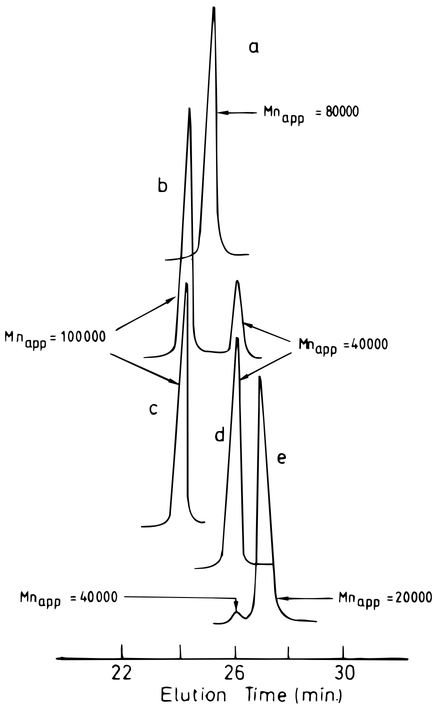

Figure 1. SEC traces of butadiene/styrene copolymers prepared with the diadduct **II** in cyclohexane (1 vol % THF added before styrene polymerization): (a) PBD central block; (b) final copolymer; (c) precipitated fraction in the (1/4; v/v) benzene/acetone mixture; (d) soluble fraction; (e) PS recovered after PBD degradation of the final copolymer.

Anionic Polymerization Initiated with Diadduct II in a Hydrocarbon Solvent. The sequential anionic polymerization of butadiene and styrene was initiated in a hydrocarbon solvent, i.e., cyclohexane or toluene, by the pure diadduct **II**. Butadiene was added into the reactor at 0 °C, and the final concentration was ca. 0.6 mol/L. The diadduct **II** was then added at a (5−8) × 10^{-4} mol/L concentration. When the temperature was raised to 40 °C, the deep red color rapidly changed to a faint orange color that persisted for the whole polymerization reaction. One may thus suspect that part of the initiator remains unreacted since the polybutadienyl anions are known to provide usually the solution with a yellow color. In this respect, the diadduct **II** has been shown to react not as a difunctional anionic initiator in hydrocarbons, but rather as a monofunctional species as a result of alkyllithium association.[1] Indeed, the sequential copolymerization of butadiene and styrene, as initiated by compound **II**, results in copolymers with unexpectedly poor mechanical properties that are more consistent with a diblock structure rather than the expected triblock one. In polar solvents, such as THF or diethyl ether, the two lithium species of diadduct **II** are activated, and initiation by monofunctional species can be neglected. However, polymerization in such polar solvents forms PBD blocks with a 1,2-microstructure rather than the 1,4-microstructure required for promoting the most desirable elastomeric properties. In order to avoid this drawback, preliminary experiments have been conducted by adding 1 vol % THF prior to the styrene polymerization.

A typical SEC trace of a butadiene/styrene block copolymer prepared under these conditions is shown in Figure 1. The expected molecular weight for the PBD block and the styrene/butadiene molar ratio were 40 000 and 0.36, respectively. A sample of PBD formed in the first step was picked out before THF and styrene addition (Figure 1a). Although a narrow and monomodal molecular weight distribution (MWD) is observed for the central PBD block ($M_{n_{app}}$ = 80 000, $M_{n_{PBD}}$ = 44 000), the SEC chromatogram of the final copolymer (Figure 1b) shows two peaks. The major peak on the high-molecular weight side ($M_{n_{app}}$ = 100 000) has been assigned to the block copolymer. The minor peak on the low-molecular weight side ($M_{n_{app}}$ = 40 000) is

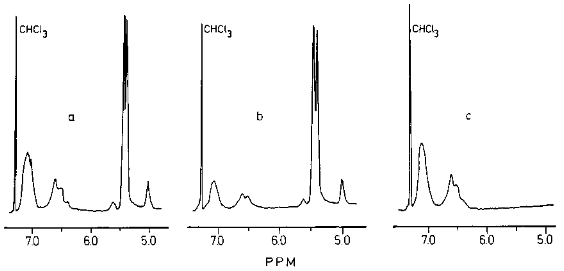

Figure 2. ^{1}H-NMR spectra of the butadiene/styrene block copolymer prepared with the diadduct **II** in cyclohexane (see Figure 1): (a) crude block copolymer; (b) precipitated fraction in the (1/4; v/v) benzene/acetone mixture; (c) soluble fraction.

characteristic of chains much shorter (by ca. 2) than the originally formed PBD chains, which can only be explained by homopolystyrene formation.

Morton and Fetters[8] reported similar observations for the styrene polymerization initiated by *t*BuLi in cyclohexane. Styrene was polymerized with *t*BuLi at 35 °C, and a monomodal MWD was observed. When a second styrene feed along with 1 vol % THF was added, formation of PS chains was observed, resulting in a bimodal molecular weight distribution. The authors suggested that only part of the *t*BuLi rapidly reacted with styrene in cyclohexane and that the final bimodal MWD resulted from the initiation of styrene by residual *t*BuLi that was activated by the THF added.

Since the solubility of block copolymers of butadiene and styrene is different from the solubility of homo-PS in a (1/4; v/v) benzene/acetone mixture, the crude SBS copolymer has been fractionated as described in the Experimental Section. SEC traces of these two fractions are shown in Figure 1c,d and confirm the complete separation of the two constitutive components of the original copolymer (Figure 1b). Figure 2 shows the ^{1}H-NMR spectra for the crude butadiene/styrene block copolymer and the soluble and precipitated fractions, respectively. The aromatic protons of PS and the vinylic protons of PBD are observed in the ranges of 6.8−7.2 and 4.4−5.5 ppm respectively for both the crude copolymer (Figure 2a) and the precipitated fraction (Figure 2b). The integration of the ^{1}H-NMR signals leads to a styrene/butadiene molar ratio of 0.36 for the crude copolymer compared to 0.21 for the precipitated fraction. In contrast, only aromatic protons are detected in the soluble fraction (Figure 2c), confirming that the minor SEC peak on the low-MW side is due to homopolystyrene.

The crude copolymer has been further reacted with hydrogen peroxide in the presence of osmium tetroxide,[6] which are conditions known for the selective degradation of PBD. The SEC trace of the recovered PS shows again a bimodal MWD (Figure 1e). The minor peak has the same molecular weight as the soluble fraction ($M_{n_{app}}$ = 40 000), and the molecular weight of the major peak is two times smaller than the soluble fraction ($M_{n_{app}}$ = 20 000). So, the minor peak observed in Figure 1b corresponds to homo-PS initiated by some residual dilithium initiator **II**, and the major peak is PS formed as a result of the selective degradation of the PBD block in the copolymer. Since the homo-PS fraction has a molecular weight two times higher than of the PS blocks (Figure 1e), the residual diadduct **II** is certainly difunctional in the presence of THF. From the ^{1}H-NMR analysis of the precipitated fraction (styrene/butadiene molar ratio = 0.21; Figure 2b) and the molecular weight of the PBD block ($M_{n_{PBD}}$ = 44 000; Figure 1a), the molecular weight of the PS blocks should be close to 10 000, assuming an ideal triblock structure. Since the molecular weight of the PS blocks is actually two times higher (20 000 for the major peak in Figure 1e), the precipitated fraction is basically a diblock copolymer. Therefore, the polymerization mechanism might be described by eq 2, where $x \gg y$.

$$(x+y)\underset{\textbf{II}}{\text{Li-DIB-Li}} + \text{BD} \xrightarrow{\text{cyclohexane}} x\text{Li-DIB-PBD-Li} + y\text{Li-DIB-Li} \xrightarrow{\text{THF + styrene}} x\text{-Li-DIB-PBD-PS-Li (or Li-PS-DIB-PBD-Li)} + y\text{Li-PS-DIB-PS-Li} \quad (1)$$

Consistently with the experimental observations, most of the initiator **II** rapidly reacts with butadiene from one end, whereas a small amount of the dilithium compound remains totally unreacted ($x \gg y$ in eq 2). Addition of 1 vol % THF triggers the activation of this residual dilithium initiator. Styrene polymerization is then initiated by one end of the PBD dilithium chains (*x*Li-DIB-PBD-Li) and by the two anionic sites of the residual lithium diadduct (*y*Li-DIB-Li). It is not clear yet why only one end of the PBD dilithium chains is active and which one is responsible for the styrene initiation [i.e., Li-DIB-PBD-*Li* or *Li*-DIB-PBD-Li].

Several SBS triblock copolymers have been prepared under the aforementioned experimental conditions. Whatever the hydrocarbon solvent used, i.e., cyclohexane or toluene, and the composition and MW of the envisioned copolymers, the same observations are reported. Furthermore, all these block copolymers have very poor mechanical properties (Table 1), which is additional evidence for the preferential formation of diblock copolymers.

Effect of Lithium Alkoxides. Many scientific papers have reported on the favorable effect of lithium alkoxides on the anionic polymerization initiated by a lithium difunctional initiator. Lo et al.[4] have observed that lithium isopropoxide was able to prevent polyisoprene with a bimodal molecular weight distribution from being formed, when [1,3-phenylenebis[3-methyl-1-(methylphenyl)pentylidene]]dilithium (DDPE-Li$_2$) was used as the initiator. Quirk and Ma[9] also noted that the MWD of SBS copolymers was narrower when the difunctional DDPE-Li$_2$ initiator was added with lithium *sec*-butoxide.

In this study, several butadiene/styrene block copolymers have been initiated in toluene by the diadduct **II** in the presence of increasing amounts of *t*BuOLi. The main characteristic features of these copolymers are listed in Table 2. In the case of samples 2, 4, and 6, THF has been added into the reaction medium before the styrene polymerization. An equimolar amount of *t*BuOLi with respect to the alkyllithium sites of compound **II** has been used in the synthesis of samples 1 and 2, whose SEC traces are quite comparable (Figure 3). The SEC trace of the PBD central block shows a shoulder on the low-molecular weight side, which tends to disappear upon the styrene polymerization. In spite of very similar molecular characteristics, sample 2 shows a much higher tensile strength than sample 1 (14.0 MPa compared to 6.0 MPa) and a larger elongation at the break, which indicates a favorable effect of THF on the crossover reaction from butadienyl anions to styrene. Both samples have much better mechanical properties than the samples prepared without any *t*BuOLi (see Table 1). The monomodal MWD of sample 2 indicates that no residual initiator **II** is left when the

Table 1. Butadiene/Styrene Block Copolymers (copo) Initiated with the Diadduct II in a Hydrocarbon Solvent[a]

sample	solvent[b]	1,2-PBD[c] (%)	PS[c] (wt %)	$M_{n_{copo}}$[d] ($\times 10^{-3}$)	M_w/M_n PBD/copo[e]	ultimate tensile strength (MPa)	elongation at break (%)
1	CHx	8.9	40	76	1.10/1.20	0.8	90
2	CHx	9.0	40	105	1.10/1.20	1.1	150
3	CHx	8.7	30	79	1.10/1.20	0.6	85
4	CHx	8.8	30	106	1.10/1.20	1.0	165
5	Tol	9.2	40	100	1.10/1.20	1.5	185
6	Tol	9.0	40	150	1.10/1.20	1.4	165
7	Tol	8.9	35	152	1.10/1.20	1.2	170

[a] 1 vol % THF added before styrene polymerization. [b] CHx = cyclohexane; Tol = toluene. [c] From ^{1}H-NMR data. [d] From SEC and ^{1}H-NMR data. [e] Bimodal MWD.

Table 2. Butadiene/Styrene Block Copolymers (copo) Initiated in Toluene with the Diadduct II in the Presence of *t*BuOLi

sample[a]	*t*BuOLi/Li	1,2-PBD[b] (%)	PS[b] (wt %)	$M_{n_{copo}}$[c] ($\times 10^{-3}$)	M_w/M_n PBD/copo	ultimate tensile strength (MPa)	elongation at break (%)
1	1.0	15	36	78	1.15/1.10	6.0	700
2	1.0	15	35	85	1.15/1.10	14.0	1000
3	2.0	16	35	92	1.20/1.10	5.5	800
4	2.0	17	36	90	1.15/1.10	14.5	1000
5	3.0	17	34	91	1.15/1.10	6.5	700
6	3.0	16	35	89	1.15/1.10	13.5	1000
7	1.0[d]	43	33	84	1.05/1.10	30.5	1000

[a] 1 vol % THF added before styrene polymerization in case of samples 2, 4, and 6. [b] From ^{1}H-NMR data. [c] From SEC and ^{1}H-NMR data. [d] Polar additive: $LiO(CH_2CH_2O)_2CH_3$.

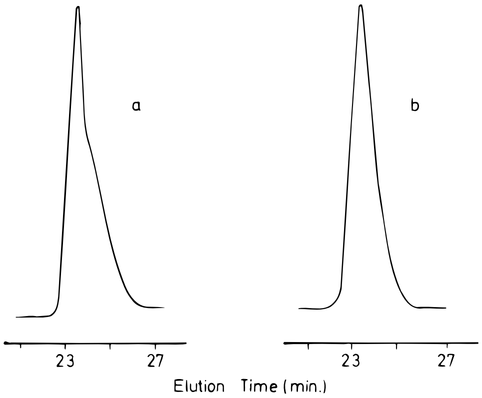

Figure 3. SEC traces of a butadiene/styrene block copolymer (Table 2, entry 1) prepared in toluene with the diadduct **II** in the presence of *t*BuOLi (*t*BuOLi/Li = 1.0): (a) PBD central block; (b) final block copolymer.

butadiene polymerization is complete as a result of the *t*BuOLi addition. Increasing the *t*BuOLi/Li ratio from 1 to 3 does not improve the ultimate mechanical properties of the final block copolymers. Furthermore, ^{1}H-NMR analysis shows that increasing amounts of *t*BuOLi slightly increases the content of 1,2-units in the PBD block. Substitution of cyclohexane for toluene, all the other conditions being the same, does not modify the molecular characteristics and mechanical properties of the resulting block copolymers.

The aforementioned results indicate that *t*BuOLi activates all of the diadduct **II** in BD polymerization. Nevertheless, it appears that only part of compound **II** initiates the BD polymerization from the two anionic sites so that two types of growing PBD chains would be formed:

Li-DIB-PBD-Li (III) Li-PBD-DIB-PBD-Li (IV)

Indeed, the shoulder observed on the low-MW side of the SEC trace (Figure 3a) might be assigned to the PBD chains of type III. The styrene polymerization initiated by the living PBD chains of types III and IV then yields diblock and triblock copolymers, respectively. The addition of THF is however instrumental in allowing triblocks to be formed from the two types of PBD chains (III and IV), which may explain the substantial improvement in the ultimate mechanical properties of SBS. It means that the effectiveness of the diadduct **II** as a difunctional initiator has been improved but not yet completely.

Lithium polyether alkoxides have been reported by some of us as more effective ligands than *t*BuOLi in living anionic polymerization of methacrylic and acrylic esters.[10] In this study, a butadiene/styrene block copolymers have been prepared in cyclohexane with diadduct **II**, in the presence of 2 equiv of lithium 2-(2-methoxyethoxy)ethoxide ($LiO(CH_2CH_2O)_2CH_3$) (Table 2, sample 7). Both the PBD central block and the final block copolymer are monomodal and symmetric. Even though, mechanical properties are much improved, as shown by a tensile strength of 30.5 MPa and an elongation at the break of 1000%, the PBD microstructure is also much higher in the 1,2-unit (ca. 43%). The block copolymers are actually quite comparable to samples prepared in the presence of diethyl ether, as reported in a previous paper of this series.[1]

Effect of Anisole. From the experimental observations discussed above, *t*BuOLi is a too weak ligand to activate the two anionic sites of diadduct **II**, whereas lithium polyether alkoxide is strong enough to make the two species active per the DIB molecule, but it also increases the 1,2-content of the PBD blocks. In a previous paper,[1] we have reported that THF and diethyl ether are effective additives for the controlled preparation of SBS triblock copolymers, although the 1,2-content of the PBD central block was also too high. Anisole is a commonly used aromatic ether for promoting anionic polymerization in hydrocarbon solvents, that has only a minor effect on the 1,4-microstructure of polydienes.[3]

Several butadiene/styrene block copolymers have been prepared with the diadduct **II** in the presence of anisole in cyclohexane at room temperature. These copolymers and their molecular characteristics are listed in Table 3. As expected, anisole has no drastic effect on the 1,2-

Table 3. Butadiene/Styrene Block Copolymers (copo) Prepared in Cyclohexane with the Diadduct II in the Presence of Anisole

sample	anisole (vol %)	1,2-PBD[a] (%)	PS[a] (wt %)	$M_{n_{copo}}$[b] ($\times 10^{-3}$)	M_w/M_n PBD/copo	ultimate tensile strength (MPa)	elongation at break (%)
1	0.5	12.5	34	100	1.05/1.10	2.5	600
2	3.0	18.0	33	99	1.50/1.30[c]	5.0	800
3	5.0	24.5	34	99	1.70/1.40[c]	4.5	700
4	10.0	31.0	33	97	1.60/1.35[c]	2.5	600
5	15.0	37.0	33	97	1.20/1.20[c]	2.0	700

[a] From ^{1}H-NMR data. [b] From SEC and ^{1}H-NMR data. [c] Copolymers with bimodal MWD.

Table 4. Butadiene/Styrene Block Copolymers (copo) Prepared in Cyclohexane with a Seeded Initiator

sample[a]	seeding technique[b]	1,2-PBD[c] (%)	PS[c] (wt %)	$M_{n_{copo}}$[d] ($\times 10^{-3}$)	M_w/M_n PBD/copo	ultimate tensile strength (MPa)	elongation at break (%)
1	A	9.0	34	96	1.05/1.05	4.5	800
2	A	9.5	33	97	1.05/1.10	6.5	900
3	B	15.5	33	116	1.15/1.20[e]	17.5	1000
4	B	16.0	30	91	1.10/1.25[e]	22.5	1000
5	C	18.5	34	122	1.20/1.30[e]	2.8	700
6	C	18.5	34	152	1.15/1.30[e]	2.2	700
7	D	15.5	34	105	1.10/1.10[e]	25.0	1000
8	D	15.0	34	106	1.10/1.10[e]	31.0	1000

[a] 1 vol % THF added before styrene polymerization in samples 2, 4, and 8. [b] Seed initiator A was prepared in cyclohexane; B was prepared in cyclohexane added with 15 vol % anisole; C was prepared in cyclohexane with 75 vol % anisole; D was prepared in cyclohexane with 15 vol % anisole and *t*BuOLi (*t*BuOLi/Li = 1.0). [c] From ^{1}H-NMR data. [d] From SEC and ^{1}H-NMR data. [e] Block copolymers with bimodal MWD.

content of PBD, which exceeds 20% when the content of the aromatic ether is higher than 3 vol %. PBD prepared in the presence of 0.5 vol % anisole has a narrow and monomodal MWD. When the anisole content is higher than 3 vol %, a bimodal MWD is observed. All of these copolymers have poor mechanical properties, which may indicate a dominant diblock structure.

Effect of the Initiator Seeding. The condition necessary to get a narrow MWD is an initiation step faster than the propagation one and termination side reactions, if any, much slower than the initiation and propagation steps. In the unfavorable case where the rate ratio of the initiation to propagation changes with the concentration of initiator or monomer, a seeding technique may be useful to restrict the undesirable broadening of the MWD. This technique consists in polymerizing first a small fraction of monomer and using these oligomers as initiator for the actual polymerization of the major monomer feed. For instance, Madani et al. have reported cases where the propagation rate from dilithium oligomers was autoaccelerated to an extent that depended on molecular weight and monomer concentration.[11] These authors reported on the favorable effect of the seeding technique on the polymerization control. Lo et al.[4] also reported that seeding was effective in narrowing the MWD of polyisoprene initiated by DDPE-Li$_2$. Roovers and Bywater also successfully used the seeding technique to prepare narrow MWD polystyrene in benzene with *tert*-butyllithium as the initiator.[12]

A seeded initiator (A in Table 4) has been prepared by reaction of the diadduct **II** with a small amount of butadiene in cyclohexane. The concentration of compound **II** was 0.03 M, thus ca. 60 times higher than the usual concentration. This seeded initiator has a rather symmetrical monomodal MWD with the expected molecular weight (MW = 2000). More butadiene and cyclohexane have then been added to the seeded initiator so as to restore the usual concentration of monomer and initiator, i.e., 30 g/L and 5×10^{-4} mol/L, respectively. After the overnight polymerization of butadiene at 40 °C, styrene has been added and polymerized for 4 h at 40 °C, or at room temperature when 1 vol % THF was added prior to styrene. The SEC traces of the samples picked out from the reaction medium show that the PBD central block and the final copolymer have rather symmetrical monomodal MWD ($1.05 \le M_w/M_n \le 1.10$). Although these block copolymers (samples 1 and 2 in Table 4) are of a high molecular weight (100 000) and narrow MWD, their mechanical properties are poor compared to the SBS Cariflex TR1102 commercialized by Shell. The tensile strength is slightly improved when styrene is polymerized in the presence of THF. It is worth noting that sample 2 (THF added before styrene polymerization) has now a monomodal MWD, which indicates that the seeding technique can prevent part of the initiator from remaining unreactive. So, the initiator seeding appears to be effective in activating all of the diadduct molecules toward butadiene, but not in promoting two active sites per molecule. Addition of a polar additive should be thus another condition strictly necessary for the seeded initiator to be an effective difunctional initiator.

Another PBD oligomer (B in Table 4) has been prepared in the presence of 15 vol % anisole in cyclohexane (MW = 2000). In contrast to the bimodal SEC traces of high-molecular weight PBD prepared under the same conditions (see Table 3), a monomodal distribution with a slight tailing on the low-MW side is observed. This tailing might be the consequence of a slow initiation by the second lithium site of diadduct **II**. Samples 3 and 4 (Table 4) have been prepared with the PBD oligomers B as initiator, and THF has been added prior to styrene polymerization in the case of sample 4. From the mechanical properties of samples 3, 4 and 1, 2, it appears that the anisole modified seeded initiator is very efficient in improving the mechanical properties of the block copolymers. The low anisole content used (<1 vol %) has no significant effect on the PBD microstructure. Nevertheless, tensile strengths of samples 3 and 4 remain smaller than the value expected for SBS triblock copolymers (ca. 31 MPa), so that combination of the seeding technique and modification by anisole is not yet effective enough in perfectly controlling the SBS triblock structure. In the presence

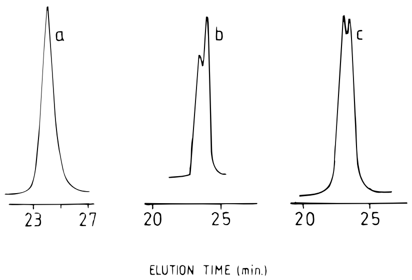

Figure 4. SEC traces of butadiene/styrene block copolymers initiated with the seeded PBD initiator D in cyclohexane (see Table 4, sample 8): (a) seeded initiator D; (b) PBD central block; (c) final block copolymer.

of anisole, two species of compound **II** might coexist and differ in the initiation rate. After complete consumption of butadiene, one anionic site of some diadduct **II** might remain unreacted and be responsible for the formation of diblock copolymers. An additional evidence for the diblocks formation has to be found in the bimodal MWD of the PBD block and the final block copolymer (Figure 4b,c). The effect of an increasing amount of anisole on the synthesis of block copolymers has been considered. A PBD oligomer (C in Table 4) has accordingly been prepared in the presence of 75 vol % anisole in cyclohexane. The MWD is again monomodal although slightly asymmetric on the low-MW side. Mn of this PBD oligomer is actually 7000, thus slightly higher than the expected value ($M_n = 6000$). Both PBD and block copolymers prepared with this seeded initiator C in cyclohexane containing ca. 3.5 vol % anisole (samples 5 and 6 in Table 4) have a well-marked bimodal MW distribution, and the mechanical properties of SBS are very poor.

Although the seeding technique is a substantial improvement for the synthesis of SBS in hydrocarbons, a too large difference in the initiation rate of the two organolithium sites of diadduct **II** remains a pending problem. Since the butadiene polymerization is drastically decreased by *t*BuOLi, this polar compound has been added to the diadduct **II**/anisole system in view of decreasing the initiation rate by the more reactive site of the dilithium initiator **II** and bringing closer the reactivity of the two anionic sites. A seeded initiator (D in Table 4) has thus been prepared as follows: *t*BuOLi, anisole, and butadiene have been added to the diadduct solution (*t*BuOLi/Li molar ratio = 1; 15 vol % anisole in cyclohexane), and butadiene has been polymerized overnight at room temperature. The SEC trace of the PBD oligomer is narrow and perfectly symmetrical (Figure 4a), and M_n is in perfect agreement with the expected value ($M_n = 2000$). Butadiene and styrene have been polymerized overnight and for 4 h, respectively, at 40 °C in cyclohexane with this seeded initiator D (samples 7 and 8, Table 4). THF has been added before styrene polymerization in the case of sample 8. The PBD central block and the final SBS copolymer have again a bimodal MWD, as shown in Figure 4b,c, even though the molecular weight distribution of the final copolymer is as narrow as 1.10. Assuming that the lower MW material is a diblock copolymer, its content might be estimated to 50% (from the area ratio of the two peaks (Figure 4c). This high amount of diblocks should have a detrimental effect on the final mechanical properties, as recently reported.[13] Surprisingly enough, sample 8 shows high mechanical performances, i.e., a tensile strength of 31 MPa, 1000% elongation at the break, and a permanent set at the break of ca. 25%. The 1,4-units content of the PBD block is ca. 85%. Therefore the low-MW component in sample 8 should be a triblock rather than a diblock copolymer. This is confirmed by the selective degradation of the PBD block that releases PS of $M_n = 18\,000$, in good agreement with the expected value for an ideal triblock structure.

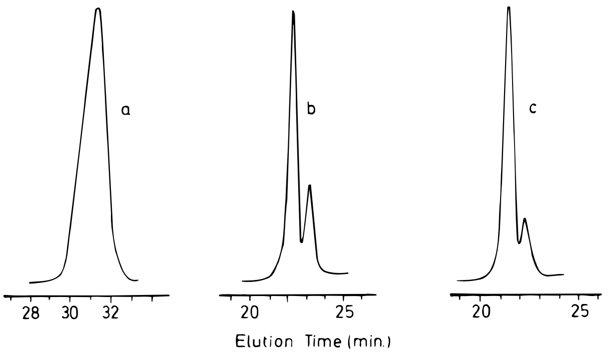

Figure 5. SEC traces of a butadiene/styrene block copolymer prepared in cyclohexane with a seeded initiator containing DEE and *t*BuOLi (Table 5; sample 1): (a) seeded initiator; (b) PBD central block; (c) final block copolymer.

Since the use of anisole is quite inconvenient in the case of industrial application, this additive has been replaced by diethyl ether (DEE) for the preparation of the seeded initiator in the presence of *t*BuOLi. The accordingly prepared PBD oligomers have a narrow and symmetrical MWD and the predicated MW (Figure 5a). The PBD and block copolymers have again a bimodal MWD (Figure 5b,c). The final block copolymers (samples 1 and 2 in Table 5) prepared in cyclohexane with this seeded initiator have comparable mechanical properties to Cariflex TR, even though THF was not used in sample 1. The substitution of diethyl ether for anisole results in some increase in the 1,2-units content of PBD.

Another seeded initiator has finally been prepared in cyclohexane with the diadduct **II** and *t*BuOLi (*t*BuOLi/Li = 3) in the absence of anisole or DEE. It has a narrow and symmetrical MWD and a predictable MW. Synthesis of block copolymers has failed without THF addition before styrene polymerization. In the absence of THF, the color change from pale yellow (characteristic of PBD-Li) to orange (characteristic of PS-Li) is very slow, and so the crossover reaction from PBD-Li to PS-Li must be. In contrast, the color changes instantaneously when 1 vol % THF is added before the styrene

Table 5. Butadiene/Styrene Block Copolymers (copo) Prepared in Cyclohexane with a Seeded Initiator in the Absence of Anisole

sample	1,2-PBD (%)	M_n (expected) PBD	PS	M_n (exptl) PBD	PS	M_w/M_n PBD/Copo	ultimate tensile strength (MPa)	elongation at break (%)	perm set (%)
1[a]	23	60000	16000	60000	16000	1.10/1.10	32.5	1000	25
2[a,c]	24	60000	16000	60000	16000	1.10/1.09	31.5	1000	25
3[b,c]	13	60000	16000	60000	16000	1.05/1.10	28.5	1000	25

[a] Seeded initiator containing DEE (15 vol %) and *t*BuOLi (*t*BuOLi/Li = 2/1). [b] Seeded initiator containing *t*BuOLi (*t*BuOLi/Li = 3/1). [c] 1 vol % THF added before styrene polymerization.

polymerization. Thus, the final block copolymer (sample 3 in Table 5) shows again high mechanical performances except for the ultimate tensile strength which is smaller by ca. 10% compared to samples 1 and 2 (Table 5). It is worth pointing out that the combination of the initiator seeding technique and weakly polar additives has also allowed poly(methyl methacrylate)/polybutadiene-based symmetrical block copolymers with a high 1,4-microstructure content to be obtained. Those copolymers were found to have much better mechanical properties, e.g., an ultimate tensile strength higher than 38 MPa and higher service temperatures than conventional SBS thermoplastic elastomers.[13]

Conclusions

The initiation of butadiene (BD) in a hydrocarbon solvent with a soluble dilithium initiator, 1,3-bis(1-lithio-1,3,3′-trimethylbutyl)benzene (**II**), has proved to be complex. Actually, there is a relatively rapid reaction between BD and a fraction of compound **II**. The initiation rate then seems to decrease rapidly, to the point where part of compound **II** would remain unreacted. When a second monomer feed along with THF is added to the reaction medium, the residual initiator is activated by THF and contributes to polymerization. Weakly polar additives, such as lithium alkoxides and aromatic ether, can prevent the residual initiator from being present, although they are unable to form pure SBS triblock copolymers. Strongly polar additives, such as THF, diethyl ether, and lithium polyether alkoxides, are effective in activating the two organolithium sites of the diadduct **II**, but they have an unacceptable effect on the PBD microstructure, since the content of 1,2-units is dramatically increased. The seeding technique is also able to prevent part of the initiator from being inactive. When anisole and *t*BuOLi are jointly used for the preparation of the seeded initiator, the PBD content of 1,2-units is low and the SBS triblock copolymers show high ultimate mechanical properties in spite of a bimodal MWD of both the PBD midblock and the final triblock copolymer. However, the selective degradation of the polydiene block confirms an essentially triblock structure.

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