Macromolecules 1994, *27*, 5957–5963

Efficiency of the *sec*-Butyllithium/*m*-Diisopropenylbenzene Diadduct as an Anionic Polymerization Initiator in Apolar Solvents

Y. S. Yu, R. Jérôme,* R. Fayt, and Ph. Teyssié

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart Tilman B6, 4000 Liège, Belgium

Received May 6, 1994; Revised Manuscript Received July 25, 1994®

ABSTRACT: The 2/1 *sec*-butyllithium/1,3-diisopropenylbenzene adduct has been prepared and evaluated as an effective, hydrocarbon soluble, difunctional initiator for the synthesis of polystyrene–polybutadiene–polystryene (SBS) thermoplastic elastomers in cyclohexane or benzene solution. The molecular weight distribution of both the PBD central block and the final block copolymer is narrow, and the expected molecular weight is obtained. However, mechanical testing, degradation of the PBD component, and use of an excess of s-BuLi compared to DIB suggest that the final copolymers are diblock instead of triblock as expected. The stoichiometric reaction of s-BuLi with DIB in an apolar solvent essentially results in the expected Li diadduct. This organolithium compound does not however react as a difunctional anionic initiator in a hydrocarbon solvent, but rather as a monofunctional compound more likely due to an association process. Addition of enough THF can make approximately two species active per DIB molecule. The addition of small amounts of triethylamine (<10 molecules per organolithium site) does not contribute to the formation of an acceptable difunctional initiator. The 1/1 addition of lithium *tert*-butoxide to the Li diadduct of DIB does not perturb the 1,4-microstructure of PBD, but it does not promote the activity of each metalated site of the initiator.

Introduction

The availability of well-defined and very efficient difunctional anionic initiators is a major interest for the on-purpose synthesis of α,ω-functional (telechelic) polymers and ABA triblock copolymers by a two-step method. A considerable effort has been devoted to the synthesis of hydrocarbon soluble difunctional organolithium compounds, able to initiate the anionic polymerization of dienes (monomer B in ABA triblocks) and to produce ultimately thermoplastic elastomers.[1-10] Indeed polar solvents, such as tetrahydrofuran (THF), lead to a high 1,2-microstructure for polybutadiene instead of a predominant 1,4-enchainment (80–90%), which is required for promoting the most desirable elastomeric properties.

Two general routes to hydrocarbon soluble difunctional initiators have been reported in the scientific literature. The first one relies upon the coupling of radical anions. As an example, Morton et al. have published the synthesis of 1,1-diphenylethylene (DPE) dimers in the presence of a fine dispersion of lithium in an anisole-containing hydrocarbon solvent.[1] The most recently reported method is based on the metalation of a precursor comprising two nonconjugated reactive double bonds. The precursor should have a low ceiling temperature in order to avoid competition between metalation and homopolymerization. 1,3-Divinylbenzene (DVB), 1,3-bis(1-phenylethenyl)benzene (PEB), and 1,3-diisopropenylbenzene (DIB) have been proposed as potential precursors.[2,10,5] Nevertheless, DVB is partly oligomerized,[9] whereas a bimodal molecular weight distribution (MWD) is reported for polymers prepared from the PEB diadduct.[11] DIB is most favorable because of a low ceiling temperature, which efficiently prevents homopolymerization to occur.[5] The reaction of DIB with *sec*-butyllithium (s-BuLi) is slow in an apolar solvent, and it is advantageously accelerated when performed at 50-60 °C. Precipitation usually occurs when the reaction is close to completion. According to Rempp et al., metalated DIB is an efficient difunctional initiator in hydrocarbon solvents.[5,8] Sharkey et al. have reported on the favorable effect of triethylamine on the DIB metalation rate and the Li diadduct solubility.[3] They have added the diadduct with a few isoprene units, in order to form a difunctional initiator of an improved solubility. Synthesis of polyisoprene of a monomodal and narrow MWD has accordingly been reported (0.1 mol of triethylamine per mol of organolithium site).[3] These encouraging conclusions have been criticized by Buchan et al. These authors have reported that the reaction of DIB with s-BuLi, in benzene or cyclohexane, leads to a mixture of di- and polyfunctional compounds rather than to a difunctional initiator, even at 55 °C and in the presence of triethylamine.[12] Recently, Hogen-Esch et al. have revisited the problem and concluded that the addition of s-BuLi to DIB in a 2/1 molar ratio produces a nearly perfect difunctional compound, when carried out in benzene, at 50 °C, for 1 h.[13] Actually, PMMA–PBD–PMMA triblock copolymers (where PMMA and PBD stand for poly(methyl methacrylate) and polybutadiene, respectively) have been synthesized as follows. PBD has been first polymerized in an apolar solvent, followed by the sequential addition of THF, DPE, and MMA, respectively. The formation of a triblock copolymer has been claimed.[13]

The key point in the present debate is that most arguments are based on size exclusion chromatography (SEC) of the final (co)polymers, rather than on their actual structure and ultimate mechanical properties, particularly when thermoplastic elastomers are concerned. Even though the diadduct results from the addition of s-BuLi to DIB, it might be associated in the apolar solvent in such a way that only part of the organolithium groups contribute to the monomer conversion. In the particular case where only half the organolithium species of the diadduct initiates the sequential polymerization of butadiene and, for example, styrene, a diblock of a narrow MWD should be formed instead of the expected triblock copolymer. The ultimate mechanical properties would accordingly be very poor. This paper focuses on that problem and reports on the mechanical performances and, above all, on the molecular structure of butadiene–styrene block copolymers

---

® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0024-9297/94/2227-5957$04.50/0

Table 1. Characterization of PBD/PS Block Copolymers Prepared by Using the s-BuLi/DIB Diadduct in Cyclohexane

	$\bar{M}_n$									
	expected[a]		experimental[b]		$\bar{M}_w/\bar{M}_n$		recovered PS			
sample	PBD block	PS block	PBD block	PS block	PBD	copolymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	ultimate tensile strength (MPa)	elongation at break (%)
1	10 000	15 000	10 000	18 000	1.05	1.30	40 000	1.35	brittle	
2	20 000	15 000	20 000	18 000	1.05	1.30	40 000	1.30	weak	
3	60 000	20 000	55 000	25 000	1.05	1.25	45 000	1.35	weak	
4	70 000	15 000	70 000	13 000	1.10	1.20	30 000	1.35	0.61	206

[a] Expected value for a SBS triblock copolymer. [b] Experimental value calculated, for a triblock structure, from SEC and ^{1}H-NMR data.

synthesized by using the 2/1 s-BuLi/DIB adduct as an initiator, in an apolar solvent.

Experimental Section

Chemicals. Butadiene (Air Liquid Co.) was condensed after passing through columns containing freshly crushed CaH_2 and then distilled over n-BuLi just prior to use. Styrene (Janssen) was dried over CaH_2 for 2 days and then added with fluorenyllithium and distilled just before use. 1,3-Diisopropenylbenzene (Aldrich) was dried over CaH_2 for 1 day, distilled from fluorenyllithium, and then diluted with dry cyclohexane (or benzene). THF was purified by refluxing over a Na-benzophenone complex Toluene, benzene, and cyclohexane (CH_x) were refluxed over CaH_2 for several days and then added with living polystyryllithium oligomers and distilled just prior to use. A commercially available s-BuLi solution (Janssen) was analyzed by the double titration method with 1,2-dibromobutane.[14] Methyl methacrylate (Aldrich) was dried over CaH_2 for 2 days and then added with triethylaluminum ($AlEt_3$) until a persistent yellow-green complex was formed and finally distilled before use. Diphenylethylene (Aldrich) was dried over n-BuLi and diluted with dry CH_x. This solution was added with diphenylmethyllithium and distilled before use.

Polymerization Procedures. Block copolymerization was carried out under an inert atmosphere in a previously flamed glass reactor equipped with rubber septums. Syringes and stainless steel capillaries were used in order to transfer solvent, monomer, and initiator. As a typical example, the hydrocarbon solvent (mainly cyclohexane) was added into the glass reactor, followed by s-BuLi and DIB, respectively. Concentration of DIB and s-BuLi was ca. 5×10^{-4} and 1.0×10^{-3} mol/L, respectively. After a 1–2 h reaction time, at 50 °C under stirring, the solution of the red initiator was cooled down to 0 °C, and butadiene was then introduced. Concentration of butadiene was ca. 20–30 g/L, depending on the requested molecular weight. Upon addition of butadiene, the red color of the initiator rapidly changed to a faint color that persisted during the whole polymerization process. Polymerization was allowed to proceed overnight at 50 °C. Either styrene or MMA was finally polymerized. Styrene was polymerized either at 50 °C for 4 h or at room temperature for 4 h in the presence of THF. When MMA was concerned, dry THF was previously added into the reactor in a well-defined THF/hydrocarbon solvent volume ratio. The living PBD chains were then end-capped with diphenylethylene (5-fold excess) and used to initiate the MMA polymerization at −78 °C. After MMA addition, the deep red color, characteristic of DPE–Li rapidly disappeared and the polymerization solution became colorless. Polymerization was terminated with a methanol/HCl mixture (previously flushed with nitrogen), and the copolymer was precipitated into methanol. IRGANOX 1010 was used as an antioxidant.

Characterization Techniques. Molecular weight and MWD were determined 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 at 40 °C was the elution solvent. A conversion factor of 0.55 was found to be appropriate to the calculation of PBD molecular weight. Composition of copolymers was analyzed by ^{1}H NMR spectroscopy (Brucker AN-400 spectrometer). UV spectra were recorded by using a Philips PU 8700 apparatus. Tensile strength and elongation at break were measured with a Adharmel Lomargy tensile tester. Samples were compression-molded at 200 °C for 5 min and cut into DIN 53448 specimen. Cross-head speed was 50 mm/min. The PBD block of copolymers was cleaved by reaction with H_2O_2 in the presence of osmium tetroxide. Block copolymer (0.5–0.6 g) was transferred into a flask containing 50 mL of 1,2-dichlorobenzene and 10 mL of H_2O_2 (35 wt % solution in water). Finally, 1 mL of a 0.003 M osmium tetroxide solution in benzene was added and the reaction mixture was heated at 90 °C for 2 h. After cooling to 25 °C, the solution was slowly poured into 300 mL of methanol under stirring. PS (or PMMA) was filtrated, washed with methanol, and dried, at 40 °C, in vacuo.

Results and Discussion

As reported in the scientific literature, DIB has been reacted with 2 equiv of s-BuLi, at 50 °C, for 1 h in cyclohexane or benzene. The addition product has been used as an initiator for the sequential polymerization of butadiene and styrene, respectively. Table 1 reports the characteristic features of the recovered polybutadiene (PBD)–polystyrene (PS) block copolymers. In agreement with Rempp et al.[8] and Hogen-Esch et al.,[13] the MWD of both the PBD central block (<1.10) and the final triblock copolymer (<1.30) is narrow, and the expected molecular weight is obtained. Nevertheless, the tensile properties of the block copolymers—particularly of sample 4, the composition of which is close to commercial SBS thermoplastic elastomers—are disappointing and might suggest that the copolymers are actually not of a triblock structure.

Since SEC does not allow diblock and triblock copolymers to be discriminated, a method based on the cleavage of the central polybutadiene block has been used in order to fill this gap. It is known that PBD in contrast to PS is cleaved into small fragments when reacted with a hydroperoxide in the presence of osmium tetroxide.[15] Thus, if a block copolymer of butadiene and styrene is synthesized and assumed to be a triblock copolymer, then PS recovered after PBD degradation should be of the expected chain length, but of a 2-fold higher molecular weight in case of formation of a diblock copolymer. The efficiency of the degradation procedure reported in the Experimental Section has been first confirmed when applied to butadiene–styrene block copolymers. The FTIR and NMR analysis of the recovered polymeric material is consistent with the complete cleavage of the PBD block after a 2 h reaction time. Indeed, the characteristic absorption bands and chemical shifts of PBD have completely disappeared, in contrast to those of PS. SEC has also supported that PS chain length does not change under the experimental conditions used for PBD degradation. The molecular weight ($\bar{M}_n$) of PS recovered after degradation of the block copolymers listed in Table 1 is reported in the same table and clearly indicates that these copolymers are essentially diblock in structure rather than triblock. Thus, when the anionic polymerization of butadiene is initiated with the 2/1 s-BuLi/DIB adduct in an apolar solvent, the polybutadienyllithium chains appear to be monofunctional toward the sequential styrene polymerization.

The first reason for the formation of a diblock copolymer might be found in the reaction of s-BuLi with DIB which

Table 2. Characterization of Polymers Initiated by the Reaction Product of an Excess of s-BuLi with DIB, in a Hydrocarbon Solvent

sample	polymer	solvent	s-BuLi (mol)	DIB (mol)	amount of monomer (g)	amount of monomer/[s-BuLi] − [DIB] (g/mol)	$\bar{M}$n	$\bar{M}$w/$\bar{M}$n
1	PS	cyclohexane	2.53×10^{-4}	8.32×10^{-5}	1.5	9 000	9 500	1.05
2	PS	cyclohexane	3.45×10^{-4}	8.32×10^{-5}	1.8	7 000	6 500	1.05
3	PBD	cyclohexane	2.53×10^{-4}	8.32×10^{-5}	2.6	15 000	15 000	1.05
4	PBD	cyclohexane	3.45×10^{-4}	8.32×10^{-5}	2.6	10 000	11 500	1.05
5	PS	benzene	1.84×10^{-4}	4.16×10^{-5}	1.8	13 000	13 500	1.05

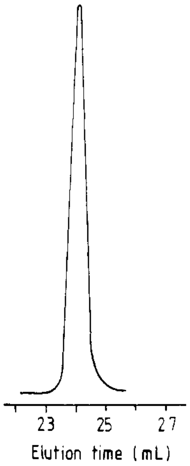

Figure 1. SEC trace of PBD initiated with the addition product of 4 mol of s-BuLi per mol of DIB, in cyclohexane (sample 4 in Table 2).

Table 3. Characterization of PBD/PMMA Block Copolymers by Using a 2/1 s-BuLi/DIB Adduct

$\bar{M}$n						recovered PMMA	
expected[a]		experimental[b]		$\bar{M}$w/$\bar{M}$n			
PBD	PMMA	PBD	PMMA	PBD	copolymer	$\bar{M}$n	$\bar{M}$w/$\bar{M}$n
30 000	10 000	30 000	10 000	1.10	1.25	20 000	1.25
40 000	10 000	43 000	9 000	1.10	1.20	20 000	1.15

[a] Calculated for a triblock copolymer. [b] Calculated from SEC and ^{1}H NMR (in case of a triblock copolymer).

would lead to a monolithium adduct. This hypothesis is however not supported by evidence reported by several research groups[8,12,13] and by the hereafter discussed experimental data. In fact, the UV and NMR spectra confirm that the double bond of DIB completely disappears upon the addition reaction under the used conditions. As previously suggested, a second assumption might rely upon the initiation efficiency of the actually formed Li diadduct which would initiate PBD chains propagating on only one side (species **I**), instead of bearing two independently growing sites (species **II**) in hydrocarbon solvents.

Li PBD–DIB Li (**I**)   Li PBD–DIB–PBD Li (**II**)

According to the previously cited papers, the synthesis of a useful difunctional initiator requires a strict control of the 2/1 s-BuLi/DIB stoichiometry, otherwise the synthesized polymer has a multimodal MWD.[11] Surprisingly enough, this conclusion has not been supported by experiments carried out under the conditions reported in the experimental part. Indeed, homopolymers of a narrow monomodal MWD have been prepared even when the s-BuLi/DIB molar ratio is higher than 2. If the diadduct is formed under these conditions, the actual initiator should consist of a mixture of diadduct and unreacted s-BuLi. The anionic polymerization of styrene and butadiene should accordingly lead to a bimodal MWD, provided that the diadduct reacts as a difunctional initiator. The size exclusion chromatogram of Figure 1 shows that PBD prepared in cyclohexane, by using a 2-fold molar excess of s-BuLi with respect to DIB, has a narrow monomodal MWD. This observation has been repeatedly reported, particularly for the experiments listed in Table 2. This table also compares the experimental $\bar{M}$n for PBD and PS to the value calculated on the assumption that the formed lithium diadduct acts as a monofunctional initiator, thus leading to species **I**. Then, the actual initiator concentration is the difference between the initial concentrations of s-BuLi and DIB, respectively. There is a very good agreement between calculated and experimental values, which gives credit to the existence of species of type **I**.

Addition of THF to the Apolar Solvent. Hogen-Esch et al. have reported the successful synthesis of PMMA–PBD–PMMA triblock copolymers of a high 1,4-microstructure for the central polydiene block.[13] Butadiene polymerization has been initiated with the 2/1 s-BuLi/DIB adduct in benzene. The apolar solvent has then been added with THF (50 vol %), which is expected to shift an aggregation equilibrium toward nonassociated species. The living polybutadienyl chains have finally been end-capped with DPE and used to initiate the MMA polymerization at −78 °C. This sequential polymerization of butadiene and MMA has been carried out according to this recipe. Table 3 shows that there is a good agreement between the experimental and theoretical molecular weights and that the final block copolymers are of a narrow MWD. Nevertheless, the degradation of these copolymers by H_2O_2 in the presence of osmium tetroxide releases PMMA (PMMA is stable under these conditions), the molecular weight of which agrees with a diblock structure. Therefore, it must be concluded that the addition of THF to polybutadienyl chains does not allow PMMA to grow from each extremity of these chains but rather from one of them. This conclusion is confirmed when the butadiene–MMA sequential copolymerization is repeated under the same conditions except for the initiator which has been prepared by using a 2-fold molar excess of s-BuLi with respect to DIB. Figure 2 shows a narrow monomodal MWD for PBD synthesized in the apolar solvent. The same observation is reported when the polybutadienyl chains have been added with DPE before the polymerization of MMA takes place in a THF/benzene (50 vol %) mixture, at −78 °C. From the butadiene polymerization, it results that the Li diadduct is apparently monofunctional and as reactive as s-BuLi in excess. Upon the addition of THF, polybutadienyl chains of type **I**, i.e. initiated by the Li diadduct, are expected to be dissociated and to initiate a triblock copolymerization. In contrast, polybutadienyl chains initiated by the excess of s-BuLi should lead to the formation of a diblock copolymer. Since this is not the case (monomodal MWD), only one of the two organolithium sites of the type **I** polybutadienyl chains participate in the MMA polymerization. An explanation might be that the species directly associated to the DIB moiety of type **I** chains is sterically hindered to the point where the end-capping with DPE is prevented to occur, which would

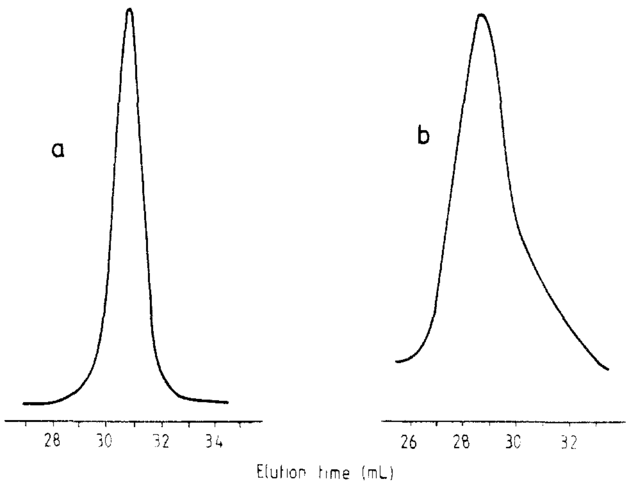

Figure 2. SEC traces of a PBD–PMMA block copolymer initiated with the addition product of 4 mol of s-BuLi per mol of DIB: (a) PBD block ($\bar{M}$n = 2200, in benzene), (b) PBD–PMMA block copolymer (in 50/50 v/v benzene/THF).

lead to the very early termination of the MMA polymerization.

In order to get a more straightforward insight into the effect of THF on the behavior of the Li diadduct prepared in an apolar solvent, homopolymerization of styrene has been first considered. When an excess of s-BuLi has been reacted with DIB, and THF has been added to the apolar solvent, PS has a multimodal MWD as shown by Figure 3. The two main populations of PS chains are formed in comparable proportions. The shortest chains (peak I) have been more likely initiated by the unreacted s-BuLi, whereas the high $\bar{M}$n fraction (peak II) should result from the Li diadduct, which acts now as a difunctional initiator. Peak III, which is comparatively smaller than the two first peaks might result from polyfunctional DIB oligomers. The assignment of the elution peaks is in agreement with the following observations. Samples a and b in Figure 3 differ from each other only by the excess of s-BuLi with respect to DIB. If the diadduct formation is complete, the unreacted s-BuLi should amount to one-third and one-half of the total amount of organolithium compounds in samples a and b, respectively. Peak I is actually smaller than peak II for sample a, whereas the two peaks are in even proportions for sample b. Peaks I and II are also of the same height in sample c, which is similar to sample b, except for the apolar solvent. When the excess of s-BuLi is increased (from sample a to samples b and c), the relative importance of DIB oligomers decreases. The same effect is promoted by the substitution of CH_x by benzene, all the other conditions being the same. These two observations are in agreement with those reported by Rempp et al.[8,16] It is clear from Figure 3 that the metalation of DIB by s-BuLi is quantitative and that the Li diadduct initiates chains growing from each extremity when the polymerization solvent is polar enough.

The conclusion that THF promotes the formation of chains of type **II** is also confirmed by the formation of the expected SBS triblock copolymers when THF (10 vol %) is added to living polybutadienyl chains in CH_x just prior to the sequential polymerization of styrene. Table 4 shows that the on-purpose degradation of the PBD block releases PS, the molecular weight of which is approximately 20% higher than expected for a pure triblock structure. The formation of an essentially triblock copolymer is also observed when only 1 vol % THF is added to the apolar solvent. As an additional piece of evidence, butadiene has been polymerized in CH_x by the addition product of s-BuLi to DIB used in a 4/1 molar ratio. Figure 4 supports conclusions drawn from Figure 2, since, in the absence of THF, the MWD of the final copolymer remains monomodal. In contrast, upon the addition of as small as 1 vol % THF to CH_x (Figure 5), the MWD of the block copolymer is split into two peaks, which should be assigned to copolymer chains initiated by difunctional (dissociated chains of type **I**) and monofunctional polybutadienyl chains, respectively.

All in all, experimental data from Figures 3–5 and from Table 4 convincingly support (i) the quasi-complete conversion of DIB into a Li diadduct, (ii) the formation of type **I** chains in an apolar solvent, i.e. chains initiated by the coordinatively associated Li adduct, and (iii) the general activation of the second organolithium species of the type **I** chains upon the addition of THF (1–10 vol %) to the apolar solvent. The latter effect indicates that the inactivity of half the organometallic sites of chains initiated by the Li diadduct should be due to a coordinative association effect.

A last piece of information is worth being mentioned. Indeed, PBD chains of a low molecular weight have been initiated with the 2/1 s-BuLi/DIB adduct, in the presence and absence of THF, respectively. The two samples have been added with enough THF before being completely

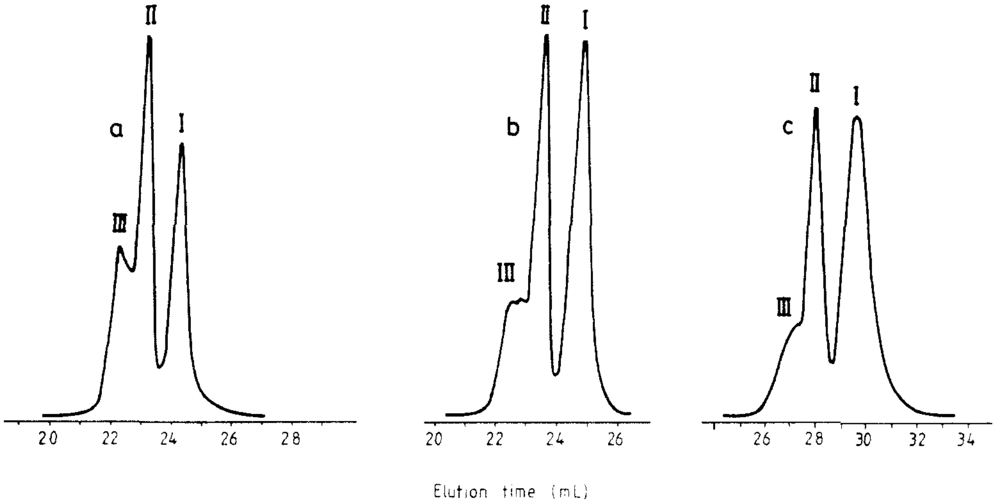

Figure 3. SEC traces of PS initiated with the addition product of a molar excess of s-BuLi to DIB in the presence of 10 vol % THF: (a) cyclohexane, s-BuLi/DIB = 3, (b) cyclohexane, s-BuLi/DIB = 4, (c) benzene, s-BuLi/DIB = 4.

Table 4. Characterization of Polystyrene (PS) Released by the Degradation of PBD–PS Block Copolymers, Prepared in Cyclohexane by Using the Lithium Diadduct of DIB as an Initiator and THF (10 vol %) Just Prior to the Polymerization of Styrene

$\bar{M}_n$							
expected[a]		experimental[b]		$\bar{M}_w/\bar{M}_n$		recovered PS	
PBD block	PS block	PBD block	PS block	PBD	copolymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
20 000	30 000	25 000	30 000	1.05	1.35	35 000	1.10
40 000	25 000	40 000	25 000	1.05	1.20	30 000	1.10
50 000	25 000	50 000	25 000	1.10	1.25	30 000	1.15

[a] Calculated from the monomer to initiator ratio (assuming a perfectly triblock copolymer). [b] Calculated from SEC and ^{1}H-NMR data (same assumption).

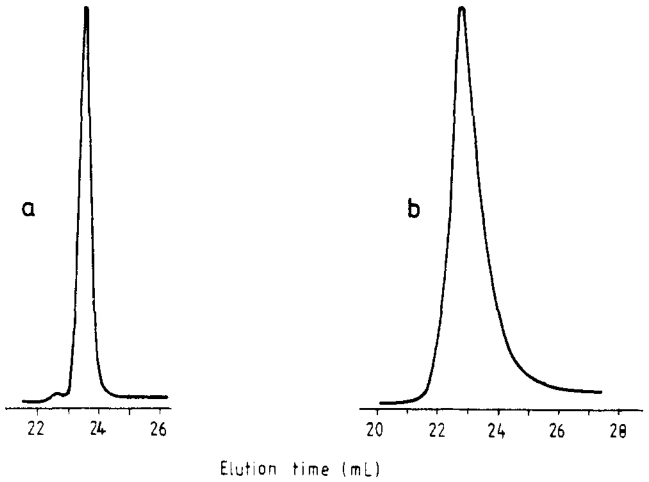

Figure 4. SEC traces of a PBD–PS block copolymer initiated with the addition product of 4 mol of s-BuLi per mol of DIB: (a) PBD block ($\bar{M}_n$ = 16 000, cyclohexane), (b) PBD–PS copolymer (cyclohexane).

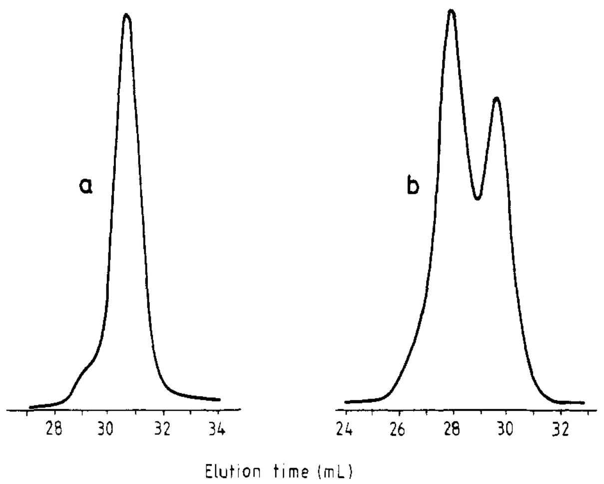

Figure 5. SEC traces of a PBD–PS block copolymer initiated with the addition product of 4 mol of s-BuLi per mol of DIB: (a) PBD block ($\bar{M}_n$ = 2200, cyclohexane), (b) PBD–PS copolymer (cyclohexane + 1 vol % THF).

carboxylated by CO$_2$. In the absence of THF, side reactions might occur leading to ketone structures at the expense of carboxylic acid groups. Depending on the polymerization conditions, species **III** and **IV** should be ultimately formed, when the polymerization solvent is free from THF or not, respectively.

HO$_2$C–PBD–DIB–CO$_2$H
(III)

HO$_2$C–PBD–DIB–PBD–CO$_2$H
(IV)

Due to the close vicinity of one carboxylic acid group to the aromatic ring of DIB in structure **III**, the UV absorption of DIB might be shifted. It has been first ascertained that a change in the PBD microstructure (mainly 1,4 in structure **III** and 1,2 in structure **IV**) has no significant effect on the UV absorption of the aromatic ring of DIB. Figure 6 compares the effect of THF on the UV absorption spectrum of α,ω-carboxylic acid polybutadiene chains. A shift from 272 nm down to 262 nm when THF is used can be regarded as an evidence for the formation of structure **III** in an apolar solvent and structure **IV** in a THF-containing polymerization medium.

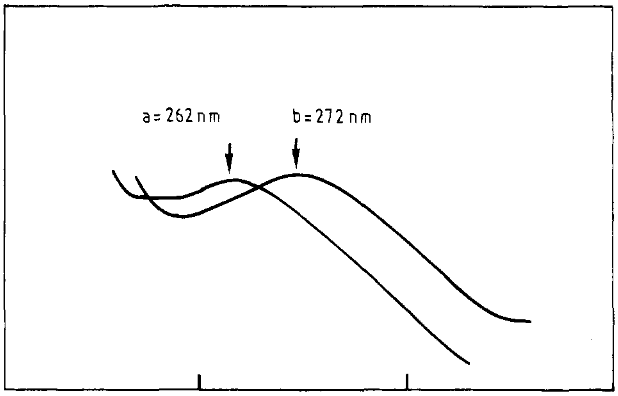

Figure 6. UV spectra of a low $\bar{M}_n$ PBD ($\bar{M}_n$ = 2000) terminated by CO$_2$. Polymerization solvent: (a) 10 vol % THF in cyclohexane, (b) cyclohexane.

Addition of Triethylamine to the Apolar Solvent. Butadiene–styrene block copolymers have been synthesized by using the initiator prepared according to the procedure reported by Sharkey et al.,[3] which consists in adding triethylamine to the Li diadduct of DIB. Although block copolymers are of a very narrow MWD, they have very poor mechanical properties, which cannot be accounted for by the PBD microstructure which is predominantly 1,4 (Table 5). The molecular weight of PS chains recovered after the degradation of the central PBD blocks is in agreement with a diblock instead of a triblock structure.

Figure 7 shows the SEC trace of PS prepared by using an initiator which consists of a 2-fold molar excess of s-BuLi compared to DIB. Various amounts of triethylamine have been added to the initiator. When the amine content is below 3.0 mol per mol of organolithium site, PS is of a narrow monomodal MWD. It is thus clear that the Li diadduct behaves as a monofunctional initiator under these experimental conditions. When the amine content is increased up to 10 mol per mol of lithium site, part of the Li diadduct acts as a difunctional initiator, since a minor fraction of chains of a molecular weight twice as high as the major component is now formed.

From the experimental observations of Table 5 and Figure 7, it must be concluded that the Li diadduct does not act as a difunctional initiator under the conditions recommended by Sharkey et al. An exceedingly high amount of amine might be necessary, which would however

Table 5. Effect of Triethylamine on the Butadiene–Styrene Copolymerization Initiated with the 2/1 s-BuLi/DIB Adduct in Cyclohexane

amine content (mol/Li$^+$)	$\bar{M}_n$ (experimental)[a]		$\bar{M}_w/\bar{M}_n$		1.4-microstructure[b] of the PBD block (%)	ultimate tensile strength (MPa)	elongation at break (%)	recovered PS	
	PBD	PS	PBD	copolymer				$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.1	70 000	13 000	1.10	1.20	84.5	0.85	60	31 000	1.25
1.0	85 000	12 000	1.05	1.20	84.5	1.10	110	25 000	1.30
3.0	95 000	15 000	1.15	1.25	88.5	0.97	90	30 000	1.25
10.0	95 000	16 000	1.10	1.20	83.5	1.50	52	30 000	1.30

[a] Calculated from SEC and ^{1}H-NMR data for a triblock SBS structure. [b] Measured by ^{1}H-NMR.

Table 6. Effect of Lithium *tert*-Butoxide (t-BuOLi/s-BuLi = 1.1) on the Butadiene–Styrene Copolymerization Initiated with the Lithium Diadduct of DIB in Cyclohexane

$\bar{M}_n$[a] (experimental)		$\bar{M}_w/\bar{M}_n$		1.4-microstructure[b] of the PBD block (%)	ultimate tensile strength (MPa)	elongation at break (%)	recovered PS	
PBD	copolymer	PBD	copolymer				$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
55 000	10 000	1.10	1.25	86.0	0.74	380	25 000	1.25
55 000	10 000	1.10	1.35	83.5	0.78	370	25 000	1.20
55 000	10 000	1.10	1.25	85.5	0.67	220	20 000	1.25

[a] Calculated from SEC and ^{1}H-NMR data for a triblock SBS structure. [b] Measured by ^{1}H-NMR.

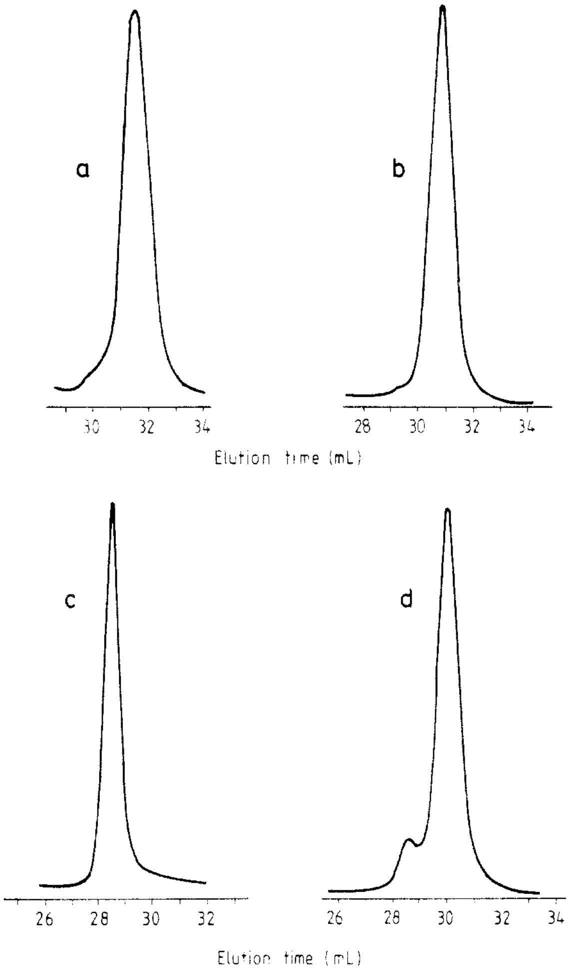

Figure 7. SEC traces of PS initiated with the 4/1 s-BuLi/DIB addition product in cyclohexane added with various amounts of triethylamine: (a) 0.1 mol of triethylamine per mol of lithium, (b) 1.0 mol triethylamine per mol of lithium, (c) 3.0 mol of triethylamine per mol of lithium, (d) 10.0 mol of triethylamine per mol of lithium.

result in an undesirable high 1,2-microstructure for the PBD block.

Addition of Lithium *tert*-Butoxide to the Apolar Solvent. The addition of s-BuLi to 1,3-bis(1-phenylethenyl)benzene is fast and leads to the formation of the corresponding dilithium species. The initiator is soluble in hydrocarbons, and it has been reported by McGrath et al. as an efficient difunctional initiator for the synthesis of homopolymers and triblock copolymers of a relatively narrow MWD.[10] There are however contradictory reports about the efficiency of the dilithium initiator which would actually produce bimodal or at least very broad MWD.[11] Quirk et al. have attributed this poor control to chain-end association effects.[11] They have proposed to improve the situation by the addition of lithium alkoxide, which would have a favorable dissociation effect.

In order to estimate the beneficial effect that lithium *tert*-butoxide might have on the butadiene–styrene sequential polymerization, the lithium diadduct of DIB has been added with 1 equiv of this alkoxide. Table 6 shows the main characteristics of the block copolymers accordingly prepared. The first piece of information is that the addition of t-BuOLi to the Li diadduct initiator in a 2/1 molar ratio has no significant effect on the microstructure of PBD. Moreover, the mechanical properties are very poor, although the PBD block and the final block copolymer exhibit a low polydispersity and a molecular weight close to the expected values (55 000 and 80 000, respectively). This observation is in agreement with the degradation of the PBD component, which releases PS chains, the length of which fits in a diblock structure instead of the expected triblock copolymer. Thus, lithium *tert*-butoxide does not appear to be a very effective dissociating agent for the Li diadduct of DIB in CH$_x$, at least when used in an equimolar amount with respect to the organolithium sites of the diadduct.

Conclusion

The most important conclusion of this investigation is that the stoichiometric reaction of s-BuLi with DIB in an apolar solvent essentially forms the expected Li diadduct. However, this organolithium compound does not behave as a difunctional anionic initiator in hydrocarbon solvents (i.e. cyclohexane, benzene, and toluene) but rather as a monofunctional compound. An association process might be at the origin of this effect, as previously suggested by Quirk et al.[11]

The addition of THF (1–10 vol % of the apolar solvent) can make approximately two species active per DIB molecule. Nevertheless, even under these experimental conditions, the control is not fine enough to get strictly difunctional chains and SBS triblock copolymers. The addition of small amounts of triethylamine (<10 mol per mol of organolithium site) does not contribute to the formation of an acceptable difunctional initiator. Higher amine contents might be requested, which would however result in an undesirable 1,2-microstructure of PBD chains. Finally, the addition of lithium *tert*-butoxide to the Li diadduct of DIB (2/1 molar ratio) does not perturb the 1,4-microstructure of PBD, but it does not promote the activity of each metalated site of the initiator.

The selective degradation of the PBD component of butadiene/styrene block copolymers has proved to be a very successful although indirect method to analyze the initiation efficiency of the s-BuLi/DIB diadduct. The use of an excess of s-BuLi together with the SEC analysis of the accordingly produced polymer chains has also contributed to a better knowledge of the associative behavior of the Li diadduct in apolar solvents.

Acknowledgment. The authors are very grateful to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" in the frame of the "Poles d'Attraction Interuniversitaire:Polymères" and Koninklijke/Shell Laboratorium, Amsterdam, for financial and scientific support. Dr. F. H. Van Der Steen and Dr. B. Van Wingerden from Shell Co. are particularly thanked for many stimulating discussions. The authors are also indebted to Mrs. Luthers for skillful technical assistance.

References and Notes

(1) Fetters, L. J.; Morton, M. *Macromolecules* **1969**, *2*, 435.

(2) Lutz, P.; Franta, E.; Rempp, P. C. R. *Hebd, Seances Acad. Sci. Ser. C* **1976**, *283*, 123.

(3) Foss, R. P.; Jacobson, H. W.; Sharkey, W. H. *Macromolecules* **1977**, *10*, 287.

(4) Tung, L. H.; Lo, G. Y.-S.; Beyer, D. E. *Macromolecules* **1978**, *11*, 616.

(5) Beinert, G.; Lutz, P.; Franta, E.; Rempp, P. *Makromol. Chem.* **1978**, *179*, 551.

(6) Fetters, L. J.; Kamienski, C. W.; Morrison, R. C.; Young, R. N. *Macromolecules* **1979**, *12*, 344.

(7) Guyot, P.; Favier, J. C.; Uytterhoeven, H.; Fontanille, M.; Sigwalt, P. *Polymer* **1981**, *22*, 1724.

(8) Lutz, P.; Franta, E.; Rempp, P. *Polymer* **1982**, *23*, 1953.

(9) Bandermann, F.; Sperikamp, H. D.; Weigel, L. *Makromol. Chem.* **1985**, *186*, 2017.

(10) Long, T. E.; Broske, A. D.; Bradley, D. J.; McGrath, J. E. *J. Polym. Sci.: Part A, Polym. Chem.* **1989**, *27*, 4001.

(11) Quirk, R. P.; Ma, J. J. *Polym. Int.* **1991**, *24*, 197.

(12) Cameron, G. G.; Buchan, G. M. *Polymer* **1979**, *20*, 1129.

(13) Ladd, B. J.; Hogen-Esch, T. E. *Polym. Prepr.* **1989**, *30*, 26.

(14) Gilman, H.; Cartledge, F. K. *J. Organometal. Chem.* **1964**, *2*, 447.

(15) Kolthoff, I. M.; Lee, T. S.; Carr, C. W. *J. Polym. Sci.* **1946**, *1*, 429.

(16) Lutz, P.; Beinert, G.; Franta, E.; Rempp, P. *Eur. Polym. J.* **1979**, *15*, 1111.