Macromolecules **1996,** *29,* 2738−2745

Difunctional Initiators Based on 1,3-Diisopropenylbenzene. 3. Synthesis of a Pure Dilithium Adduct and Its Use as Difunctional Anionic Polymerization Initiator[†]

Y. S. Yu, Ph. Dubois,[‡] R. Jérôme,* and Ph. Teyssié

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

Received August 8, 1995; Revised Manuscript Received January 2, 1996[⊗]

ABSTRACT: The addition reaction of *tert*-butyllithium (*t*-BuLi) to 1,3-diisopropenylbenzene (1,3-DIB) has been studied. Under optimized conditions, i.e., reaction in cyclohexane at −20 °C and dropwise addition of 1,3-DIB to a 1:1 *t*-BuLi−triethylamine (Et_3N) complex followed by a 1 h postreaction period, a pure diadduct is formed without concomitant oligomerization of 1,3-DIB. The behavior of this diadduct has been investigated, in apolar and polar solvents; triblock copolymers have been prepared and found to have interesting mechanical properties.

Introduction

Great attention has been paid to the modification of commercially available thermoplastic elastomers, for example, polystyrene−polybutadiene−polystyrene (SBS) triblock copolymers, over the past decades.[1−5] Indeed, the strength of these thermoplastic elastomers relies on the ability of the glassy polystyrene domains to yield under stress and undergo inelastic deformation. The strength of the SBS thermoplastic elastomers markedly drops above 60 °C, i.e., as the glass transition temperature (T_g) of the polystyrene domains is approached.[6,7] The availability of end blocks of a higher temperature resistance might be a valuable answer to that problem. Poly(methyl methacrylate) (PMMA) is such a potential candidate, since its T_g is around 130 °C when the syndiotactic content reaches 80%.[8] So far, no well-defined PMMA−PBD−PMMA triblock copolymer has been reported in the scientific literature. A key problem for the synthesis of triblock copolymers containing PMMA outer blocks is the inability of PMMA anionic species to initiate the polymerization of BD. The use of a difunctional initiator for BD is thus the only way to go, which explains why a lot of patents and papers have claimed the synthesis of difunctional initiators, and particularly of organolithium ones since they give a high percentage of the 1,4-diene microstructure necessary for optimal elastomeric properties.[9−19]

Two general methods to prepare such difunctional initiators have been investigated, i.e., the coupling of radical anions, and the use of a precursor having two reactive double bonds which further react with 2 equiv of a monofunctional organolithium compound. One example for the radical anion coupling has been given by Morton et al.[1] More recent interest has focused on precursors containing two nonconjugated double bonds, of a high ceiling temperature so as to avoid competition between metalation and homopolymerization. Although bis-1,1-diphenylethylene (BDPE) compounds have been reported as useful precursors of efficient difunctional initiators,[10,18,19] high cost and purification problems may stem their use on an industrial scale. Since 1,3-diisopropenylbenzene (1,3-DIB) is much cheaper and is commercially available, considerable effort has been devoted to its conversion into an efficient difunctional anionic initiator. At first, Rempp et al. have claimed that reaction of 2 mol of *sec*-butyllithium (*sec*-BuLi) with 1 mol 1,3-DIB could meet that challenge in anionic polymerizations.[11] Also, Foss et al. have reported on a favorable effect of triethylamine on 1,3-DIB metalation rate and Li diadduct solubility.[9] However, Cameron et al. have criticized these conclusions[17] and found that a mixture of oligomers and diadduct results from this addition reaction. Finally, Hogen-Esch et al. have revisited the problem and concluded that the addition of *sec*-BuLi to 1,3-DIB in a 2/1 molar ratio produces a nearly perfect difunctional compound, when carried out in benzene at 50 °C for 1 h.[4]

However, investigations in our laboratory have recently demonstrated that the conclusions from the later authors cannot explain all the experimental features, and a mechanism for the addition reaction and the anionic initiation of anionic polymerization by the *sec*-BuLi/1,3-DIB diadduct has been proposed and assessed.[20,21] In fact, the ceiling temperature of 1,3-DIB is somewhat higher than 50 °C, and oligomers are always the main product of the addition reaction of *sec*-BuLi onto 1,3-DIB. Under the conditions used to prepare the difunctional initiator solution, i.e., mixing of 1,3-DIB and *sec*-BuLi in a 1:2 stoichiometric ratio in cyclohexane, a mixture of *sec*-BuLi, diadduct, and oligomers is accordingly obtained. When that mixture is used as an initiator for polymerization in the presence of a polar solvent such as THF, initiation by at least monofunctional, difunctional, trifunctional, and tetrafunctional derivatives has been observed.[21] But in apolar solvents, such a mixture gives rise to a polymer with a very narrow molecular weight distribution (MWD) and a functionality of two. It is, however, characterized by a sharp difference in the reactivity of the two sites to the point where the lithium diadduct as well as multilithium oligomers behave in hydrocarbon media as if they are monofunctional initiator.[20] Again, addition of a sufficient amount of THF is able to promote initiation by each di- and multilithium species. This paper reports on the preparation, characterization, and use of a pure dilithium initiator from 1,3-DIB.

Experimental Section

Chemicals. Styrene (Janssen) was dried over CaH_2 for 2 days, then added with fluorenyllithium, and distilled just

---

[†] For the first paper in this series, see ref 20.

[‡] Research Associate by the Belgian National Fund for Scientific Research (FNRS).

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

0024-9297/96/2229-2738$12.00/0

before use. Butadiene (air liquid CO_2) was condensed after passing through a column containing freshly crushed CaH_2 and then distilled over *n*-BuLi 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. Commercially available *tert*-butyllithium and *sec*-butyllithium (Janssen) were analyzed by the double titration method with 1,2-dibromobutane. Cyclohexane, benzene, and diethyl ether were refluxed over CaH_2 for several days. Tetrahydrofuran (THF) was purified by refluxing over a Na−benzophenone complex. All solvents were added with living polystyryl Li oligomers and distilled just prior to use.

Preparation of *tert*-BuLi/1,3-DIB Diinitiator. Optimized reaction conditions include dropwise addition of 1,3-diisopropenylbenzene in cyclohexane to a stirred cyclohexane solution of a 1:1 *tert*-butyllithium−triethylamine complex at −20 °C, followed by a 1 h postreaction period at the same temperature.

Polymerization Procedures. Block copolymerization was carried out under inert atmosphere in a previously flamed glass reactor equipped with rubber septum. Syringes and stainless steel capillaries were used in order to transfer solvent, monomer, and initiator. Butadiene was slowly added to the initiator solution of known concentration at 0 °C. Thereafter, the reaction mixture was kept at 40 °C in a hydrocarbon solvent or at room temperature in the presence of a polar solvent, for 4 h for styrene polymerization and overnight for butadiene polymerization.

Characterization Techniques. 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. All NMR spectra were obtained with a Bruker AM 400 superconducting magnet system operating in the FT mode at 100.6 MHz (^1H) and 155.5 MHz (^7Li), using a deuterium lock (10 volume % C_6D_6 in cyclohexane). ^1H chemical shifts were referred to $(CH_3)_4Si$. ^7Li-NMR shifts were referred to a 0.2 M LiCl solution in D_2O. Tensile strength and elongation at break were measured with a Adharmel Lomargy tensile tester: samples were cyclohexane cast and cut into DIN 53448 specimen, and cross-head speed was 200 mm/min. GC-MS were recorded on HP5890-VGAUTOSPEC Q. Selective degradation experiments were carried out with hydrogen peroxide in the presence of osmium tetroxide as described in a previous paper.[20]

Results and Discussion

Attempts at the Preparation of a Pure Lithium Diadduct of BuLi/1,3-DIB. So far, many efforts to prepare a lithium diadduct using 1,3-DIB as a precursor have failed due to the occurrence of oligomerization: the reaction of 2 equiv of *sec*-BuLi to 1,3-DIB yields indeed a mixture of lithium diadduct, multilithium oligomers, and unreacted *sec*-BuLi in hydrocarbon solvents at temperatures from 20 to 50 °C.[21] The formation of poly(1,3-DIB) is attributed to a ceiling temperature, higher than the investigated range, and as expected, an increase in temperature will be in favor of the diadduct formation (Figure 1a,d). Figure 1d clearly illustrates that the formation of higher molecular weight materials is limited in favor of the diadduct, which is the main product when the reaction temperature is increased up to 80 °C. Unfortunately, it has also been found that the lithium diadduct is decomposed at such a high temperature, by observation of new vinyl resonances, at 4.8−5.6 ppm in the ^1H-NMR spectrum. It must be noted that although unreacted isopropenyl bonds are detected in the product withdrawn in the early stages of reaction, they are no longer visible when the conversion of 1,3-DIB is complete.[21] The experiments also show that all of the 1,3-DIB has been consumed within 20 min at 80 °C, since gas chromatography does not detect its presence anymore. So, the vinyl resonances observed in the ^1H-NMR spectrum upon heating up to 80 °C cannot derive from unreacted isopropenyl groups. As shown below, the loss of LiH by thermolysis of a lithium diadduct could indeed produce a new olefinic bond.[22]

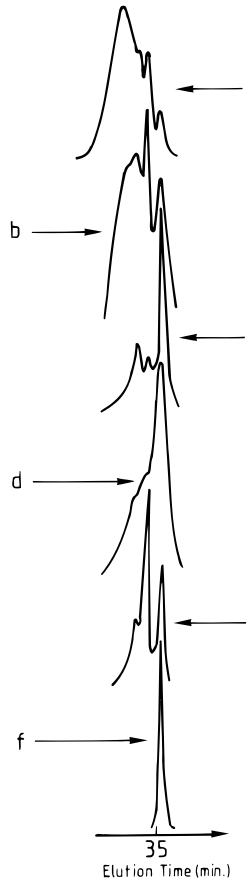
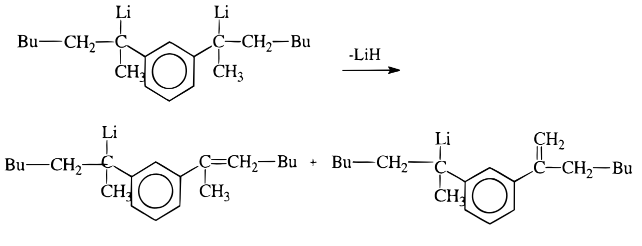


Figure 1. SEC traces of BuLi/DIB adducts prepared in cyclohexane. (a) *sec*-BuLi/1,3-DIB adduct from a 2/1 molar ratio at 50 °C for 1 h; (b) *sec*-BuLi/1,3-DIB adduct from a 4/1 molar ratio at 50 °C for 1 h; (c) *t*-BuLi/1,3-DIB adduct from a 2/1 molar ratio at 50 °C for 1 h; (d) *sec*-BuLi/1,3-DIB adduct from a 2/1 molar ratio at 80 °C for 1 h; (e) *sec*-BuLi/1,3-DIB adduct from a 2/1 molar ratio in the presence of equivalent Et_3N at −20 °C for 1 h; (f) *t*-BuLi/1,3-DIB adduct from a 2/1 molar ratio in the presence of equivalent Et_3N at −20 °C for 1 h.



It is worth noting that the thermally degraded samples had changed from a dark red to a black-purple color with concomitant formation of solids. A previous study has shown that the amount of oligomers markedly decreases with reaction time when all 1,3-DIB is consumed, and that a mixture of diadduct and dimer is the final reaction product at 50 °C after a longer reaction time (20 h).[21] Thermal decomposition has similarly been observed under these conditions, since the vinyl resonances have also been detected in ^1H-NMR spectra of the final products. The thermal degradation of

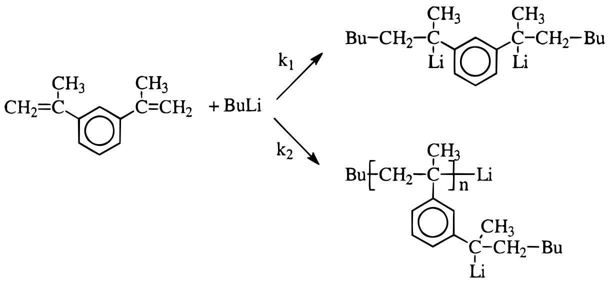
Table 1. Characterization of Polybutadienes Initiated by Thermally Aged Initiator in Cyclohexane[a]

initiator[b]	M_n(calcd)	M_n(exptl)	M_w/M_n
A	2 000	2 000	1.05
A	60 000	60 000	1.15
B	2 000	13 000	1.20
B	60 000	400 000	2.35
C	2 000	18 000	1.20
C	60 000	410 000	1.80

[a] A small amount of anisole is used as additive (ca. 0.5 vol % in cyclohexane) in the butadiene polymerization. [b] Initiator A is prepared at 50 °C for 1 h; initiator B is prepared at 50 °C for 20 h; initiator C is prepared at 80 °C for 1 h.

lithium species is also evidenced by the results listed in Table 1, which indicate a loss of control of polybutadiene molecular weight when a thermally aged initiator is used. In order to reject the argument that the loss of active species in apolar solvents is due to aggregation through lithium μ-bridges between diLi adducts, leading to a precipitated complex,[9] a small amount of anisole has been used as additive to prevent such aggregation processes.

When BuLi is added to 1,3-DIB, there is a competition between the addition reaction and polymerization of metalated DIB.



If the addition rate is much higher than the polymerization rate ($k_1 \gg k_2$), the formation of oligomers will be limited. The initiation rate is expected to be increased by increasing the BuLi/DIB molar ratio. Indeed, when a 4-fold molar excess of *sec*-BuLi is reacted with 1,3-DIB in cyclohexane at 50 °C for 1 h, the protonically terminated material contains more diadduct product than the product from the 2:1 molar ratio (Figure 1a,b).

The relative temperature effect on the addition and polymerization steps depends on the activation energy of these two processes. A temperature decrease leads to a decrease of the polymerization rate more important than that of the addition, i.e., a favorable situation for the formation of the expected diadduct. However, it has been reported that the addition rate of 1,3-DIB and *sec*-BuLi is unacceptably slow in hydrocarbons at low temperature.[19] So, it is necessary to use a weakly polar additive, such as triethylamine, to increase the reaction rate under such conditions. This is the reason why an equimolar amount of Et_3N has been added to the 2/1 (mol/mol) *sec*-BuLi/1,3-DIB reaction mixture in cyclohexane at −20 °C. 1,3-DIB is not detected anymore by gas chromatography after 1 h, which indicates complete conversion of 1,3-DIB. The SEC trace of the recovered product shows that diadduct and dimers are the main components and that high MW materials have been reduced to very low amounts (Figure 1e). Comparison of the SEC traces of the *sec*-BuLi/1,3-DIB product and the *t*-BuLi/1,3-DIB one prepared under the same conditions (Figure 1a,c) shows that the latter one contains much more diadduct than the former. Therefore, the 2:1 reaction of *t*-BuLi and 1,3-DIB carried out in the presence of Et_3N in cyclohexane at −20 °C for 1 h may lead to a diadduct of a higher purity.

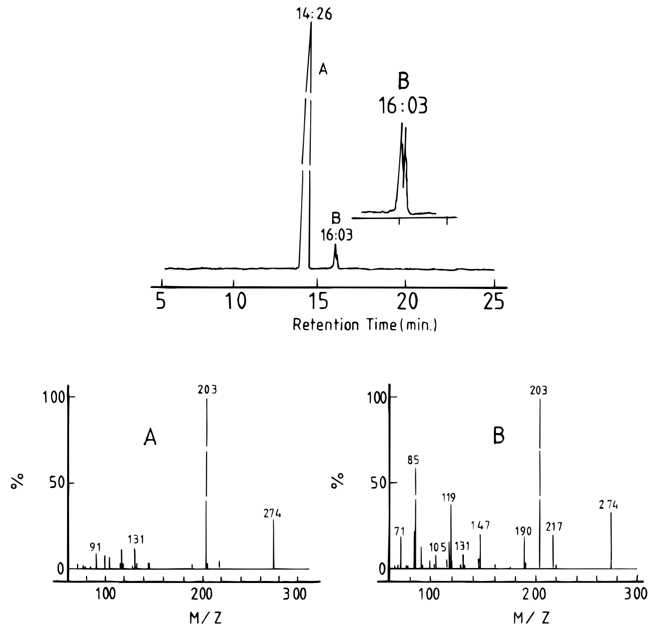


Figure 2. GC-MS of the *t*-BuLi/1,3-DIB adduct prepared in the presence of 1 equiv of Et_3N at −20 °C for 1 h.

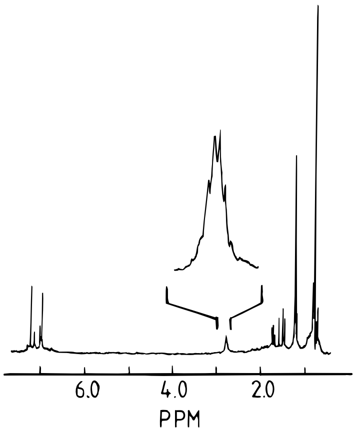


Figure 3. ^{1}H-NMR spectrum of the *t*-BuLi/1,3-DIB adduct prepared in the presence of 1 equiv of Et_3N at −20 °C for 1 h.

Characterization of the *t*-BuLi/1,3-DIB Diadduct Prepared in the Presence of Et_3N at Low Temperature. The addition product of *t*-BuLi and 1,3-DIB in a 2/1 molar ratio, in the presence of 1 equiv of Et_3N in cyclohexane at −20 °C for 1 h, has been identified by SEC, GC-MS, and ^{1}H-NMR. Under the same reaction conditions, features of the SEC trace of the *t*-BuLi/1,3-DIB adduct (Figure 1f) are quite different from those for the *sec*-BuLi/1,3-DIB adduct (Figure 1e); i.e., high MW materials have practically disappeared. The high purity of the *t*-BuLi/1,3-DIB adduct is also supported by GC-MS as reported in Figure 2, which shows two elution peaks characterized by the same mass of 274 in agreement with that structure. Note that peak B at a longer retention time is split into two parts. No compound of a mass higher than 274 is detected, which indicates that the *t*-BuLi/1,3-DIB adduct is free from oligomers. The difunctionality of this adduct has been verified by ^{1}H-NMR spectroscopy after deactivation with methanol (Figure 3). Comparison of ^{1}H-NMR resonances of the benzylic protons at 2.5−3.0 ppm (vs

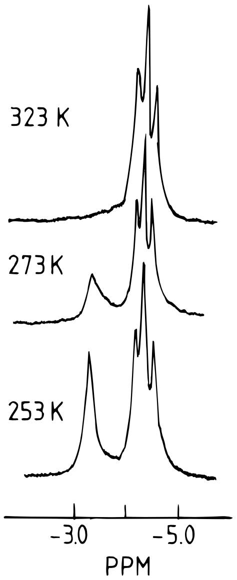
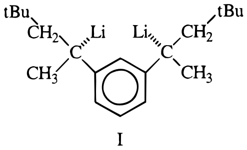


Figure 4. ^{7}Li-NMR spectrum of the *t*-BuLi/1,3-DIB dilithium prepared in the presence of 1 equiv of Et_3N at −20 °C for 1 h.

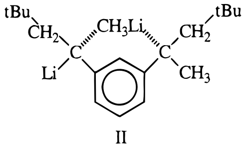
tetramethylsilane) with the aromatic protons at 6.9−7.2 ppm gives an integrated peak area ratio of 0.5, and comparison of total peak ratio for aliphatic protons (from 0.5 to 3.0 ppm) to aromatic protons (at 6.9−7.2 ppm) gives a value of 7.5. These two ratios are in perfect agreement with the expected diadduct structure, the purity of which can also find some confirmation from the sharpness of the ^{1}H-NMR resonance signals.

^{7}Li-NMR Study of *t*-BuLi/1,3-DIB Dilithium. The *sec*-BuLi/1,3-DIB adduct has previously been studied by ^{7}Li-NMR spectroscopy,[21] showing that the *sec*-BuLi/1,3-DIB adduct in cyclohexane has several resonance peaks assigned to unreacted *sec*-BuLi and multilithium compounds. Approximately 30 mol % of *sec*-BuLi remains unreacted at complete conversion of 1,3-DIB, which fits DIB oligomerization. The *t*-BuLi/1,3-DIB reaction product prepared in the presence of Et_3N at −20 °C has also been studied by ^{7}Li-NMR (Figure 4), and as expected, is quite different from the *sec*-BuLi/1,3-DIB one.[21] Note first the complete disappearance of the peak for *t*-BuLi (at −1.0 ppm), which indicates complete conversion, and that, simultaneously, the amount of 1,3-DIB oligomerization is negligible.

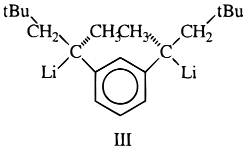
At 323 K, the ^{7}Li-NMR spectrum shows three singlets in the −4.5 ppm range. In agreement with the results of GC-MS reported above, stereoisomers of the diadduct are more likely responsible for this observation. It may be established that the *t*-BuLi/1,3-DIB adduct has three stereoisomeric configurations, as shown:



I



II



III

At 273 K, a new ^{7}Li resonance is observed at −3.2 ppm, indicating a slow exchange between aggregates and free species at least within the NMR time scale. The assignment of these spectra is straightforward and highlights the aggregation of the DIB−Li_2 diadduct under these conditions. From Figure 4, it also appears that the relative importance of the aggregates increases when the temperature decreases. The shape of the triplet at −4.0 to −4.5 ppm does not change with temperature, suggesting that the distribution of these three isomers is independent of temperature.

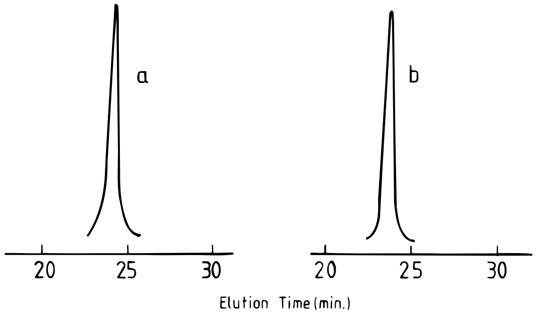


Figure 5. SEC trace of SBS prepared from the *t*-BuLi/1,3-DIB adduct in cyclohexane. (a) Central PBD block; (b) final copolymer.

Behavior of the *t*-BuLi/1,3-DIB Adduct in Apolar Solvent. Identification of the initiator structure and particularly its Li content is not sufficient to guarantee its efficiency for the synthesis of living polydienes having two equireactive living end groups, i.e., suitable for the synthesis of ABA triblock copolymers. If the two organolithium groups are of different reactivity (and particularly if one end is “dormant”), initiation of the second monomer may be incomplete and AB diblocks consequently may be formed. The efficiency of a difunctional initiator for the synthesis of ABA triblock copolymers may be tested by different methods: degradation of the central block and/or evaluation of the physicomechanical properties. In other words, if this *t*-BuLi/1,3-DIB adduct behaves as an efficient difunctional initiator for the polymerization of monomers such as butadiene and styrene, the resulting SBS triblock copolymers should exhibit good properties, in addition to a narrow molecular weight distribution and an experimental total M_n in agreement with the calculated values.

A sequential polymerization of butadiene and styrene has accordingly been initiated by the *t*-BuLi/1,3-DIB adduct. Its solution in cyclohexane has a deep red color. When butadiene is added to this dilithium initiator solution, the color rapidly changes to a faint orange, which is the sign of a fast initiation step, and that faint orange color persists throughout the polymerization (suggesting that there might still exist unreacted lithium species directly associated to the DIB moiety). In the polymerization solution, the butadiene concentration is 31 g/L and the initiator concentration is 5.15×10^{-4} mol/L; i.e., at 100% conversion, the PBD M_n should be 60 000. The polymerization temperature is 40 °C for butadiene and styrene; butadiene polymerization is carried out overnight. After styrene addition, a color change from faint orange to deep orange takes a long time, indicating a slow crossover reaction from butadiene to styrene. After the color change is complete, styrene polymerization is maintained for an extra 4 h. SEC traces of a sample picked out before styrene addition and of the final copolymer are shown in Figure 5. Both the PBD central block and the final copolymer have a monomodal and narrow MWD, and the molecular weights are close to the expected values. However,

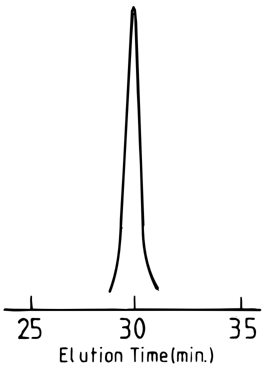


Figure 6. SEC trace of PS as initiated with a mixture of AMS-Li and *t*-BuLi/1,3-DIB adduct in cyclohexane.

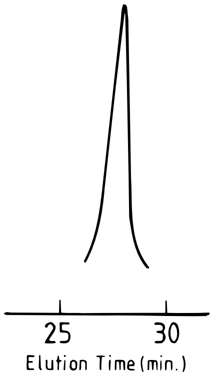


Figure 7. SEC trace of PS prepared from the *t*-BuLi/1,3-DIB adduct in THF.

the mechanical properties of the sample are very poor; in particular, the tensile strength is below 2 MPa, suggesting that the copolymer has an essentially diblock structure. Moreover, after selective degradation of the PBD block,[20] the molecular weight of the recovered polystyrene is about 2 times higher than the expected value, attesting quantitatively for the diblock structure of the polymer.

Another polymerization experiment has been carried out in cyclohexane, using a mixture of the *t*-BuLi/1,3-DIB adduct and of a structurally similar monofunctional initiating species, i.e., α-methylstyrene lithium (AMS-Li). One milliliter (0.91 g) of styrene monomer is added to a cyclohexane solution containing 9×10^{-5} mol of dilithium and monolithium compounds, respectively. Polymerization is then carried out overnight at room temperature in order to ensure complete styrene polymerization. SEC trace of the sample obtained from this polymerization displays a monomodal distribution as shown in Figure 6, and the MW is in good agreement with the value calculated from the ratio of styrene over dilithium plus monolithium initiators ($M_n = 5000$); the *t*-BuLi/1,3-DIB adduct thus really behaves as a monofunctional initiator in apolar solvent.

Behavior of the *t*-BuLi/1,3-DIB Adduct in Polar Solvent. It has been reported earlier that polystyrene initiated with the *sec*-BuLi/1,3-DIB adduct in THF shows a multimodal MWD:[21] initiation by difunctional, trifunctional, and tetrafunctional species provides polymers with 2, 3, and 4 times higher M_n's compared to a monofunctional initiator.

When the *tert*-BuLi/1,3-DIB adduct is used for styrene polymerization in THF, the SEC trace of the product obtained displays a monomodal and narrow MWD as shown in Figure 7, which gives credit to a unique structure of this difunctional initiator. Peaks derived from initiation by monofunctional and multifunctional species are not detected.

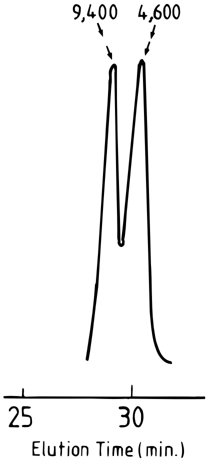


Figure 8. SEC trace of PS prepared from a mixture of AMS-Li and *t*-BuLi/1,3-DIB adduct in THF.

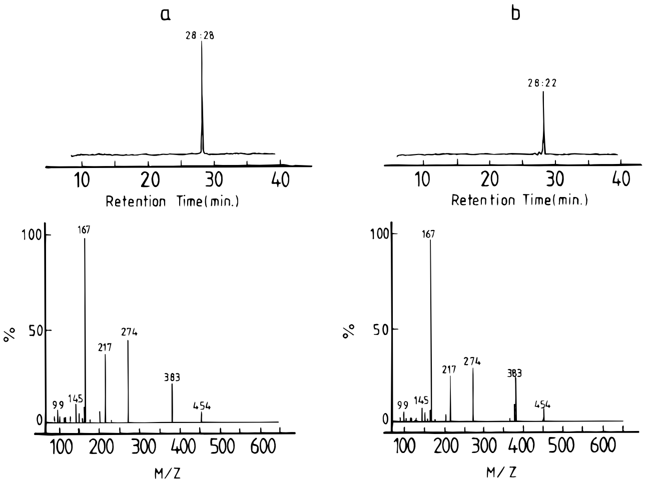


Figure 9. GC-MS spectrum of the reaction product of DPE and *t*-BuLi/1,3-DIB adduct. (a) In cyclohexane; (b) in THF.

Indeed, another styrene polymerization experiment has been initiated in THF, with a mixture of AMS-Li and *t*-BuLi/1,3-DIB adduct. One milliliter of styrene is added to THF containing 1.5×10^{-4} mol of AMS-Li and 5×10^{-5} mol of *t*-BuLi/1,3-DIB adduct. This time, the SEC trace of the resulting product displays the well-resolved bimodal distribution shown in Figure 8. The M_n of the higher MW peak is double that of the lower M_n, which indicates that the rate of the difunctional initiating species is equal to that of the monofunctional species. Comparison of areas of lower MW and higher MW peaks gives a ratio of 1.5, in good agreement with the relative Li ratio of monofunctional and difunctional species. Furthermore, initiation by species with more than two active sites per molecule can be neglected.

Structure of the Reaction Product of Diphenylethylene (DPE) and the *t*-BuLi/1,3-DIB Adduct. Addition reactions of 2 equiv of DPE and of the *t*-BuLi/1,3-DIB adduct have been carried out for 2 days, in cyclohexane and in THF, at 50 °C and at room temperature, respectively. GC-MS has been used as the analytical tool for identification of the reaction product (Figure 9). For both reactions in cyclohexane and THF, the same features are observed in the spectrum, and the molecular mass of the products derived from both reactions is equal to 454, which indicates clearly that DPE reacts only with one end of the *t*-BuLi/1,3-DIB

Table 2. Characteristics of SBS Triblock Copolymers As Initiated with the *t*-BuLi/1,3-DIB Adduct

sample no.	polar solvent	content (vol %)	1,2-PBD[a] (%)	PS[b] (wt %)	M_n[c] ($\times 10^{-3}$)	M_w/M_n	tensile strength (MPa)	elongation at break
1	THF	1.0	85	34	110	1.10	12.5	800
2	THF	3.0	85	34	105	1.10	12.0	800
3	Et_2O	10.0	46	33	105	1.10	31.5	1000
4	Et_2O	7.5	45	35	105	1.10	32.5	1000
5	Et_2O	5.0	45	33	105	1.10	30.0	1000
6	Et_2O	2.5	45	35	105	1.10	32.0	1000
7	Et_2O	1.0	33	35	110	1.35	19.0	1000
8[d]	Et_2O	7.5	45	35	105	1.10	32.0	1000

[a] From ^{1}H-NMR data. [b] From ^{1}H-NMR of the SBS copolymers. Expected value was 34 wt % for all samples. [c] Experimental value obtained from SEC and ^{1}H-NMR analysis. Expected value was 100 000 for all samples. [d] Initiator stored for 1 month at −20 °C.

dilithium, even in THF. Such a 50% efficiency of the end-capping reaction cannot be due to aggregation of the diadduct, since THF is known to be able to destroy the aggregation complexes. It has thus to be related both to steric hindrance, when bulky side groups of DPE might stem its reaction with isopropenyl Li attached to another very bulky group, and perhaps to a local reactivity being modified by former addition to the first double bond.

An earlier paper[20] has reported on the unsuccessful synthesis of a PMMA−PBD−PMMA triblock copolymer with the dilithium initiator. We have supposed that the organo Li species directly attached to the DIB moiety in Li−DIB−PBD−Li chains was sterically hindered to the point where end-capping with DPE was prevented from occurring, leading to a very early termination of the methyl methacrylate polymerization on that side:

$$\text{Li−DIB−Li} + \text{BD} \xrightarrow[\text{cyclohexane}]{40\ °\text{C}} \text{Li−DIB−PBD−Li} \xrightarrow[\text{THF}]{\text{DPE}} \text{Li−DIB−PBD−DPE−Li} \xrightarrow[-78\ °\text{C}]{\text{MMA}} \text{X−DIB−PBD−DPE−PMMA−Li}$$

In other words, similarly to the reaction described above, the two bulky side groups of DPE prevent it from reacting with DIB−Li attached to a long PBD chain, although it reacts easily with PBD−Li under the same conditions, leading to the formation of diblock copolymers.

Preparation of SBS Triblock Copolymers in the Presence of a Polar Solvent. As aforementioned, the SBS prepared with the *t*-BuLi/1,3-DIB adduct in cyclohexane has a low tensile strength, suggesting that the copolymer also has a diblock structure. Although the reason why diblock copolymers are exclusively formed is not clearly apparent up to now, it might involve an aggregation due to μ-bridge coordination.

Solvents are known to exert a strong influence on the mode of association of organolithiums. In polar aprotic solvents, these compounds are solvated and the degree of association is lower. THF has been known to provide for two active species per DIB molecule;[20] since diethyl ether is also a solvent of similar donicity, several SBS triblock copolymers have been prepared with the *t*-BuLi/1,3-DIB adduct in the presence of THF or diethyl ether. Their characteristics, indicative of pure products, are given in Table 2. All samples have been prepared with the same *t*-BuLi/1,3-DIB adduct except for sample 8 synthesized with a dilithium initiator previously stored at −20 °C for 1 month. A total of 1.0−3.0 volume % THF and 1−10 volume % diethyl ether in cyclohexane have been used, respectively, for the polymerization of butadiene and styrene at room temperature, overnight for butadiene and 4 h for styrene. After butadiene addition, the red color of the initiator is rapidly converted into a faint yellow, characteristic of butadienyllithium. After completion of butadiene polymerization, styrene is added and the color immediately changed to orange, characteristic of styrenyllithium. The SEC traces are all monomodal and symmetrical (Figure 10) with the exception of sample 7 for which it is rather broad (as shown in Figure 11).

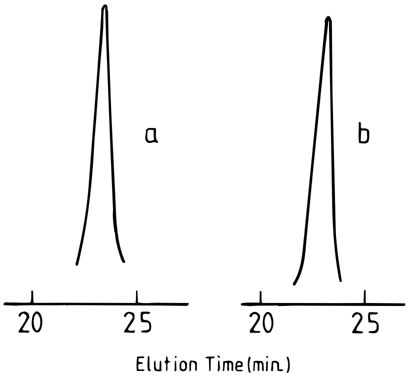


Figure 10. SEC trace of SBS prepared from the *t*-BuLi/1,3-DIB adduct in cyclohexane containing 7.5 vol % diethyl ether. (a) PBD central block; (b) final copolymer.

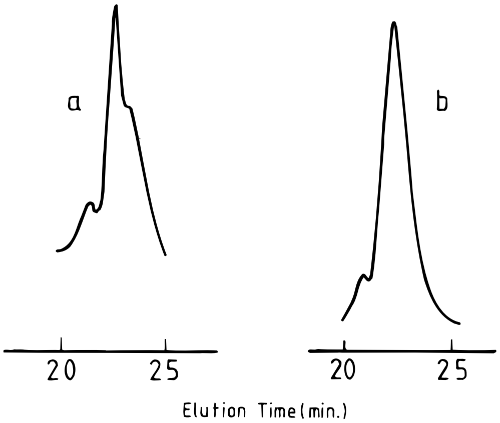


Figure 11. SEC trace of SBS prepared from the *t*-BuLi/1,3-DIB adduct in cyclohexane containing 1.0 vol % diethyl ether. (a) PBD central block; (b) final copolymer.

^{1}H-NMR analysis of the PBD chains microstructure yields almost constant 1,2-content, approximately 85%, when the amount of THF used changes from 1.0% to 3.0% in volume. When the diethyl ether content goes from 2.5% to 10% in volume, approximately 45% of the butadiene monomeric units are in the 1,2 configuration; when reduced below 1 vol %, the 1,2-content could be brought down to 32.5%. The SBS's prepared in the presence of 2.5−10% diethyl ether have good mechanical properties (tensile strength ca. 30 MPa), comparable to

Table 3. Effect of Aging of *t*-BuLi/1,3-DIB Dilithium on the PBD Molecular Parameters

sample no.	time (days)	temp (°C)	$M_n{}^a$ ($\times 10^{-3}$)	M_w/M_n
1	0		80	1.1
2	2	−20	80	1.1
3	5	−20	80	1.1
4	15	−20	80	1.1
5	30	−20	80	1.1
6	2	20	80	1.1
7	5	20	90	1.1
8	15	20	100	1.3
9	30	20	140	3.1

[a] Theoretical $M_n = 80\,000$.

the tensile strength reported in Shell's technical manual for commercial product CARIFLEX TR1101/1102 prepared by the coupling process, and to those given by Lo et al.,[19] with difunctional initiators of the BDPE. It is worthy to mention that the test specimens have been prepared by film casting from cyclohexane. When the test specimens are prepared by compression molding at 180 °C, the tensile strength falls below 15 MPa. Sample 7 has an expectedly low tensile strength: it is here apparent that when the diethyl ether content is below 1 vol %, a part of the dilithium initiator still behaves like a monofunctional initiator, leading to the formation of diblock copolymers, source of poorer mechanical properties. On the other hand, a predominantly 1,2-microstructure might be responsible for the poorer mechanical properties of samples 1 and 2 in Table 2.

Storage Stability of the *t*-BuLi/1,3-DIB Adduct. From a convenience standpoint, an important feature of an initiator is its stability in time. That of the *t*-BuLi/1,3-DIB adduct has been studied at −20 and 20 °C. The state of that adduct with respect to storage time has been monitored by the molecular weight of polybutadiene prepared from it: Table 3 reports the characteristics of PBD's prepared with adducts aged from 2 to 30 days in cyclohexane in the presence of 7.5% diethyl ether.

An increase in MW should result as the total number of moles of initiator is reduced by aging. In addition, a monofunctional initiation yields a diblock copolymer responsible for a broadening of MWD. In practice, these M_n's and MWD's are not affected as long as the *t*-BuLi/1,3-DIB adduct is stored at −20 °C (samples 1−5 in Table 3). Moreover, no loss of tensile strength is observed for the SBS triblock copolymer prepared with the adduct stored for 1 month (sample 8 in Table 2). When the initiator is stored at room temperature, however, the M_n has increased with storage time, and after 15 days, a bimodal distribution is observed in the SEC traces.

Conclusion

A pure *tert*-butyllithium/1,3-diisopropenylbenzene diadduct can be obtained under optimized preparation conditions, i.e., a reaction temperature of −20 °C and dropwise addition of 1,3-diisopropenylbenzene (1,3-DIB) in cyclohexane to a stirred cyclohexane solution of a 1:1 *t*-BuLi−Et_3N complex followed by a 1 h postreaction period. GPC, ^{1}H-NMR, GC-MS, and ^{7}Li-NMR confirm the formation of the expected diadduct characterized by three stereoisomeric configurations.

Although the *t*-BuLi/1,3-DIB adduct is completely soluble in an apolar medium, it behaves as if it is a monofunctional initiator for butadiene (BD) and styrene polymerization. In polar solvents, such as tetrahydrofuran (THF), the two ends of the *t*-BuLi/1,3-DIB dilithium adduct are activated, and initiation by monofunctional species and species with more than two active sites per molecule can be neglected.

Accordingly, a styrene−butadiene−styrene (SBS) triblock copolymer free from diblocks can be obtained using that *t*-BuLi/1,3-DIB diadduct as initiator in the presence of THF or diethyl ether. The 1,2-microstructure of PBD chains is ca. 85% or 45%, when the amount of THF or diethyl ether changed from 1 to 3 vol % or 2.5 to 10 vol %, respectively. The SBS synthesized in the presence of diethyl ether (from 2.5% to 10%) displays good ultimate mechanical properties (tensile strength ca. 30 MPa) comparable to those of commercial products prepared by the coupling process, and others reported in the literature. When the diethyl ether content is below 1 vol %, a part of the dilithium initiator still behaves like a monofunctional initiator, probably because of aggregation phenomena, leading to the formation of diblock copolymers responsible for the poorer mechanical properties. A predominant 1,2-microstructure might be responsible for the poorer mechanical properties of the sample prepared in the presence of THF.

Interestingly, when diphenylethylene (DPE) reacts with the *t*-BuLi/1,3-DIB adduct, in cyclohexane or THF, the reaction only takes place at one end of the dilithium compound. That gives strong support to our previous proposal to explain the failure of the direct synthesis of PMMA−PBD−PMMA triblock copolymers in hydrocarbon solvents.[20]

The *t*-BuLi/1,3-DIB adduct is stable for at least 1 month when stored at −20 °C, although storage at room temperature is not recommended.

In a future paper, we shall report the initiation mechanism by this *t*-BuLi/1,3-DIB adduct in hydrocarbon solvents and the preparation of triblock copolymers with a lower level of 1,2-microstructure.

Acknowledgment. The authors are deeply indebted to Koninklijke/Shell Laboratorium (Amsterdam) for financial support and scientific discussions, particularly with Dr. F. H. van der Steen and Dr. B. Van Wingerden. We also express our gratitude to Mrs. Luthers for skillful technical assistance, to Miss Zune for ^{7}Li-NMR recording, and to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" (Brussels) for general support to the laboratory through an Interuniversity Attraction Pole Grant.

References and Notes

(1) Fetters, L. J.; Morton, M. *Macromolecules* **1969**, *2*, 453.
(2) Soum, A.; Fontanille, M.; Aboudalle, A. *Polymer* **1988**, *29*, 1528.
(3) Foss, R. P.; Jacobson, H. W.; Cripps, H. N.; Sharkey, W. H. *Macromolecules* **1979**, *12*, 1210.
(4) Ladd, B. J.; Hogen-Esch, T. E. Polym. Prepr. **1989**, *30*, 261.
(5) Long, T. E.; Brosker, A. D.; Bradley, D. J.; McGrath, J. E. *J. Polym. Sci.: Part A, Polym. Chem.* **1989**, *27*, 4001.
(6) Krass, G.; Rollmann, W. *J. Polym. Sci., Polym. Phys. Edn.* **1976**, *14*, 1133.
(7) Matsuo, M.; Veno, T.; Hormio, H.; Churiyio, S.; Asi, H. *Polymer* **1968**, *9*, 425.
(8) Long, T. E.; Allen, R. D.; McGrath, J. E. In *Recent advances in mechanistic and synthetic aspects of polymerization*; Fontanille, M., Guyot, A., Eds.; NATO ASI Series; Reidel Publishing Cie: 1987; Vol. 215, p 79.
(9) Foss, R. P.; Jacobson, H. W.; Sharkey, W. H. *Macromolecules* **1977**, *10*, 287.
(10) Tung, L. H.; Lo, G. Y.-S.; Beyer, D. E. *Macromolecules* **1978**, *11*, 616.
(11) Beinert, G.; Lutz, P.; Franta, E.; Rempp, P. *Makromol. Chem.* **1978**, *179*, 551.

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

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

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

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

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

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

(18) Tung, L. H.; Lo, G. Y.-S. *Macromolecules* **1994**, *27*, 1680.

(19) Tung, L. H.; Lo, G. Y.-S. *Macromolecules* **1994**, *27*, 2219.

(20) Yu, Y. S.; Jérôme, R.; Fayt, R.; Teyssié, Ph. *Macromolecules* **1994**, *27*, 5957.

(21) Yu, Y. S.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. Mechanism of *sec*-butyllithium/1,3-diisopropenylbenzene reaction and initiation by their adduct in apolar solvent. *Macromolecules*, in press.

(22) Kaminski, C. W.; Morrison, R. C.; Rathman, T. L. *Curr. Appl. Sci., Med. Technol.* **1985**, 315.

MA951164G