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Studies on Dilithium Initiators. 1. Hydrocarbon-Soluble Initiators 1,3-Phenylenebis(3-methyl-1-phenylpentylidene)dilithium and 1,3-Phenylenebis[3-methyl-1-(methylphenyl)pentylidene]dilithium

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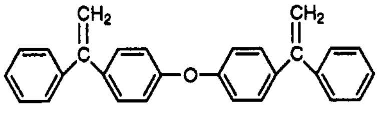
ABSTRACT: The title initiators were prepared by the addition reaction of *sec*-butyllithium to two double 1,1-diphenylethylene (DDPE) compounds, 1,3-bis(1-phenylethenyl)benzene (PEB) and 1,3-bis[1-(methylphenyl)ethenyl]benzene (MPEB). The initiator based on MPEB was found to be soluble in toluene, cyclohexane, and *n*-hexane representing aromatic, cycloalkane, and alkane hydrocarbons. The initiator based on PEB was soluble in toluene and cyclohexane but not in *n*-hexane. The addition reaction was found to be clean and fast for both dilithium initiators and the reaction solutions could be used directly for initiating anionic polymerization. Kinetics of the formation reactions, the stability of the resulting initiators, and the use of the initiators for making butadiene and isoprene block copolymers with styrene were investigated.

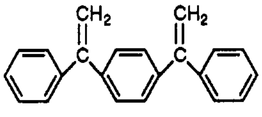
Introduction

Earlier, we reported[1] four useful dilithium initiators (DLI) prepared by the addition of *sec*-butyllithium (s-BuLi) to four double 1,1-diphenylethylene (DDPE) compounds (**I–IV**).



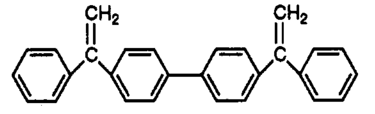
(I)

bis[4-(1-phenylethenyl)phenyl] ether



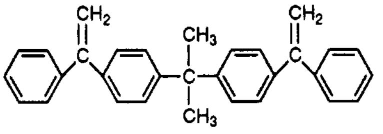
(II)

1,4-bis(1-phenylethenyl)benzene



(III)

4,4′-bis(1-phenylethenyl)-1,1′-biphenyl

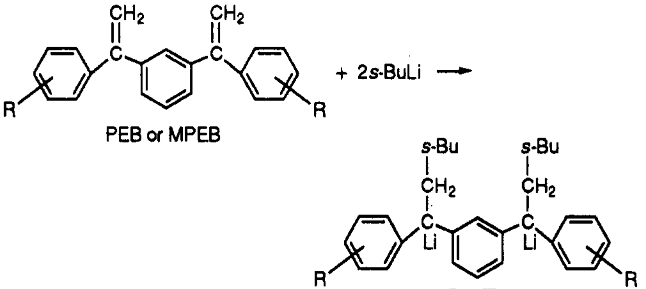


(IV)

2,2′-bis[4-(1-phenylethenyl)phenyl]propane

Because s-BuLi adds rapidly to the 1,1-diphenylethylene group, the reaction proceeds readily to completion in benzene and toluene without requiring the presence of any polar additives. The four initiators derived from the above DDPE compounds, similar to many DLI published in literature, were not directly soluble in hydrocarbon solvents. However, freshly prepared DLI from the four DDPE compounds above were in the form of fine suspensions and were effective in initiating diene polymerization. A more useful form of the DLI was made by seeding with (contacting with a small amount of) isoprene or butadiene monomer to make the DLI soluble. A styrene–butadiene–styrene (SBS) triblock copolymer of good tensile strength was prepared from these DLIs. When oligomeric poly(styryllithium) was used to replace s-BuLi in the addition reaction with the DDPE compounds, soluble DLI formed directly.[2] The triblock SBS made from the directly soluble initiators prepared from poly(styryllithium), however, had a low tensile strength.

Further investigation led to the discovery that DLI of a much higher solubility could be prepared by reacting s-BuLi with two other DDPE compounds, 1,3-bis(1-phenylethenyl)benzene (PEB) and 1,3-bis[1-(methylphenyl)ethenyl]benzene (MPEB).



R = H; DDPE = PEB;
I = 1,3-phenylenebis(3-methyl-1-phenylpentylidene)dilithium
R = CH$_3$; DDPE = MPEB;
II = 1,3-phenylenebis[3-methyl-1-(methylphenyl)pentylidene]dilithium

The initiators **I** and **II** are the only dilithium initiators to have direct solubilities in hydrocarbons including benzene, toluene, cyclohexane, and also *n*-hexane for **II** without requiring seeding with another monomer, without requiring the use of polar additives, and without requiring another oligomeric or polymeric segment to be incorporated. Although the use of **I** and **II** to prepare unique telechelic polybutadienes[3] and block copolymers[4] has been reported and patents[5] on these initiators were issued, the detailed properties of these useful initiators have never been reported. The kinetics of the addition reaction of s-BuLi with PEB in cyclohexane has been reported by Broske et al.[6] The same reaction in toluene has been reported by Leitz and Höcker.[7] However, the concentrations studied by both were an order of magnitude more

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dilute than those required for practical use. In this paper the studies on the rates of the addition reactions of s-BuLi with both PEB and MPEB in toluene, cyclohexane, and *n*-hexane at concentrations useful in the preparation of **I** and **II** are reported. The use of **I** and **II** in the preparation of SBS triblock copolymers, the studies on the oxidative stability of PEB and MPEB, and the studies on the solvent effect on the storage stability of **I** and **II** are also discussed.

Results and Discussion

Addition Reaction of s-BuLi with PEB and MPEB. The addition reaction using reactants in stoichiometric amounts was investigated in three different solvents: toluene, cyclohexane, and *n*-hexane representing aromatic, cycloalkane, and alkane hydrocarbons. Conditions of the reactions are shown in Table 1.

Table 1. Conditions of the Addition Reactions of s-BuLi with DDPE

run	DDPE	solvent	DDPE conc (M)	temp (°C)	DLI	DLI solubility
1	PEB	toluene	0.043	31–33	I	soluble
2	PEB	cyclohexane	0.031	30–33[a]	I	soluble
3	PEB	*n*-hexane	0.029	30–33[a]	I	ppt after 2 h
4	MPEB	toluene	0.039	30[b]	II	soluble
5	MPEB	cyclohexane	0.028	30–33[c]	II	soluble
6	MPEB	*n*-hexane	0.028	30–33[c]	II	soluble

[a] First 6 h, room temp afterward. [b] First 3 h, room temp afterward. [c] First 5 h, room temp afterward.

As shown in Table 1, 1 was soluble in toluene and cyclohexane but not in *n*-hexane. **II** was soluble in all three solvents. The exact solubility of the DLI was not determined. Concentrations more than double of those shown in Table 1 have been used in our laboratory as the stock solutions of the initiators in toluene and cyclohexane. Schulz and Höcker[8] reported solubilities of 0.1 M in benzene and toluene for **I**.

During the course of the addition reaction of s-BuLi to PEB, samples were withdrawn, quenched with methanol, and analyzed by GPC for unreacted DDPE, monoadduct, and diadduct. In toluene, the rate was rapid. After 30 min the reaction was essentially complete and the chromatogram appeared clean without any contamination from monoadduct. In *n*-hexane, precipitate started to form after 2 h. The reaction rate in *n*-hexane appeared to be a little faster than the rate in cyclohexane. At 48 h only the diadduct peak was visible in *n*-hexane, while in cyclohexane a small peak of unreacted PEB was still detectable. Based on these observations, the relative rates in the three solvents are toluene ≫ *n*-hexane > cyclohexane. In cyclohexane and in *n*-hexane, during the intermediate stages of the addition reaction, the peak for monoadduct was always very small, indicating that the second double bond in PEB was much faster reacting than the first. The same was observed by Broske et al.[6] in cyclohexane in higher dilutions. In toluene the monoadduct peak was more prominent, indicating that the addition of s-BuLi to the two double bonds in PEB was more nearly equal in rate as was reported by Leitz and Höcker[7] also in higher dilutions.

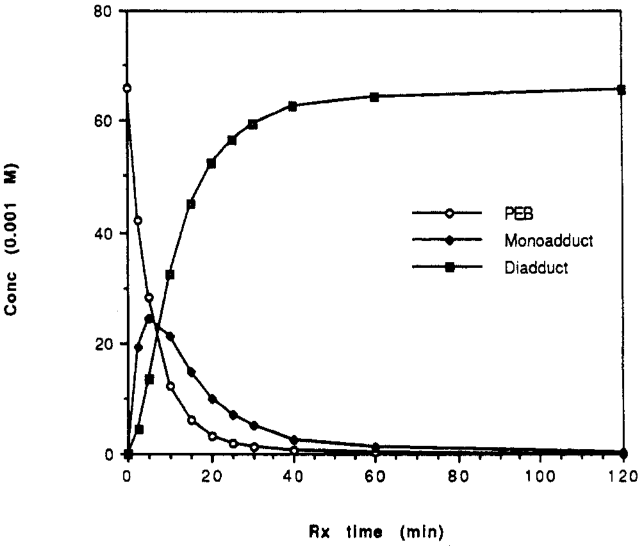


Figure 1. Concentrations of PEB, monoadduct, and diadduct for the reaction of s-BuLi with PEB in toluene at 20 °C.

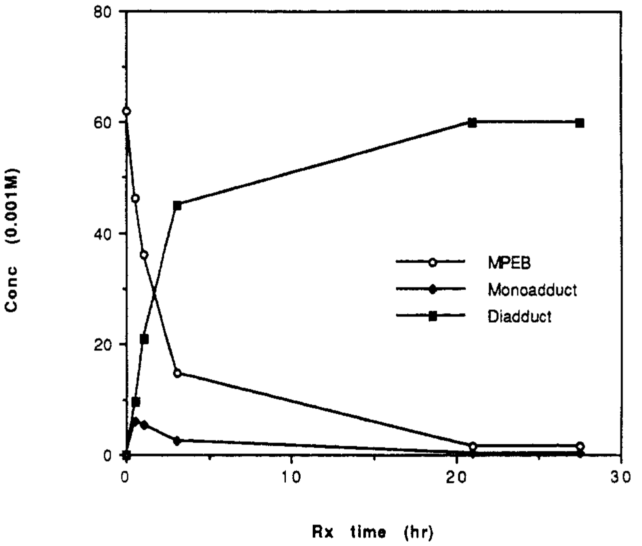


Figure 2. Concentrations of MPEB, monoadduct, and diadduct for the reaction of s-BuLi with MPEB in cyclohexane at room temperature.

The rates of addition of s-BuLi to MPEB in the three solvents can clearly be ranked also as toluene ≫ *n*-hexane > cyclohexane. It is interesting to note that the same ranking was observed by Hsieh[9] in the initiation rates of styrene, butadiene, and isoprene polymerization by n-BuLi. Similar to the PEB reaction, the addition of s-BuLi to the second double bond of MPEB was also faster than that to the first in cyclohexane and *n*-hexane. The addition to the two double bonds was at about equal rates in toluene. Thus the two DDPE compounds behaved very similarly, with the addition of s-BuLi to PEB being slightly faster than the addition to MPEB. At room temperature the reaction took more than 2 days to complete in cyclohexane. At 50 °C and 0.07 M the reaction is completed in about 3 h for both PEB and MPEB.

Quantitative determination of the components was not possible from GPC chromatograms because the monoadduct peak could not be separated cleanly from the diadduct peak. To gain more quantitative information, a PEB reaction in toluene and a MPEB reaction in cyclohexane were repeated by using GC (gas chromatography) as the analytical tool. The results are plotted in Figures 1 and 2. For the PEB reaction in toluene, the features of the kinetic curves are similar to those reported by Leitz and Höcker[7] for the same reaction in toluene at a concentration about 10 times more dilute. The agreement shows the near equal reactivity of the two double bonds in PEB was not affected by concentration changes. For the addition reaction to MPEB in cyclohexane, the data shown in Figure 2 are similar to the cyclohexane data of PEB determined by Broske et al.[6] at a concentration about 15 times more dilute. The agreement with Broske et al. supports the earlier observations that MPEB behaved the same as PEB

Table 2. Properties of SBS Triblock Copolymers

sample no.	DLI	block type	styrene (%)	mol wt ($\times10^{-3}$)	M_w/M_n	tensile (psi)	elong (%)
1	I	pure	36	116	1.25	2990	1000
2	I	pure	34	111	1.25	3400	930
3	I	tapered	51	120	1.26	4530	750
4	I	tapered	48	143	1.25	3390	800
5	II	pure	32	114		3160	790
6	II	pure	35	119	1.23	4400	910
7	II	tapered	47	112	1.34	3370	930
8	II	tapered	47	134	1.14	3080	840

[a] Based on monomer feed. Analysis of % styrene on several final triblocks agreed with feed.

and that the relative rates of the two double bonds were not affected by concentration changes.

Styrene–Butadiene–Styrene (SBS) Triblock Copolymers. One of the major uses of DLI is for the preparation of diene containing triblock copolymers. Properties of the triblock are therefore the ultimate test of the effectiveness of the DLI. Several pure and tapered SBS triblocks were prepared. Their properties are given in Table 2. The DLI used was freshly prepared in toluene from freshly purified PEB or MPEB before each polymerization run. The polymerization solvent was also toluene. The molecular weights were peak molecular weights computed from GPC data assuming additivity of the logarithms of the molecular weight of the blocks.[10] The GPC chromatograms, except that for sample 6, were all monomodal and symmetrical. The chromatogram for sample 6 was also monomodal but had a high molecular weight shoulder on the peak. Despite the variations in M_w/M_n, the tensile strengths, 3000 psi and above, compared favorably with the tensile strengths reported earlier[1] on SBS prepared using DLI from DDPE compounds **I**–**IV**. The higher tensile strengths in Table 2 are also comparable to the tensile strength reported in Shell's Brochure for SBS prepared by the coupling process.

Preparation of SIS (styrene–isoprene–styrene) triblocks, however, was met with some difficulties. The molecular weight distributions of SIS samples were broad and distinctly bimodal. The GPC chromatogram of a typical SIS prepared by **I** is shown in Figure 3. The tensile strength was about a factor of 3 lower than that of the SIS prepared by the coupling process. The problem in SIS preparation prompted the investigation into the use of polar additives with **I** and **II**. The use of an alkoxide[11] was helpful, and a better additive was pentamethyldiethylenetriamine (PMDETA).[12] The nature of the bimodal distribution and the effect of additives on the polymerization behavior of DLI **I** and **II** are discussed in detail in parts 2 and 3 of this series (following papers in this issue).

Stability of PEB and MPEB. The compound 1,1-diphenylethylene has a tendency to be oxidized to benzophenone when exposed to air.[13] By analogy, PEB and MPEB are expected to be sensitive to air. Indeed, SBS prepared from DLI made from aged DDPE was found to give a low tensile strength. To gain knowledge of the stability of the DDPE compounds, two PEB samples with different exposures to air were analyzed by GC. The GC chromatogram of the sample stored under nitrogen for 2 years showed 98.9% PEB, 0.6% monoketone, and a small amount of other impurities and was essentially identical to that of freshly purified PEB. The GC chromatogram for the sample having been exposed to air for 6 months showed 86.9% PEB, 9.5% monoketone, 2.4% diketone, and other impurities. The diketone was identified by comparison with the GC chromatogram of a pure diketone sample. The monoketone was identified by gas chromatography/mass spectrometry. Infrared spectra of the two PEB samples were also examined. The absorption of the carbonyl stretching mode at about 1650 cm^{-1} was observed in the air-exposed sample but not in the sample stored under nitrogen for 2 years.

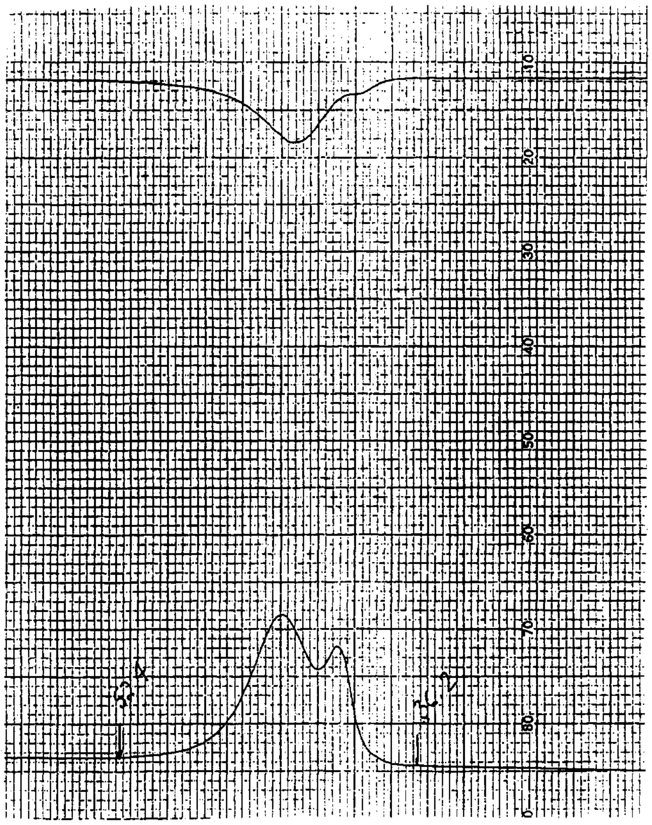
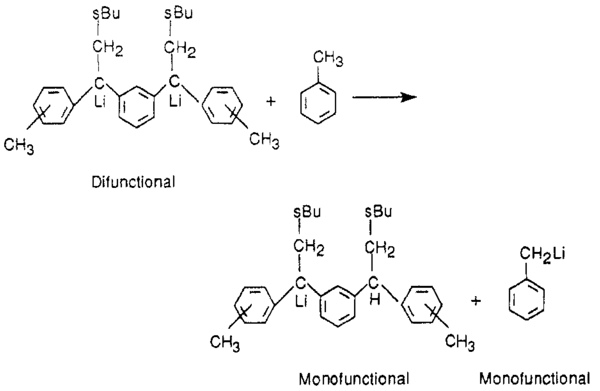


Figure 3. GPC chromatogram of a typical SIS triblock copolymer made in cyclohexane without polar additives.

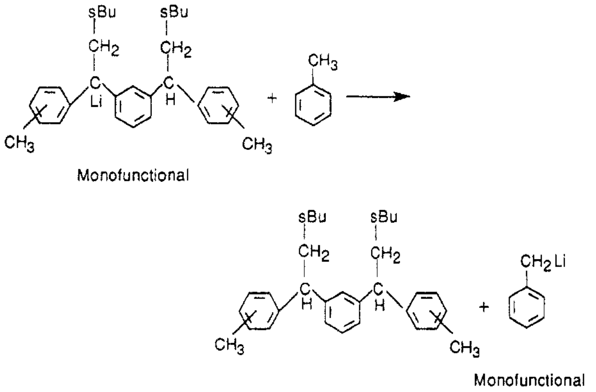
During the reaction of s-BuLi with PEB or MPEB, monoketone and diketone will also react with s-BuLi. The resultant sites from the ketones will not initiate the anionic polymerization of dienes and styrene. The presence of monoketone will generate monofunctional initiators and ultimately lower the tensile properties of block copolymers prepared.

Storage Stability of DLI. As described earlier in this paper, the reaction of s-BuLi with PEB or MPEB in toluene was completed in 30 min at 30 °C. This is a convenient rate to prepare DLI for working at laboratory scale. However, it is known that chain transfer via metallation can occur in some anionic polymerization systems especially to toluene.[14] DLI **II** contains two tolyl groups which may also be susceptible to metallation. For these reasons, the stability of **II** was studied in both cyclohexane and toluene. The concentration of the two solutions of **II** were 0.07 M in toluene and 0.06 M in cyclohexane. The state of **II** with respect to storage times was monitored by the tensile strength of the SIS made from it. PMDETA was used as an additive in the preparation of SIS.

The properties of 10 SIS triblock copolymers prepared with **II** of 2–55 days old in toluene are given in Table 3. Metallation of toluene by the first site of **II** splits **II** into two monofunctional initiators as shown by the reaction in eq 1. A reduction of the molecular weight should result as the total number of moles of initiator increased. Metallation by the second site does not create any additional monofunctional species as shown in eq 2 and should not cause additional harm.



(1)



(2)

Monofunctional initiator creates a diblock which causes a loss of tensile strength.[15] The polystyrene end block for SIS at 140 000 molecular weight is at the critical value of 10 000 for sharp phase separation in SIS.[15] Thus a reduction of molecular weight for the present SIS should also contribute to the loss of tensile strength. In Table 3 there is a reduction of the molecular weight and a large loss of tensile strength. Both fit the hypothesis that metallation was the main cause for the deterioration of DLI in toluene. Therefore, freshly prepared DLI should be used for polymerization if toluene is used to take advantage of the high rate of s-BuLi addition to PEB or MPEB. Interestingly, the molecular weight distribution was not affected as the metallation reaction progressed. The M_w/M_n ratios in Table 3 remain constant, and there were no observable differences between the shapes of the GPC chromatograms for the SIS made with fresh **II** and **II** of 55 days.

The properties of SIS triblock copolymers prepared with **II** in cyclohexane are given in Table 4. No loss of tensile strength was observed for SIS prepared with **II** in cyclohexane stored over a 3-month period. The molecular weight, however, had increased with storage time. A small amount of impurities introduced from the repeated withdrawal of DLI from the stock solution is suspected. When a DLI site is terminated by any impurity, a monofunctional initiating site is created but there should be no change of the moles of initiator. One would expect a loss of tensile strength but no change in molecular weight. The increase of the molecular weight with no loss of strength reflects that there was a net loss of initiator concentration without a significant amount of monofunctional site created. The termination reaction for the most part must have taken out both reactive sites on a molecule of **II** before affecting another. The termination reaction must therefore be very localized or the reactivity of the second site on **II** toward termination was much faster than the first. Metallation of the tolyl groups on **II** would have created monofunctional initiating species but would have kept also the total initiator concentration constant with no increase in M_n. Data in Table 4 showed that metallation of **II** must be minor in comparison to the termination by impurities during storage. Conceivably by tightening the control of impurities in storage, one could keep **II** in cyclohexane stable for a very long time. Even though **I** was not tested, one would expect that its stability is not any different.

Table 3. Stability of II in Toluene

age of **II** (days)	Sty (%)	M_n (GPC) ($\times10^{-3}$)	M_w/M_n	tensile (psi)	elong (%)
2	14.9	147	1.07	3050	1250
5	15.1	138	1.07	2590	1240
9	15.1	142	1.06	2120	1260
12	15.0	142	1.07	1900	1310
14	15.0	152	1.07	2450	1300
20	15.4	145	1.06	2080	1300
29	15.2	142	1.06	1590	1430
35	15.1	137	1.06	1440	1420
42	15.2	132	1.05	1550	1490
55	15.0	136	1.05	1400	1470

Table 4. Stability of II in Cyclohexane

age of **II** (days)	sty (%)	M_n (GPC) ($\times10^{-3}$)	M_w/M_n	tensile (psi)	elong (%)
3	14.8	144	1.06	2930	1310
4	15.1	139	1.07	2720	1280
7	15.2	138	1.06	2780	1290
8	14.9	148	1.07	3160	1270
14	15.0	143	1.08	2940	1330
22	15.4	143	1.07	2910	1250
35	15.0	145	1.06	2690	1290
50	15.2	152	1.07	3250	1310
58	14.7	153	1.06	3740	1290
67	15.4	155	1.07	2950	1300
77	15.1	148	1.07	2630	1300
105	14.8	152	1.06	2960	1280

The stock DLI solutions in the above experiments were terminated with deuterated acetic acid after the above experiments and analyzed by ^{1}H NMR—for **II** in toluene (sample A) after a storage time of 78 days and for **II** in cyclohexane (sample B) after 116 days. As shown in Figure 4, there was 26% benzylic protons in sample A and 5% in sample B as calculated from the relative integration areas of benzylic protons at about 4 ppm and aromatic protons at about 7 ppm. These percentages represent the amount of **II** terminated by some kind of active protons prior to the intentional termination with deuterated acetic acid. The 5% loss of **II** in cyclohexane corresponded closely to the small increase of molecular weight in Table 3. The 26% loss of **II** in toluene is the 78 days sample. When prorated to 55 days, the loss should be 18%. If the two sites on **II** chain-transferred equally, the resulting monofunctional initiator should be about 33% and a reduction of molecular weight should be about 15%. A diblock content of 33% should give a sharp drop of the tensile strength in agreement with the data in Table 3. A reduction of 15% molecular weight is also in the range of that shown in Table 3.

Experimental Section

Chemicals. Isoprene, purchased from Goodyear Tire and Rubber Co., was purified by passing through an activated alumina column and vacuum distilled in the presence of dibutylmagnesium before use. 1,3-Butadiene, rubber grade purchased from Phillips Petroleum Co., was purified by passing through an activated alumina column before use. Styrene, commercial grade, was purified by passing through an activated alumina column and vacuum distilled in the presence of calcium hydride before use. Cyclohexane, *n*-hexane, toluene, THF, methanol, and 2-propanol were purchased from either Burdick and Jackson Laboratory

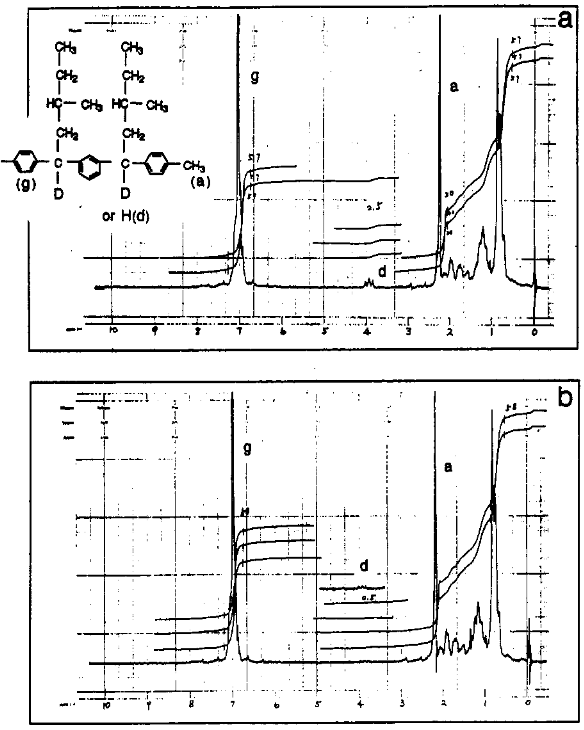


Figure 4. (a) ^{1}H NMR spectrum of deuterium-terminated DLI (stored 78 days in toluene). (b) ^{1}H NMR spectrum of deuterium-terminated DLI (stored 116 days in cyclohexane).

(distilled in glass grade) or Fisher Scientific Co. (HPLC grade). s-BuLi, 12 wt % in cyclohexane, was purchased from the Lithium Corporation of America and was used directly. Its exact concentration was determined by the double titration method of Gilman.[16] Pentamethyldiethylenetriamine (PMDETA) was purchased from Alfa Products and purified by vacuum distillation in the presence of calcium hydride.

PEB was prepared in the laboratory by the isophthaloyl dichloride acylation of benzene in the presence of an equivalent amount of $AlCl_3$ to give the diketone which was then converted to PEB via methyl Grignard and dehydration reactions. The same procedure was used to prepare MPEB except that toluene was acylated instead of benzene. Crude PEB and MPEB were purified through recrystallization from methanol.

Addition Reactions of s-BuLi with PEB or MPEB. The addition reactions of s-BuLi with PEB or MPEB were carried out in either a 100-mL or a 250-mL round-bottomed flask equipped with a side arm. The flask after thoroughly purged with nitrogen was kept at atmospheric pressure of nitrogen through a mineral oil bubbler. Nitrogen was purified by bubbling through a solution of sodium naphthalene in tetraethylene glycol dimethyl ether. The side arm was capped with a rubber septum for the introduction of reactants and withdrawal of samples. Magnetic stirring bars were used for the agitation.

In a typical run, PEB or MPEB was weighed into the flask and degassed three times. Solvent, toluene, cyclohexane, or *n*-hexane, was added to the flask through the rubber septum by a syringe. After the replacement of a new rubber septum, the solution was again degassed three times. A water bath was used to maintain a constant temperature. Subsequently, a s-BuLi solution in cyclohexane was added through the septum. Samples were withdrawn from the flask at various times also through the septum. For each sample, a few milliliter aliquot was taken with a syringe and transferred into a nitrogen-filled bottle which contained a small amount of acetic acid as the terminator. The lithium acetate salts were separated by centrifugation, and the resultant solution was used directly for GC analysis. For GPC analysis, the solvent was removed from the solution by purging with nitrogen and the resultant product was used.

Preparation of DLI for Storage Stability Studies. Stock solutions of DLI were prepared in 500-mL stainless steel tubes. Before each use, the DLI solution was transferred into a 100-mL glass flask under a nitrogen atmosphere. The exact amount of DLI was then transferred from the flask to the reactor by a syringe.

Preparation of SIS Triblock Copolymer. A 1.3-L jacketed reactor with a hollow auger agitator was used for all polymerizations. The lower, jacked part of the reactor was constructed of stainless steel. The upperpart was glass to permit observations of color changes and viscosity changes during a polymerization experiment. The inlets for solvent and reagent addition passed through a stainless steel plate sealing the top of the reactor, and a sample port was located at the bottom.

In a typical experiment, cyclohexane was added to the reactor directly from a holding tank through an activated alumina column and degassed three times in the reactor, and the small excess amount was drained out from the discharging tube to retain 675 mL in the reactor. Subsequently, 125 mL of isoprene (85 g) was added by a syringe. After mixing well, an aliquot of 50 mL of the feed solution was withdrawn by using a syringe for external titration with the DLI to determine the impurities in the solution and the amount was very small. A 0.5-mL solution of cyclohexane containing 0.24 mmol PMDETA was then added. The jacket temperature was set at 55 °C. When the solution temperature reached about 53 °C, DLI was added to start the polymerization of isoprene. A nitrogen pressure of 10–14 psi was maintained in the head space of the reactor during the polymerization. About 40 min after the addition of DLI, 15 mL (13.6 g) of styrene was added. After another 30 min 2 mL of 2-propanol was added to terminate the living chains. Carbon dioxide was bubbled through the polymer solution, and then 1 g of di-*tert*-butylhydroxytoluene was added. The polymer was recovered by vacuum drying.

Preparation of SBS Triblock Copolymers. The DLI **I** or **II** was prepared in toluene from freshly purified PEB or MPEB just before each polymerization run. The polymerization apparatus and techniques for SBS were similar to that described earlier.[1] The polymerization reactor was a round-bottomed glass flask, and the solvent was toluene. The flask and connecting accessories were baked before use and were kept at atmospheric nitrogen pressure during the polymerization. A dry-ice condensor was provided to keep vapors of solvents and monomers from escaping through the outlet connected to the nitrogen bubbler. For making pure SBS triblock copolymers, toluene was introduced into the flask by siphon and then degassed once. Butadiene monomer was added into the flask which was calibrated volumetrically for measuring the quantity of the butadiene added. A small amount of s-BuLi was added to react with the estimated quantity of impurities in the solution. The solution was heated with a water bath of 50–60 °C, and DLI was added. When butadiene polymerization was completed, styrene monomer and a small amount of THF were added. After styrene polymerization was completed, methanol was added. The resulting polymer was precipitated in methanol and vacuum dried. The dried polymers were analyzed by GPC and tensile properties. For making tapered SBS triblock copolymers, the styrene monomer was added before the initiation of butadiene polymerization and no THF was used.

Analysis. Gel permeation chromatography (GPC) measurements were made on a Waters 150C GPC equipped with six Varian MicroPak TSK columns and a UV photometer as the second detector.

The gas chromatograms were made on a Hewlett-Packard Model 5840A instrument with either a 25 m or a 12-m OV-101 methyl silicone capillary column.

The ^{1}H NMR spectra were determined on a Varian EM-390 spectrometer operating at 90 MHz. Polymer samples were prepared as ca. 12% w/v in perchloroethylene.

Tensile properties of the triblock copolymers were tested at 23 °C on specimens compression molded at 190 °C. The 0.025-in. thick 3-in. long dumbbell-shaped specimens were cut from the molded sheet. The cross-head speed was 20 in./min.

Conclusions

Hydrocarbon-soluble DLI **I** and **II** were prepared from the addition of s-BuLi to two DDPE compounds, PEB and MPEB. The DLI from PEB was soluble in toluene and cyclohexane but not in *n*-hexane, while the DLI prepared from MPEB was soluble in all three solvents.

Except that DLI **II** formed from MPEB was soluble in *n*-hexane, the kinetics of the addition reaction of s-BuLi to the two DDPE compounds were similar. In toluene the two double bonds on the DDPE were about equally reactive; in cyclohexane and *n*-hexane the second double bond was more reactive after the first had reacted. In toluene the initiators formed rapidly and cleanly from the addition reaction and could be used directly for initiating anionic polymerization. The initiators, however, were not stable for storage in toluene. In cyclohexane, longer times or slightly elevated temperatures were required for the formation of the initiators, but they could be stored in cyclohexane for much longer times.

The two DLI behaved similarly in polymerization. Tensile strengths from 3000 to over 4000 psi were obtained for SBS triblock copolymer prepared when the DLIs were used directly. However, polar additives were required to promote the polymerization for preparing SIS triblock copolymers of high tensile strength.

PEB oxidized in air to the corresponding monoketone and diketone but was found stable for years when stored under nitrogen. The same is expected for MPEB.

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