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Studies on Dilithium Initiators. 3. Effect of Additives and Seeding

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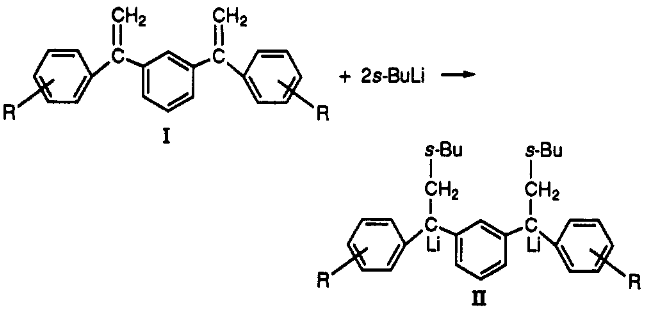
ABSTRACT: The effect of additives and seeding on the molecular weight distribution of diene polymers prepared by two hydrocarbon-soluble dilithium initiators, 1,3-phenylenebis(3-methyl-1-phenylpentylidene)-dilithium and 1,3-phenylenebis[3-methyl-1-(methylphenyl)pentylidene]dilithium, was investigated. Without any additives or seeding, the distribution of polyisoprene was bimodal and broad by the standard of polymers prepared by anionic polymerization. A particularly effective additive was *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA). Distribution with M_w/M_n of 1.07 was obtained with the microstructure of the polyisoprene only slightly affected. Several lithium alkoxides narrowed the distribution but not as effectively as PMDETA. Lithium alkoxides, however, kept the microstructure of the polyisoprene unchanged. Another tertiary amine, *N,N,N′,N′*-tetramethylenediamine, was also less effective than PMDETA. Seeding, by reacting the initiator with a fractional amount of isoprene first and then with the rest of the monomer, also made narrow distribution polyisoprene. The distributions of polybutadiene prepared by the dilithium initiators were also made narrower by the same techniques.

Introduction

Polymers of 1,3-butadiene and isoprene with narrow molecular weight distribution and good elastomeric properties are made by anionic polymerization in hydrocarbon solvents with organolithium initiators. Industrially, butyllithium is used to produce polybutadiene and the triblock copolymers of styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS). Preparation of telechelic polydienes and diene triblock copolymers with endblock compositions other than styrenic polymers requires the use of a dilithium initiator. Because of the strong association of organolithium compounds, most of the dilithium initiators need a polar additive to make them soluble in hydrocarbon solvents. Dilithium compound **II**, derived from the addition reaction of *sec*-butyllithium (s-BuLi) to either of the two double 1,1-diphenylethylene (DDPE) copounds, 1,3-bis(1-phenylethenyl)benzene (PEB) or 1,3-bis[1-(methylphenyl)ethenyl]benzene (MPEB), was shown earlier[1] to be hydrocarbon soluble and convenient to use.



R = H; **I** = PEB,
II = 1,3-phenylenebis(3-methyl-1-phenylpentylidene)dilithium
R = CH_3; **I** = MPEB,
II = 1,3-phenylenebis[3-methyl-1-(methylphenyl)pentylidene]dilithium

Triblock SBS prepared from **II** had a tensile strength comparable to that prepared by conventional butyllithium initiators. Triblocks of polybutadiene and of polyisoprene with a copolymer of styrene and α-methylstyrene as the end block were also prepared.[2] The molecular weight distributions of the butadiene block copolymers initiated by **II**, however, are slightly broader than the distributions of butadiene polymers initiated by butyllithium. The weight- to number-average molecular weight (M_w/M_n) for butadiene polymers initiated by butyllithium is usually between 1.05 and 1.08 as versus 1.1 and 1.2 when initiated by **II**. When **II** was used to initiate isoprene polymerization, the distribution of the polymer became considerably broader and often bimodal in shape. The properties of styrene–isoprene–styrene (SIS) initiated by **II** were also poor. Later[3] it was found that **II** reacted quickly with isoprene to form an adduct with several units of isoprene attached, but further polymerization of isoprene from the adduct was very slow. In most difunctional polymerization systems, a small amount of monofunctional initiating species is likely to be present. Because of the difference in the rate of propagation, 2–3% monofunctional initiating species contributed 10–20% material in the final polymer and the molecular weight distribution became bimodal. In triblocks, the 10–20% material from monofunctional initiating species became diblock when styrene was added, and the strength of the final SIS product was weakened by its presence. The slow propagation of oligomeric isoprenyldilithium was observed also by Madani et al.[4] in isoprene polymerization initiated by another dilithium initiator. They attributed the phenomenon to the intramolecular association of the isoprenyldilithium and found that the extent of the propagation slowing was concentration and molecular weight dependent. The slow propagation of low molecular weight isoprene chains in difunctional lithium initiated polymerization therefore appeared to be general and not just characteristic of compound **II**. To fully realize the advantages of dilithium initiation in anionic polymerization, some modification of the polymerization conditions was required. In this work, several methods to achieve this end were investigated.

Results and Discussion

Solvents are known to exert a strong influence on the mode of diene polymerization. In polar aprotic solvents, the organolithium compounds are more ionic and the diene monomer polymerizes more in the 1,2 addition mode (or

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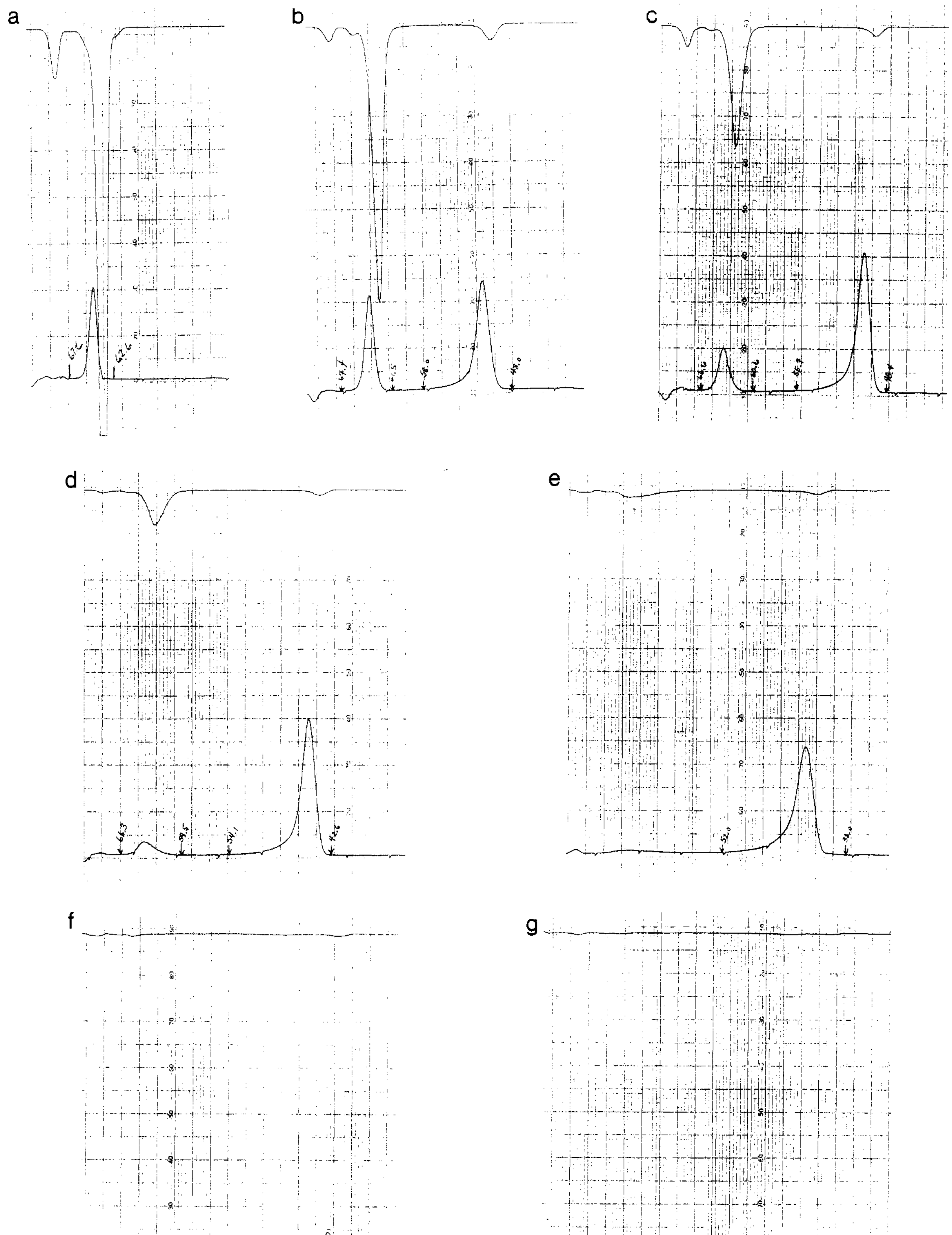

Figure 1. GPC chromatograms of samples taken from isoprene polymerization in cyclohexane using **II** alone as the initiator. Min is the time when the sample was taken; % is the monomer conversion. The upper curve is the chromatogram from the UV detector, and the lower curve is from the differential refractive index detector. (a) Terminated **II**. (b) 2.5 min, 1.9%. (c) 5 min, 4.1%. (d) 10 min, 9.5%. (e) 20 min, 22.7%. (f) 30 min, 56.9%. (g) 70 min, 97.7%.

3,4 in the case of isoprene). As a result, the polydiene has more branches, has a high glass transition temperature, is less likely to enter into strain crystallization, and in general has poorer elastomeric properties. However, a small amount of tertiary amine or ether compounds may alter the mode of association of organolithiums in hydrocarbons without drastically changing the mode of diene polymerization. Triethylamine was used by Foss et al.[5] in the preparation of dilithium initiators from the addition reaction of s-BuLi to *m*-diisopropenylbenzene. Fetters and Morton[6] used anisole in the preparation of another initiator, 1,4-dilithio-1,1,4,4-tetraphenylbutane, and found that the diene polymerization in the presence of a small amount of anisole proceeded substantially in the 1,4 addition mode. Additives of similar kind were therefore investigated to see if they would help narrow the distribution by reducing the excessive association in diene oligomers initiated by **II**.

Madani et al.[4] reported that the rate of propagation from dilithium oligomers was autoaccelerated, and the extent of autoacceleration was molecular weight and concentration dependent. The observation of Madani et al. made the use of the "seeding technique" also promising. Seeding requires no additivies; microstructure should not be affected, and removal of addivites from products would not be necessary. The latter advantage might be an important consideration in commercial uses of the polymer. Seeding was therefore also studied.

Effect of Alkoxides. Earlier, lithium isopropoxide was reported[7] to have prevented the formation of bimodal molecular weight distribution in polyisoprene initiated by **II**. The use of other lithium alkoxides was disclosed in a U.S. patent.[8] Quirk and Ma[9] reported that lithium *sec*-butoxide produced narrow distribution polybutadiene and polystyrene initiated by **II**.

To investigate how lithium alkoxide influenced the development of molecular weight distribution during isoprene polymerization, two isoprene polymerization experiments initiated by **II** were carried out in cyclohexane under similar conditions, one with lithium isopropoxide added and the other without. In the polymerization with lithium isopropoxide, 2-propanol was added to the isoprene–cyclohexane feed in the reactor. An equivalent amount of s-BuLi was added to react with the alcohol. The amount of lithium isopropoxide created was at a ratio of 0.4 per each lithium of **II** (an equivalence ratio of 0.4) used for initiation. A 0.07 M toluene solution of **II** based on PEB was then injected into the feed mixture to start the polymerization. The concentration of **II** in the polymerization was about 0.001 M and the concentration of isoprene about 1.5 M. As in an earlier investigation,[3] the development of bimodal distribution was followed by GPC chromatograms of samples taken during the polymerization. In Figure 1 are the GPC chromatograms of samples from the polymerization without lithium isopropoxide. As reported before,[3] at 2.5 min (chromatogram b), the peak for the terminated **II** in chromatogram a moved to a lower retention volume (higher molecular weight) and showed less UV intensity, reflecting that isoprene units had attached to nearly all of **II** in the mixture at this point of polymerization. Another peak at higher molecular weight in chromatogram b had been identified[3] as the polyisoprene polymerized from a small amount of monofunctional initiators present inadvertently in the polymerization mixture. The large difference between the two peak molecular weights in chromatogram b showed that further polymerization from the **II**–isoprene adduct was very slow in comparison with the rate of normal isoprene polymerization in cyclohexane. As the polymerization progressed further, the two peaks skewed toward each other. The lower molecular weight peak of the adduct diminished in size. The tail of the skewed higher molecular weight peak grew to a new broad distribution. The progression created an illusion of "melting" of the adduct peak into the formation of the main peak. This melting illusion was probably a manifestation of the autoacceleration of the isoprene propagation rate observed by Madani et al.[4] The GPC chromatograms from the polymerization in the presence of lithium isopropoxide have the same melting characteristic in the sequence except that melting occurred faster. At 30 min the two peaks merged into one and the distribution was no longer bimodal.

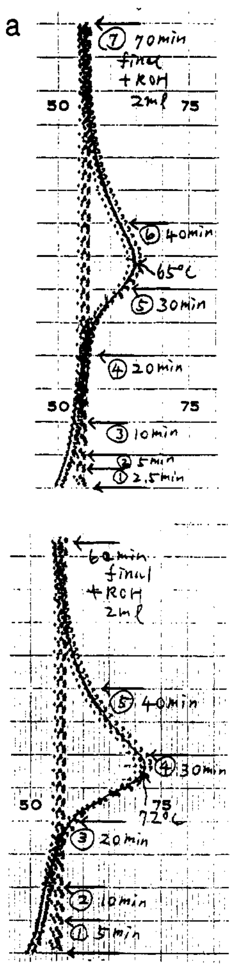

Figure 2. Temperature profiles of two isoprene polymerization runs. (a) Run with **II** alone as the initiator. (b) Run with **II** and lithium isopropoxide as the additive.

The temperature profiles of the two polymerization experiments are shown in Figure 2. Recorded in the profiles were the set temperature of the reactor jacket an the thermocouple readings of the polymerization mixture. Although the reactor had temperature controls, the highly exothermic polymerization proceeded in a semiadiabatic manner. The major exothermic peak in the temperature profile corresponded to the period of fast polymerization from the dilithio chains and the accompanying rapid rise in the viscosity of the polymerization solution. In the profile for the experiment made with lithium isopropoxide, the exothermic peak occurred sooner and the temperature rise was higher.

These results show that alkoxides had effectively promoted the propagation rate of isoprene from the adduct of II–isoprene. The final polyisoprene polymerized with and without lithium isopropoxide had identical amounts (about 7%) of 3,4 addition and the glass transition temperatures of the two polyisoprenes as measured by DSC were also identical at −57 °C.

The M_w/M_n of polyisoprene made with lithium isopropoxide at various other amounts and with other alkoxides is shown in Table 1. The M_n for the samples was included in Table 1 because, under the same polymerization conditions, the distribution is molecular weight dependent. It appeared that an amount of lithium isopropoxide greater than 0.5 equivalence to **II** provided little additional beneficial effect. Other alkoxides had about the same effect as isopropoxide. Lithium methoxide, on the other hand, apparently had no effect.

Table 1. M_w/M_n of Polyisoprene Prepared in Toluene with II and an Alkoxide

alkoxide	alkoxide/Li in II	M_n	M_w/M_n
none	0	42 300	1.50
isopropoxide	0.11	39 400	1.35
isopropoxide	0.21	32 600	1.30
isopropoxide	0.50	34 500	1.19
isopropoxide	0.89	40 500	1.16
isopropoxide	1.01	35 600	1.24
ethoxide	0.48	103 500	1.15
tert-butoxide	0.10	41 300	1.35
methoxide	0.88	53 800	1.66

The distribution of polybutadiene and SBS initiated by **II** are usually monomodal[1] when their molecular weights were greater than 100 000. Bimodal distribution was reported by Quirk and Ma[9] for lower molecular weight polybutadienes initiated by **II**. They reported lithium *sec*-butoxide at a 0.5 equivalence ratio to **II** produced monomodal distribution polybutadiene and a SBS triblock at a molecular weight as low as 26 000. In this study, two butadiene–styrene copolymerizations initiated by **II** were carried out in toluene, one with 0.37 equiv of lithium isopropoxide added and the other without any. In these experiments, butadiene and styrene monomers at a weight ratio of 2:1 were mixed together in toluene before initiation. The final polymers both at a M_n of about 140 000 were tapered triblock copolymers with polybutadiene at the center and end blocks of polystyrene. The tapered sections between the blocks were dictated by the reactivity ratios of the two monomers. No samples were taken during the polymerization. The GPC chromatograms for the two final SBS samples are shown in Figure 3. The SBS made without isopropoxide has a distribution with a hint of bimodality and a M_w/M_n of 1.17. The distribution of the SBS made with lithiumisopropoxide was narrow and monomodal with a M_w/M_n ratio of 1.08.

The above results show that the effect of alkoxide on butadiene polymerization initiated by **II** was similar to that on isoprene polymerization. The difference between the rates of polymerization from the inadvertently present monofunctional initiation and the difunctional polymerization was smaller in butadiene polymerization than in isoprene polymerization.

Effect of *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA). A particularly effective additive found for promoting isoprene polymerization initiated by **II** was PMDETA.[10] Narrow monomodal distribution polyisoprene with M_w/M_n below 1.1 appeared not attainable by the use of alkoxides but was easily obtained by the use of PMDETA. An experiment with samples taken at different stages of isoprene polymerization in cyclohexane was made with **II** and PMDETA at a ratio of 0.18 to the Li in **II**. Figure 4 shows the GPC chromatograms of the samples. At 5 min the chromatogram again shows two peaks as in the other isoprene polymerizations. The two peaks, however, were much closer in molecular weight than before. In the chromatograms for the next sample taken at 10 min, the two peaks had already merged to a monomodal distribution. The melting of the lower molecular weight peak was no longer observable. In the isoprene polymerization made at a higher PMDETA/Li ratio of 0.47, no bimodal distribution was observed at any stage of the polymerization. For the 0.18 PMDETA/Li polymerization, the exothermic temperature rise started more quickly and reached a maximum at an earlier time than the other two temperature profiles shown in Figure 2. The viscosity of the polymerization mixture was noticeably lower when PMDETA was used. Because of a much lower viscosity, at 0.47 PMDETA/Li the heat of polymerization dissipated very quickly and the temperature rise became barely visible. The lower temperature in the run kept the polymerization at a slower rate at the later stages. At PMDETA/Li of 0.98, no exothermic peak was observed. The temperature stayed at the control

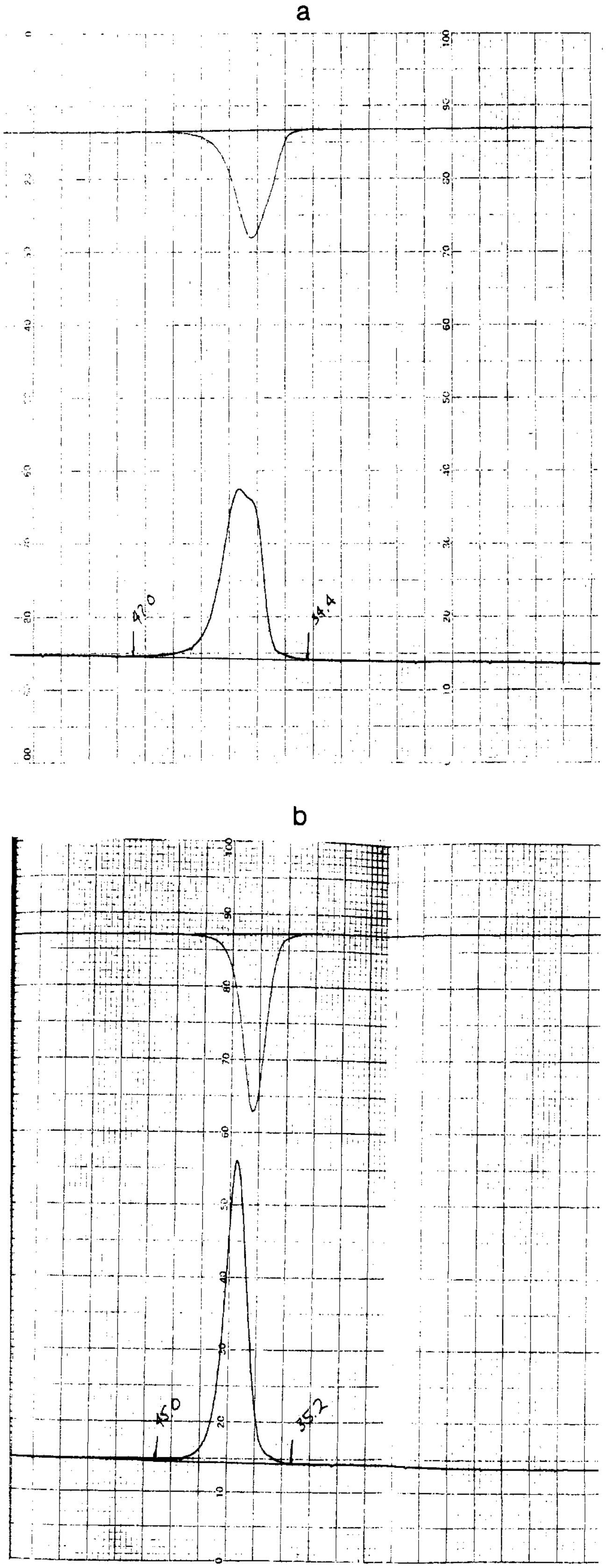

Figure 3. GPC chromatograms of a tapered SBS triblock copolymer prepared in toluene. (a) SBS prepared with **II** as the initiator. (b) SBS prepared with **II** and lithium isopropoxide as the additive.

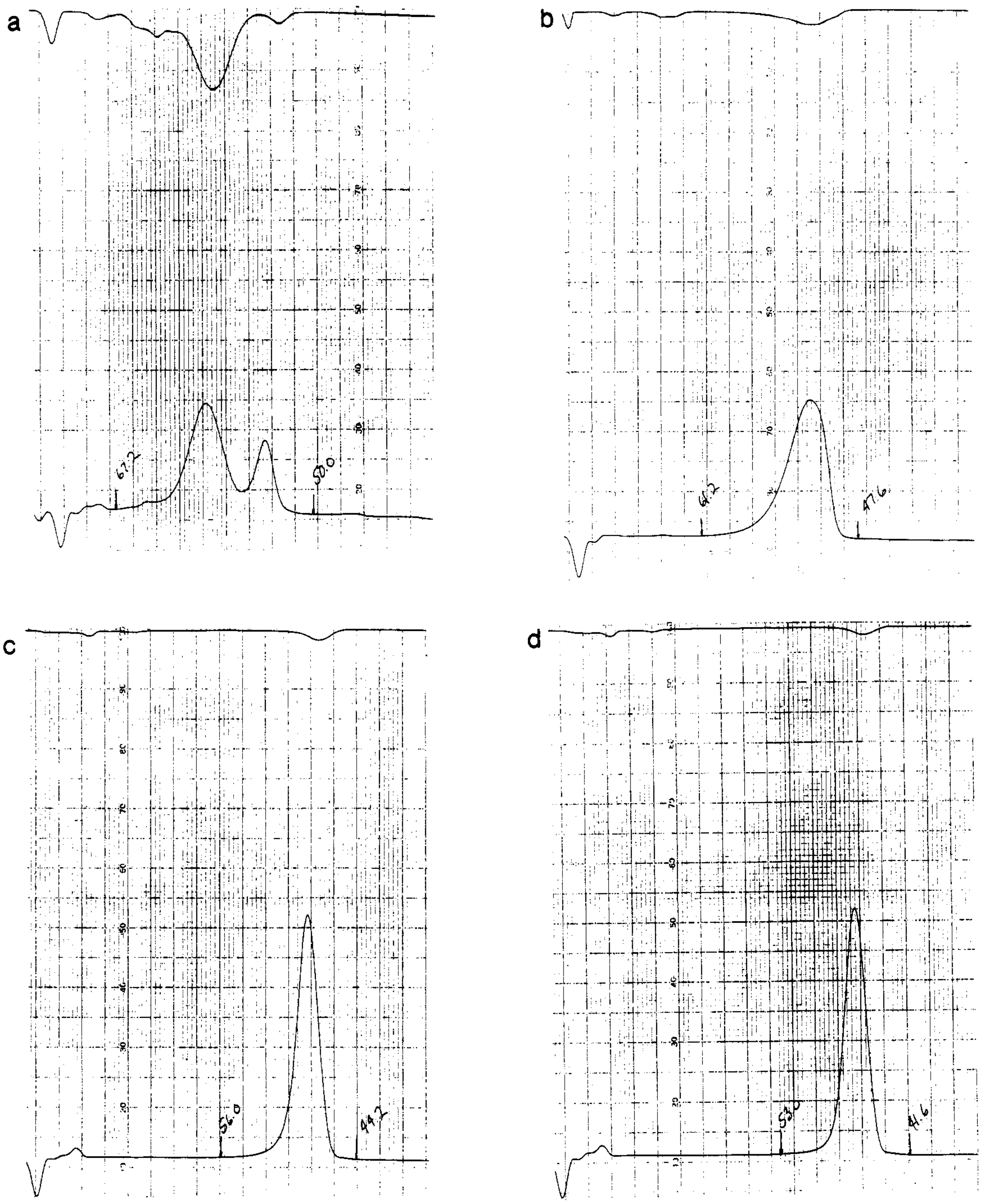

Figure 4. GPC chromatograms of samples taken from isoprene polymerization in cyclohexane using **II** as the initiator and PMDETA at PMDETA/Li = 0.18 as the additive. Min is the time when the sample was taken; % is the monomer conversion. The upper curve is the chromatogram from the UV detector, and the lower curve is from the differential refractive index detector. (a) 5 min, 4.0%. (b) 10 min, 16.8%. (c) 15 min, 50.9%. (d) 60 min, 96.9%.

Table 2. Microstructure and T_g of Polyisoprene Prepared in Cyclohexane with II and PMDETA

PMDETA/Li	M_n	M_w/M_n	3,4%	T_g (°C)
0	121 000	1.53	7.1	-56.6
0.18	82 000	1.07	10.8	-54.5
0.47	72 000	1.06	29.2	-39.0
0.98	51 000	1.09	50.4	-9.6

Table 3. Tensile Properties of SIS Prepared in Cyclohexane with II and PMDETA

PMDETA/Li	3,4 in PI (%)	Sty (%)	M_n	M_w/M_n	tensile (psi)	elong (%)
0.17	10.8	15.1	143 000	1.08	3180	1350
0.09	8.4	14.9	127 000	1.09	1350	1410
0.04	8.2	15.3	135 000	1.20	1420	1370
0	7.5	15.4	159 000	1.44	880	1470

temperature of the reactor jacket throughout the polymerization. As a result, the rate languished and only 56% isoprene in the mixture polymerized after 2 h.

The microstructure and the glass transition temperature (T_g) of the polyisoprene made at several PMDETA/Li ratios are shown in Table 2. It appears that PMDETA/Li higher than 0.18 did not narrow the distribution any further but 3,4 addition in the polyisoprene increased, making the T_g higher than desired.

Several SIS triblock copolymers were also prepared with **II** and PMDETA/Li at 0.17 and lower. Their properties are shown in Table 3. The results in Tables 2 and 3 show that at a 0.17 to 0.18 PMDETA/Li ratio, polyisoprene and SIS triblock copolymers initiated by **II** were comparable in properties and molecular weight distribution to those made with conventional butyllithium initiators. The 3,4 content in the polyisoprene was slightly higher than the polyisoprene made without PMDETA. The 0.17 to 0.18 PMDETA/Li ratio appeared to be an optimum amount of PMDETA to use with **II**. Larger amounts of PMDETA would raise the 3,4 and glass transition temperatures in polyisoprene to an undesirable level. Weaker and broader distribution SIS triblocks were obtained if smaller amounts of PMDETA were used.

In butadiene polymerization initiated by **II**, a much lesser amount of PMDETA was required to produce very narrow distribution polymers. Tapered SBS initiated by **II** in cyclohexane had a distribution similar to that made in toluene with a M_w/M_n ratio of about 1.17. Tapered SBS made with 0.0125 PMDETA/Li reduced the M_w/M_n to 1.06. The 1,2 content of the polybutadiene center block changed from 11% to about 16%.

Table 4. Microstructure of Polyisoprene Prepared in Cyclohexane with II and TMEDA

TMEDA/Li	M_n	M_w/M_n	3,4%
0	121 000	1.53	7.1
0.24	82 000	1.13	10.1
0.51	132 000	1.07	32.0

Effect of *N,N,N',N'*-Tetramethylethylenediamine (TMEDA). Another commonly used chelating additive for promoting anionic polymerization in hydrocarbon solvents is TMEDA. Dumas et al.[11] studied the effect of both PMDETA and TMEDA on isoprene polymerization. In this study, two isoprene polymerization initiated by **II** were conducted, one with TMEDA added at a TMEDA/Li ratio of 0.24 and the other at a TMEDA/Li ratio of 0.51. The GPC chromatograms of the samples taken in the two experiments had the same features as those in Figure 1 except that the melting happened faster. For polymerization with TMEDA/Li at 0.24 the final polymer still had a high molecular weight shoulder on the monomodal peak. The final polymer for the polymerization with TMEDA/Li at 0.51 had a narrow and symmetrical distribution like the distribution for the final polymer prepared with PMDETA/Li at 0.18 as shown in Figure 4. However, in the case when PMDETA was used, melting was not observed. Melting was still clearly observable in the polymerization with TMEDA/Li. As shown in Table 4, in comparison to PMDETA, more TMEDA is needed to narrow the MWD with a consequent higher increase of the 3,4 content in polyisoprene.

Effect of Seeding. Narrow molecular weight distribution is obtained in polymerization when the rate of initiation is comparable or faster than the rate of propagation and the rate of termination is very slow or nonexistent. In some polymerizations, where the relative rate of initiation is unfavorable for the preparation of narrow distribution polymer, seeding[12] is a technique used to overcome this deficiency. In the "seeding" technique, a small fraction of monomer to be polymerized is used to react with the initiator first. The rest of the monomer is then introduced to the seeded initiator to complete the polymerization. Questions on the effectiveness of the technique have been raised.[13] However, if the relative rates of initiation and propagation are influenced by the concentration of the initiator or the monomer, then seeding may be used to change the distribution in an advantageous manner. Roovers and Bywater[14] used it successfully to prepare narrow distribution polystyrene in benzene with *tert*-butyllithium initiation.

In isoprene polymerization initiated by **II** there is ample evidence that the rate-controlling step is the propagation from the adduct of **II**–isoprene and the propagation is autoaccelerated as reported by Madani et al.[4] Madani et al. reported also that autoacceleration was less pronounced at high initiator concentrations. Polymerization at a higher concentration of **II** in one step to reach the desirable molecular weight in practical polymers will create a severe heat dissipation problem. Dividing the polymerization into two steps, as in seeding, should allow the early propagation to be carried out at a higher concentration without the danger of a run-away polymerization. A two-step polymerization was carried out to test if seeding was useful. In the first step, the full amount of **II** was used to initiate one-fourth the normal amount of isoprene in the same fractional amount of cyclohexane. The concentration of **II** was at 0.0035 M, about 4 times the normal. At the end of the first step, more isoprene and cyclohexane were added to restore the concentrations of all components to normal. Finally after all isoprene was polymerized, styrene was added to make a SIS triblock of 15% styrene and 85% isoprene. The GPC chromatograms of the samples taken during the polymerization showed the melting feature of the low molecular weight peak to form the main peak, but the melting occurred at a much lower molecular weight than the polymerization at normal concentrations as shown in Figure 1. The M_n of the polyisoprene at the end of the first step was only 38 400. The GPC chromatogram of the polyisoprene collected at the end of the first step is shown in Figure 5a. The distribution was still bimodal, but the main peak from difunctional initiation was more dominant than that in the distribution of the polyisoprene of 121 000 molecular weight made at normal concentrations. At the end of the second step, the distribution of the polyisoprene is monomodal as shown in Figure 5b. The M_n was 113 000 and the M_w/M_n ratio was 1.18. The chromatogram of the final SIS is shown in Figure 5c. The SIS has a M_n of 142 000 and a M_w/M_n ratio of 1.12. The rupture strength was 3330 psi at an elongation of 1350% which compared favorably with the SIS made with PMDETA shown in Table 3.

Four more seeding experiments were carried out with about $^1/_{10}$ of the monomer and solvent used in the first step. In two of the experiments, a small amount of PMDETA was used. The properties and characteristics of the final SIS of the four experiments together with a normal polymerization using PMDETA for comparison are shown in Table 5. The GPC chromatograms of the five final SIS polymers were all monomodal and symmetrical.

The above results show that seeding is effective in narrowing the distribution of **II** initiated polyisoprene and it is also effective in improving the properties of SIS. The addition of a small amount of PMDETA with seeding did not substantially improve the properties further, but it did serve the purpose of reducing the viscosity of the polymerization mixture.

Experimental Section

Materials. Polymerization-grade isoprene was purchased from Goodyear Tire and Rubber Co. and was purified by passing through an activated alumina column and vacuum distilled in the presence of dibutylmagnesium just before use.

Styrene was obtained from Dow production facilities and was purified by passing through an activated alumina column and vacuum distilled in the presence of calcium hydride just before use.

1,3-Butadiene was rubber grade from Phillips Chemical Co. Butadiene after passing through an activated alumina column in the liquid state was collected in a stainless steel weighting tube and then transferred to the polymerization reactor.

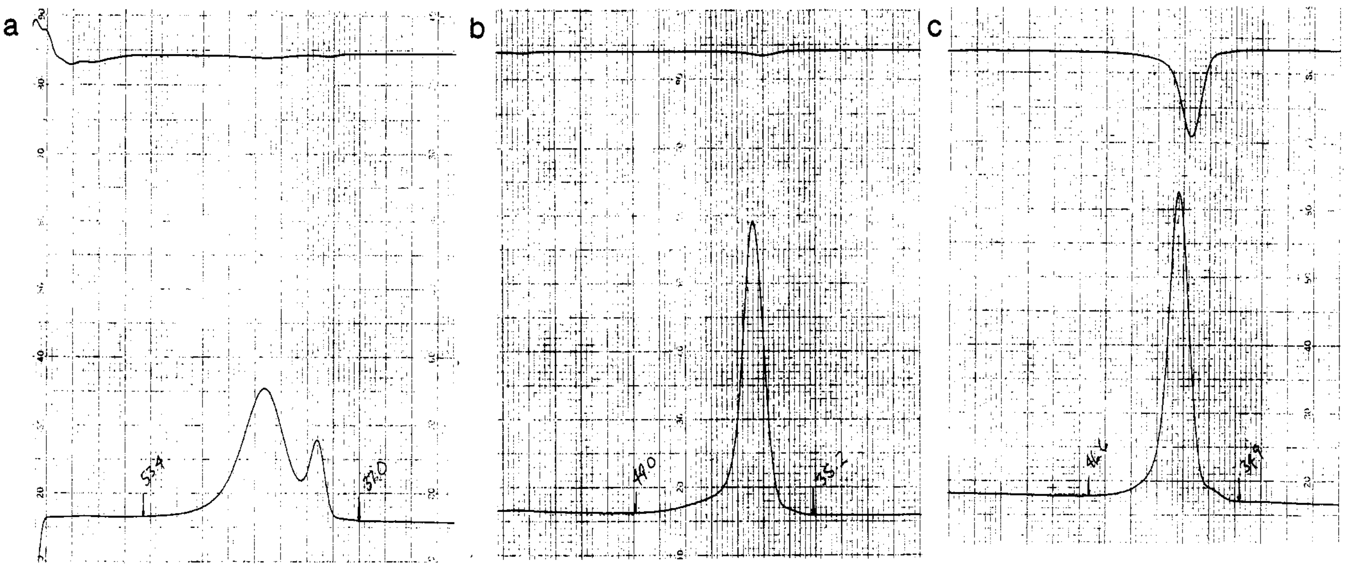

Figure 5. GPC chromatograms of samples taken from isoprene polymerization in cyclohexane using **II**: 1st step, seeding; 2nd step, isoprene and styrene polymerization. (a) Polyisoprene at the end of the first step, 60 min, 99.6%. (b) Final polyisoprene before the addition of styrene. (c) Final SIS.

Table 5. Characteristics and Tensile Properties of SIS Prepared with Seeded II

PMDETA/Li	3,4 in PI (%)	Sty (%)	M_n	M_w/M_n	tensile (psi)	elong (%)
0	7.6	15.2	144 000	1.17	3360	1300
0	7.6	15.7	121 000	1.13	3360	1120
0.05	8.4	15.8	126 000	1.12	3260	1310
0.05	8.1	15.2	142 000	1.10	3470	1290
0.17[a]	10.0	15.4	133 000	1.08	2900	1280

[a] A normal unseeded single-step polymerized SIS.

Toluene and cyclohexane both were purchased distilled-in-glass grade. Both solvents were dried by activated alumina before use.

PMDETA, TMEDA, s-BuLi, methanol, ethanol, propanol-2, and *tert*-butyl alcohol were all purchased reagent-grade materials and were used directly.

Initiator. Compounds **II** based on PEB and on MPEB were both used. 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 instead of benzene was acylated. Crude PEB and MPEB were purified through recrystallization from methanol.

Stock solutions of **II** were prepared in 500-mL stainless steel tubes by reacting equivalent amounts of *sec*-butyllithium with PEB or MPEB. Before each use, the solution was transferred into a 100-mL glass flask under a nitrogen atmosphere. The exact amount of the solution of **II** was then transferred from the flask to the reactor by a syringe.

Polymerization. Most of the polymerization experiments were carried out in a 1.3-L stainless steel reactor described earlier.[1] A 2-L reactor of similar construction was used for butadiene polymerization. Both reactors were provided with controlled heating jackets and devices for cooling. Polymerization was carried out in them under mild nitrogen pressure. The polymerization experiments listed in Table 1, however, were carried out in a 1-L round-bottomed glass flask. 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. A water bath was used to heat or cool the reactor. Procedures for the polymerization experiments were similar to those described earlier.[1,3]

Seeding was carried out in the stainless steel reactor in the same manner as in a normal isoprene polymerization except that the amounts of solvent and monomer were greatly reduced in the first step.

Analysis. Gel permeation chromatography (GPC) measurements were made on a Waters 150C instrument equipped with a six Varian MicroPak TSK columns and a UV photometer as the second detector. Samples from polymerization reactions were terminated with methanol and washed before use in GPC determinations.

Tensile properties of the triblock copolymer were tested at 23 °C on compression-molded specimens. 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.

Glass transition temperatures were determined on a DSC instrument.

Conclusions

Several alkoxides were effective in preventing the formation of bimodal molecular weight distribution in polyisoprene initiated by **II**. Lithium ethoxide, isopropoxide, and *tert*-butoxide produced monomodal and narrow distributions by promoting the propagation rates from the adduct of **II** with isoprene. The optimum amount of lithium isopropoxide was at a 0.5 equivalence ratio to the lithium in **II**. At this amount of alkoxide, the microstructure of the polyisoprene remained unchanged from the polyisoprene prepared without any alkoxide added. Lithium isopropoxide narrowed the molecular weight distribution of butadiene polymers too. Lithium methoxide, however, was not effective.

A particularly effective additive to **II** was PMDETA. At the optimum amount of 0.17–0.18 PMDETA/Li ratio, the 3,4 vinyl content in polyisoprene showed only a slight increase. Using PMDETA at this level, a narrow monomodal distribution of M_w/M_n of 1.07, which was not attainable by the addition of alkoxides, was made. High tensile strength SIS was also made by using PMDETA as the additive to **II**. Narrow distribution butadiene polymers can also be made using PMDETA as the additive. The amount needed was much less than that required for polyisoprene.

TMEDA was also effective, but more had to be used. For the same amount of narrowing, TMEDA had a more adverse influence on the microstructure of polyisoprene.

Seeding was effective in making monomodal distribution polyisoprene and SIS of high tensile strength.

These results are consistent with the view that the initial compound **II**-isoprene adduct is the rate barrier for making narrow distribution polymers. The methods demonstrated in this study should enable **II** to be used efficiently in making other diene triblock copolymers or telechelic polydienes which are not readily prepared by monofunctional initiators.

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