Studies on Dilithium Initiators. 4. Effect of Structure Variations

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ABSTRACT: New double 1,1-diphenylethylene (DDPE) compounds with different substituent groups on 1,3-bis(1-phenylethenyl)benzene (PEB) and samples of 1,3-bis[1-(methylphenyl)ethenyl]benzene (MPEB) with different methyl group positions on the phenyl rings were prepared. Included in the preparation was also a non-DDPE diolefinic compound in which the center phenyl ring of PEB was replaced by a saturated one. The behavior of isoprene polymerization initiated by the dilithium initiators obtained by the addition reaction of *sec*-butyllithium (s-BuLi) with these diolefinic compounds was studied. The slow propagation from the initial initiator–isoprene adduct observed for the initiators based on PEB and MPEB was not affected by any of the structural variations. Structural variations, however, had an influence on the relative reaction rate of the two double bonds on the diolefinic compounds with s-BuLi. Replacement of the center phenyl ring with a saturated cyclohexane ring drastically reduced the double bond reaction rate with s-BuLi.

Introduction

A family of dilithium initiators (DLI) prepared by the addition reaction of *sec*-butyllithium (s-BuLi) with compounds containing two 1,1-diphenylethylene functional groups (DDPE; double 1,1-diphenylethylene compounds) have been reported.[1] Unlike other DLI, they can be made in hydrocarbon solvents without the presence of any polar additives. The reaction was swift, and the DLI can be made nearly free of residual reactants and other by-products. Among the members of the DLI reported, the ones derived from the DDPE compounds, 1,3-bis(1-phenylethenyl)benzene (PEB) and 1,3-bis[1-methylphenyl)ethenyl]benzene (MPEB) are most interesting because of their solubilities in hydrocarbon solvents.[2] Useful high strength styrene–butadiene–styrene and other butadiene triblock copolymers[3,4] have been prepared from these DLI. However, styrene–isoprene–styrene (SIS) triblock copolymer made from them was weak and had a broad bimodal molecular weight distribution.

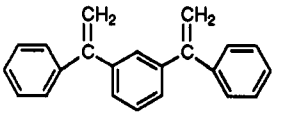
The formation of the bimodal distribution in isoprene polymerization has been attributed to the inadvertent presence of monofunctional initiator (MFI) in the DLI systems and the slow propagation from the initial addition product of isoprene with the DLI.[5] The initiation by a MFI and the subsequent propagation were fast, and the polyisoprene derived from it became the high molecular weight peak of the bimodal distribution. The initiation of isoprene by a DLI, though not slow, led to a very slow propagation from the initial addition product of isoprene with the initiator. The main peak of lower molecular weight and broader molecular weight distribution was the polyisoprene from the DLI. Complete elimination of MFI from any DLI system was difficult. As low as 2–3% of MFI would cause the formation of bimodal distribution and a deterioration of SIS properties.

This slow propagation of isoprene from the initial DLI–isoprene adduct was believed to be caused by a strong intramolecular association of the adduct. Polar additives, particularly *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), have been shown to promote the propagation effectively from the DLI–isoprene adduct and produce narrow distribution polyisoprene and high strength SIS.[6] The propagation from the DLI–isoprene is believed to be autoaccelerating as reported by Madani et al.[7] in their study on the polymerization behavior of another DLI derived from the reaction of s-BuLi with a non-DDPE diolefinic compound. Because there is a concentration dependence of the autoaccelerating propagation rate, the seeding technique has been also used effectively to narrow the distribution of polyisoprene and increase the strength of SIS.[6] In this study, the effect of the structure of the DLI on the intramolecular association of the DLI–isoprene adduct and the ensuing polymerization behavior was investigated.

In varying the structure, the main feature of PEB and MPEB, one center phenyl ring shared by the two 1,1-diphenylethenylene functional groups, will be preserved. Putting a methyl group on each of the outer phenyl rings of PEB has made the DLI derived from MPEB soluble in *n*-hexane.[2] Further variance on the substituents therefore might influence the intramolecular association of the derived DLI–isoprene adduct. A non-DDPE diolefin compound, in which one of the phenyl rings in the compound is replaced by a saturated one, as a precursor to DLI is included because a change of the aromaticity of the initiator might alter the characteristics of association in hydrocarbon solvents.

Results and Discussion

The simplest molecule that contains two 1,1-diphenylethylene functional groups is the DDPE compound PEB.



PEB

The two 1,1-diphenylethylene groups share the center phenyl ring at the meta position. If the sharing of the center ring is at the para position, the initiator derived from it is not soluble in hydrocarbon solvents.[1] When a stoichiometric amount of s-BuLi is added to PEB, the resulting DLI (as shown in Scheme 1) is soluble in toluene, benzene, and cyclohexane but not in *n*-hexane.

When a methyl group is attached to each of the outer phenyl rings on PEB, the DDPE compound is MPEB. The initiator derived from MPEB is soluble in *n*-hexane in addition to the other three solvents. Since the isomeric

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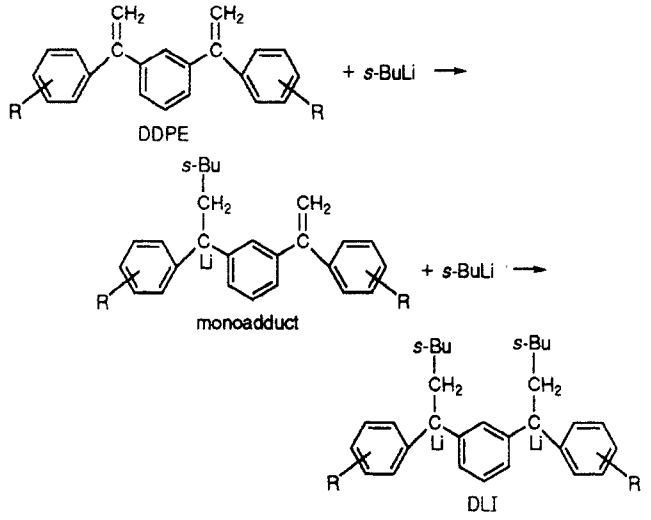
Scheme 1



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

position on the center phenyl ring dictates the solubility of the DLI derived from PEB, it is also possible that the positions of the methyl group on the outer rings may have an effect on the behavior of the DLI derived from MPEB.

Effect of Methyl Positions on MPEB. In the first set of experiments, isoprene polymerization using initiators derived from MPEB with different methyl positions on the outer phenyl rings was studied. In the synthesis of MPEB, toluene is acylated by isophthaloyl chloride to give a diketone which is then converted to the diolefin via methyl Grignard and dehydration reactions. Using $AlCl_3$ as the catalyst for the acylation, the methyl groups at the outer phenyl rings assumed predominantly para positions but some at meta and ortho positions were also present. In a normal preparation, roughly 84% of MPEB had both methyl groups in the para position. The next most abundant isomer, at about 13%, was a para on one ring and an ortho on the other. The combination of para–meta was about 2%. The other three possible isomers, ortho–ortho, meta–meta, and ortho–meta, each was present at less than 0.5%. By recrystallization of crude MPEB from methanol, a *p,p* isomer of 98% was obtained. In addition, nondiolefinic impurities were greatly reduced by the recrystallization. From the mother liquor, a MPEB sample of 49%, *p,p* isomer was recovered. Dilithium initiators were prepared from the above three MPEB samples, and they were used to initiate isoprene polymerizations in cyclohexane. For comparison, another isoprene polymerization was made under the same conditions with a DLI prepared from PEB. The isomer contents of the *p,p*-enriched MPEB, MPEB-A, the normal *p,p* MPEB, MPEB-B, and the *p,p* lean MPEB, MPEB-C, were analyzed by GC, and the results are listed in Table 1. The products of their reaction with s-BuLi were also analyzed by GC and are listed in the same table.

The samples taken during the isoprene polymerizations were analyzed by GPC. The chromatograms for the polymerization initiated by the DLI derived from MPEB-A are shown in Figure 1. They have the same feature as reported before.[5] The early stage chromatograms contained two sharp peaks. The one at low molecular weight was the initiator–isoprene adduct. The other at higher molecular weight was the polyisoprene polymerized from a small amount of monofunctional initiators present inadvertently in the polymerization mixture. As the

Table 1. GC Analysis of Isomer Contents in MPEB and Reaction Products of s-BuLi with MPEB and PEB in Cyclohexane

DDPE	principal isomers *p,p*	principal isomers *p,o*	unreacted DDPE (%)	monoadduct (%)	diadduct (DLI) (%)
MPEB-A	98.0	1.4	0.4	0.2	99.4
MPEB-B	84.2	13.4	0.6	0.4	99.0
MPEB-C	48.7	44.1	0.5	0.6	98.9
PEB			0.7	0.1	99.2

Table 2. GPC Analysis of Polyisoprene Prepared with DLI from PEB and MPEB with Variation in the Position of the Methyl Group on the Outer Phenyl Rings

DLI from	M_n ($\times 10^{-3}$)	M_w/M_n	bimodal peak MW ($\times 10^{-3}$) main pk	bimodal peak MW ($\times 10^{-3}$) high MW pk	high MW peak wt %	high MW peak mol %
MPEB-A	130	1.85	136	707	19.7	4.3
MPEB-B	120	1.94	130	616	24.9	5.8
MPEB-C	133	1.79	136	515	31.5	9.4
PEB	124	1.94	129	664	24.0	5.4

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 peak. The new broader peak later became the main peak of the bimodal distribution. The progression created an illusion of "melting" of the adduct peak into the formation of the main peak. The polyisoprene made with the DLI from MPEB-A, the diolefin with enriched *p,p* isomer, had the least amount of the high molecular weight peak, and the polyisoprene made with the DLI from MPEB-C, the diolefin with lean *p,p* isomer, had the most. Table 2 shows the results calculated from the final GPC chromatograms of the runs.

It is difficult to conclude whether there is any effect of the methyl position on MPEB to the isoprene polymerization behavior. The high *p,p* isomer DLI produced a polyisoprene with the least amount of monofunctional peak in it, but the initiator solution also had the highest amount of diadduct as shown in Table 1. If the *p,p* isomer had a positive influence on the propagation rate of isoprene from the initiator–isoprene adduct, then the two peaks of the bimodal distribution should be closer together. This was not observed.

Four SIS samples were also made using the four initiators described above. Unlike the isoprene polymerization runs where no additives were used with the DLI, in SIS polymerization *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) was used as an additive.[6] The molecular weight distributions of all SIS samples were monomodal and narrow. The tensile properties of the samples are listed in Table 3. The differences in tensile strength of all four SIS samples were small and barely exceeded the reproducibility of the tensile testing experiment. Nevertheless, it is interesting to note that they ranked exactly the same as the diadduct content in the initiator solutions listed in Table 1 and also the same as the amount of high molecular weight peak in the bimodal polyisoprene prepared with these same initiator solutions without PMDETA (Table 2).

The good correlation of the diadduct content in the initiator solutions with the results of polymerization lended confidence to the GC analysis shown in Table 1. The GC data showed a significant difference of the relative amounts of unreacted DDPE and monoadduct in the four initiator solutions. A previous kinetic study by Broske et al.[8] reported that, in cyclohexane, the second double bond on

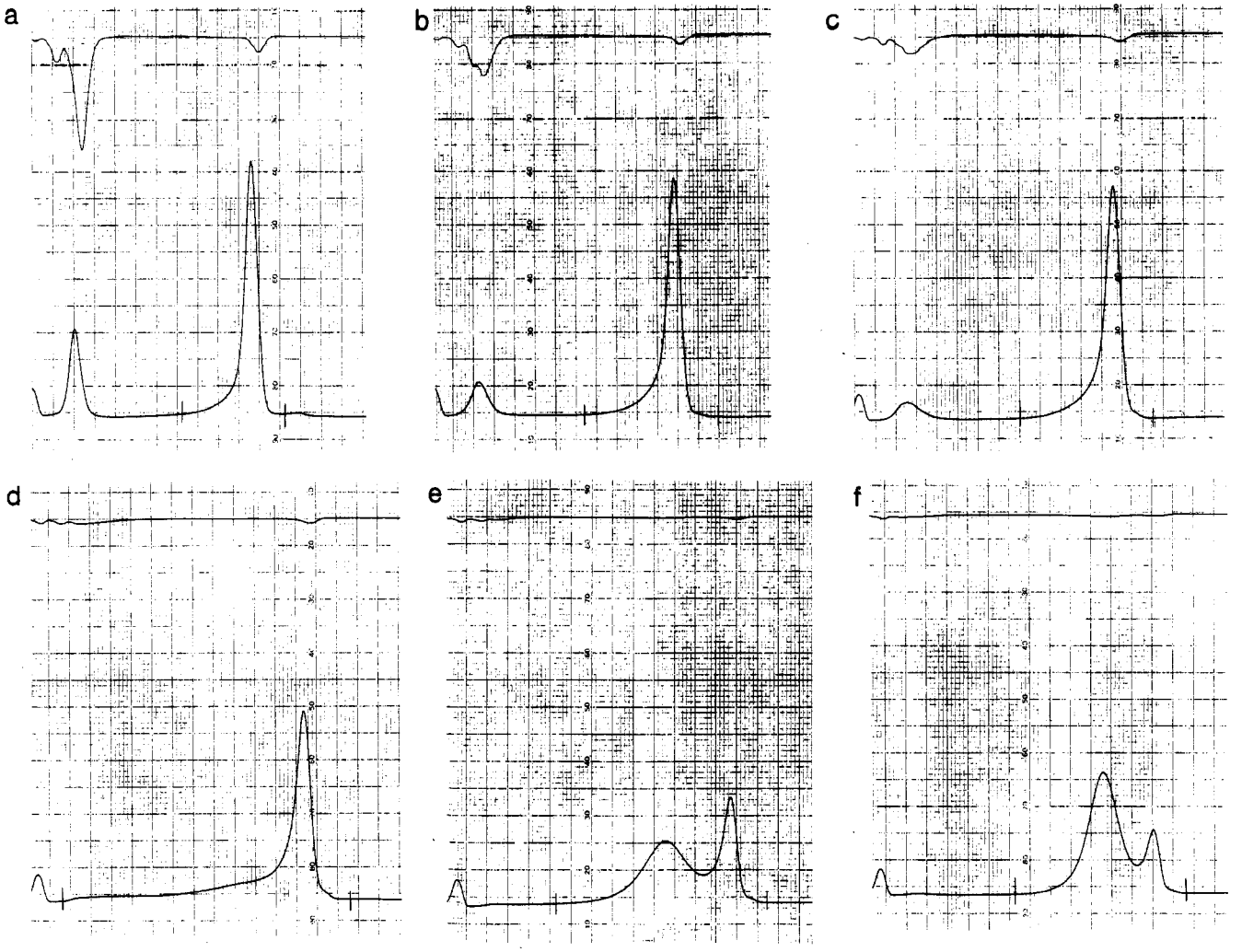


Figure 1. GPC chromatograms of an isoprene polymerization run initiated by DLI from MPEB-A. Min is the time when the sample was taken; % is the monomer conversion. The upper curve is the chromatogram from the UV detector, and the lower curve is from the differential refractive index detector. (a) 5 min, 4.5%. (b) 10 min, 8.2%. (c) 15 min, 12.5%. (d) 25 min, 25.5%. (e) 30 min, 52.9%. (f) 70 min, 97.0%.

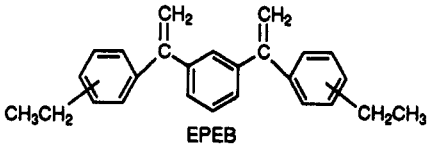
Table 3. Properties of SIS Triblock Copolymers Prepared with DLI and with PMDETA Added

DLI from	PMDETA/Li mol ratio	Sty (%)	M_n ($\times 10^{-3}$)	M_w/M_n	tensile (psi)	elong (%)
MPEB-A	0.17	14.8	144	1.08	3210	1320
MPEB-B	0.17	14.9	145	1.08	3170	1360
MPEB-C	0.16	15.1	145	1.09	2940	1340
PEB	0.17	15.1	143	1.08	3180	1350

PEB was more reactive than the first toward s-BuLi. In a separate study[2] the same preference was found in the reaction of s-BuLi with MPEB. However, a direct comparison of the two kinetics (s-BuLi with PEB and MPEB) was not possible because the condition of the reactions were not the same. The higher ratio of mono-adduct to unreacted DDPE for MPEB in comparison to PEB shown in Table 1 indicates that the second double bond in PEB is more reactive than that in MPEB. Similarly the ratios for the three MPEB samples indicate that the reactivity of the second double bond was reduced more by the methyl group in the ortho position than that in the para position even though it was still more reactive than the first in all three MPEB samples.

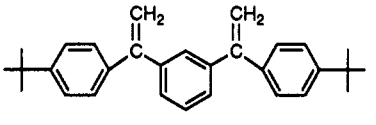
Effect of Other Substituents on PEB. In the next set of experiments, the effect of other substituents on the DDPE structure was investigated. The first three DPPE compounds were prepared to determine the effect of the substituent group on the outer phenyl rings.

In 1,3-bis[1-ethylphenyl)ethenyl]benzene (EPEB), the methyl groups on MPEB were replaced by the larger ethyl groups. In 1,3-bis[1-(4-*tert*-butylphenyl)ethenyl]benzene



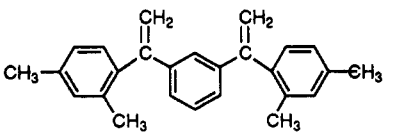
EPEB

(TBPEB), the substituents were the bulky *tert*-butyl groups. In 1,3-bis[1-(2,4-dimethylphenyl)ethenyl]benzene



TBPEB

(DMPEB), an additional methyl group was put on each of the outer phenyl rings of MPEB.

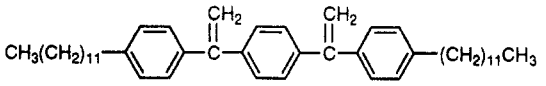


DMPEB

Table 4. GC Analysis of DLI Prepared in Toluene from New DDPE Compounds

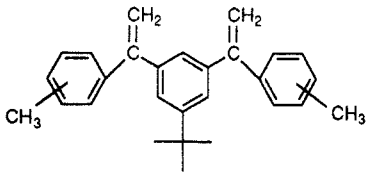
DDPE	unreacted DDPE (%)	monoadduct (%)	diadduct (DLI) (%)
EPEB	0.2	4.5	95.3
TBPEB	0.6	2.3	97.1
TBMPEB	0	1.9	98.1
DMPEB	1.2	6.7	92.1

In addition to the variation on the substituents on the outer phenyl rings, a DDPE compound was prepared to see if there is any effect by replacing the meta position of the center phenyl ring by a para one. The DLI from *p*-PEB was found to be insoluble in hydrocarbon solvents. The DDPE compound, 1,4-bis[1-(4-dodecylphenyl)ethenyl]-benzene (DPEB) was made with dodecyl groups on the outer phenyl rings to increase the solubility.



DPEB

Another DDPE compound was made to test the effect of a substitution on the center phenyl ring. The DPPE with a bulky *tert*-butyl group on the center phenyl ring was 5-*tert*-butyl-1,3-bis[1-(methylphenyl)ethenyl]benzene (TBMPEB).



TBMPEB

The DLI derived from the above five DDPE compounds were all soluble in toluene. The purification steps after synthesis of the DDPE compounds were not done as elaborately as those in the preparation of PEB and MPEB. Most of the DDPE compounds were not as easily crystallizable from alcohol solutions as PEB and MPEB. As a result, more impurities were found in the samples than those found in PEB and MPEB. In EPEB, TBPEB, and TBMPEB the impurity level was about 2% as measured by GC. In DMPEB, it was about 1%. In DPEB, the impurities were also about 1% as measured by GPC since its volatility was not high enough for GC determination.

The addition reaction of s-BuLi to PEB and MPEB was observed[2] to be completed in less than 2 h in toluene at room temperature. In cyclohexane the same reaction took more than 48 h. The DLI solutions in toluene, however, cannot be stored for extended period on account of the metallation reaction of the DLI with toluene.[2] To take advantage of the fast reaction rate, toluene was nevertheless used as the solvent in the preparation of DLI from the above five DDPE compounds. The DLI solutions so prepared were used the next day for the isoprene polymerization. The only exception was the DLI prepared from DMPEB which had a 4-day storage before use. On the basis of the stability study reported earlier,[2] DLI loss to metallation in toluene should not be excessive in this storage period. The addition reacion of s-BuLi to all five DDPE compounds in toluene was found to be similar to that of s-BuLi to PEB and MPEB. The reaction was essentially complete in about 2 h at room temperature. Analyses of the DLI samples are shown in Table 4. The

Table 5. GPC Analysis of Polyisoprene Prepared with New DLI

DLI from	M_n ($\times 10^{-3}$)	M_w/M_n	bimodal peak MW ($\times 10^{-3}$) main pk	bimodal peak MW ($\times 10^{-3}$) high MW pk	high MW peak wt %	high MW peak mol %
EPEB	106	1.51	112	272	35.3	14.8
DPEB	106	1.43	100	225	46.4	23.0
TBPEB	109	1.51	110	286	32.8	13.0
TBMPEB	146	1.44	153	336	39.7	18.5
DMPEB	151	1.31				

DLI from DPEB was not analyzed because of its lack of adequate volatility for GC.

The monoadduct contents shown in Table 4 are higher than those of unreacted DDPE, indicating that in toluene the reactivities of the two double bonds on the DDPE compounds were comparable. The same observations was reported for PEB.[2]

Isoprene polymerizations using the five DLI samples were conducted in cyclohexane. The GPC chromatograms of samples from the runs all have the same features as those in Figure 1. The relative sizes of the bimodal peaks and the difference of the molecular weights of the peaks varied as before in the study of the methyl positions on MPEB. The calculated results from the GPC chromatogram of the final polyisoprene sample in each of the runs are shown in Table 5.

All five polyisoprene samples had more high molecular weight peaks than the polyisoprene made with DLI from PEB and MPEB. This is not surprising since the DLI samples were not as pure as the DLI from PEB and MPEB used in the earlier isoprene polymerization runs. However, the correlation between the amount of diadduct in the DLI solution and the amount of high molecular weight peak produced in the isoprene polymerization broke down for the TBMPEB sample. Compared to the DLI from EPEB, TBPEB, and TBMPEB, the DLI from TBMPEB had the highest diadduct content but produced more high molecular weight peaks in polyisoprene than the other two.

Four SIS triblocks were made using DLI with PMDETA added. The initiator from DMPEB was not used to prepare SIS. Fresh initiators from DPEB and TBPEB were used in the SIS preparation. The initiators from EPEB and TBMPEB were, however, the same batch used in the earlier isoprene polymerization. The fresh initiator from TBPEB was analyzed by GC to have 99.1% diadduct, 0.7% monoadduct, and 0.2% unreacted diolefin—a much higher content of diadduct than the batch used for isoprene polymerization. The diadduct content in the latter initiator batch from TBPEB was similar to that in the DLI of PEB and MPEB-B, and the tensile strength of the SIS was also comparable. The DLI from DPEB was not analyzed. The properties of the SIS are listed in Table 6.

The high tensile strength of the SIS indicated that the second batch of DLI from DPEB was also higher in diadduct content than the first. It is interesting to note that the tensile strength of the SIS from a 3-day-old DLI from TBMPEB was worse than the tensile strength of the SIS from a 14-day-old DLI from EPEB. This indicated that the DLI could not have undergone metallation to toluene in any appreciable extent. The tensile strength of SIS made using DLI from EPEB and TBPEB correlated well with the amount of high molecular weight peak in polyisoprenes.

In a previous study,[5] the high molecular weight peak of the bimodal distribution was identified as polyisoprene

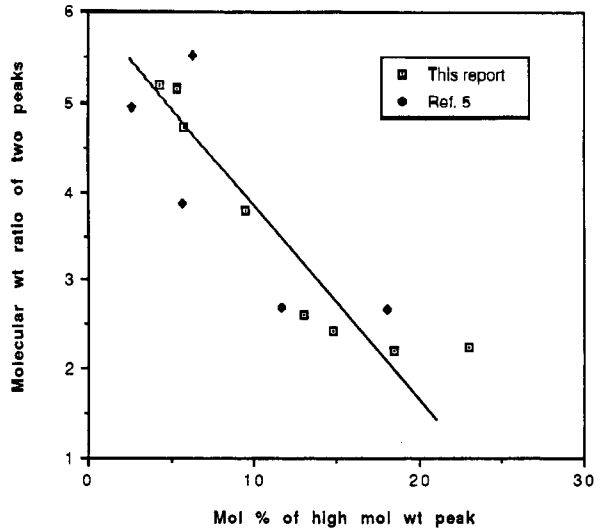


Figure 2. Correlation between peak ratios in bimodal polyisoprene with the amount of high molecular weight peak in the distribution.

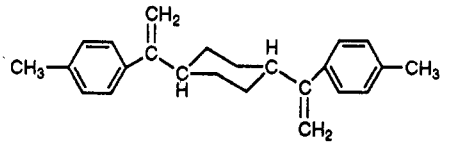
Table 6. Properties of SIS Triblock Copolymers Prepared with New DLI and with PMDETA Added

DLI from	DLI age (days)	PMDETA/Li mol ratio	Sty (%)	M_n ($\times 10^{-3}$)	M_w/M_n	tensile (psi)	elong (%)
EPEB	14	0.14	15.0	165	1.08	2390	1470
DPEB	1	0.17	14.8	150	1.08	2940	1350
TBPEB	1	0.17	14.8	144	1.07	3180	1320
TBMPEB	3	0.17	14.7	153	1.08	2190	1340

chains originating from the inadvertent presence of MFI in the DLI system and the main peak as polyisoprene chains from DLI. The time of the appearance of the main peak in the bimodal distribution was observed to coincide with the time of the large exothermic peak in the temperature profile of the polymerization. Also observed was a connection between larger high molecular weight peaks and smaller differences in the peak molecular weights of the bimodal distribution. Apparently the polymerization of chains initiated from MFI could cause a slight rise of reaction temperature which then promoted the propagation rate of isoprene initiated from the DLI-isoprene adduct. The coincidence of the timing of the exothermic peak in the reaction temperature profiles with the timing of the appearance of the main peak in GPC chromatograms existed in all the runs. In Figure 2, the ratio of the two peak molecular weights was plotted vs the mol % of the high molecular weight peak in the chromatogram of the final polyisoprene. In addition to the points representing the result of the current study, the data from a previous isoprene polymerization study[5] were also included. In the earlier study, DLI with deliberately added impurities were used in some of the polymerizations. The points nevertheless are all correlatable by the line in Figure 2. Thus the differences in the amount of high molecular weight peak observed in the present work were caused mainly by the amount of impurities in the DLI systems. Had the structure of any DLI influenced the rate of propagation from the DLI–isoprene adduct, the point representing it would have to be displaced from the correlation zone.

Unlike the large effect shown by the addition of PMDETA or by seeding on the behavior of DLI-initiated isoprene polymerization, the structure variation had hardly any detectable effect. What has been observed indicated that the slow propagation from the DLI–isoprene adduct was dictated only by the nature of the isoprenyllithium association. The rate-controlling step is the propagation from the DLI–isoprene adduct and not the initiation of isoprene polymerization by DLI. It is thus probably a general phenomenon for all dilithium-initiated polymerizations.

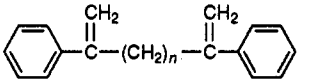
DLI with Cyclohexane as the Center Ring. The high solubility of the current family of DLI may be attributed to the bulky steric hindrance of the phenyl rings that prevent extensive intermolecular association of the organolithium functionality in hydrocarbon solvents. Aromaticity of the rings no doubt contributed also to the ionic nature of the carbon–lithium bonds. Replacement of one of the phenyl rings with a saturated one was suggested by McGrath[9] to be a route to alter the behavior of the DLI in hydrocarbon solvents. A diolefin compound with cyclohexane as the center ring, 1,4-bis[1-(4-methylphenyl)ethenyl]cyclohexane (MPECH), was prepared.



MPECH

The same path to make MPEB was used in MPECH synthesis, except that 1,4-diacid chloride of *trans*-cyclohexane instead of isophthaloyl chloride was used to acylate toluene.

The addition reaction of s-BuLi with MPECH was first carried out in toluene between 23 and 40 °C using a stoichiometric amount of both reagents. The reaction was extremely slow and precipitation occurred during the reaction. Because the reaction mixture turned quickly to a dark red color, the precise moment of precipitation could not be determined. The precipitate was in the form of a very fine suspension. The GC analysis of the samples taken is shown in Table 7. At the end of 7 days, a significant proportion of the double bonds remained unreacted. No indication of dimerization or oligomerization of MPECH into higher molecular weight compounds was observed. Prolonged heating was not advisable because of the danger of metallating toluene[2]. If cyclohexane was used as the solvent to avoid metallation, the reaction rate would be much slower yet. The change of the center ring had indeed altered the behavior of the DLI. The diolefin MPECH acted more like the diolefins used by Guyot et al.[10] with a parafinic group in the center.



Guyot et al. used a large excess of s-BuLi to make the precipitated form of the DLI. After the precipitate was separated from the solution, it was solubilized by seeding with a diene monomer. Triethylamine (TEA) was used to accelerate the reaction of s-BuLi with diisopropenylbenzene[11,12] in preparation of another DLI. In a second reaction of MPECH with s-BuLi, TEA was used as an additive. The reaction was carried out in toluene using stoichiometric amounts of s-BuLi to MPECH and a 1:1 amount of TEA to s-BuLi. The reaction proceeded much faster but appeared to have reached a plateau after 3 h as shown in Table 8. Precipitation occurred again despite the presence of TEA. It is unclear whether the plateau was caused by the reaching of an equilibrium in the reaction itself or by the metallation reaction with toluene. Approximately 15% of the s-BuLi added was unaccounted for by the amount of mono- and diadducts in the product.

Table 7. GC Analysis of the Addition Reaction of s-BuLi to MPECH in Toluene

reaction time and temp	MPECH (%)	monoadduct (%)	diadduct (%)	impurities (%)
20 min at 23 °C	95.9	3.3	0	0.8
1 h at 23 °C	89.6	9.2	0.1	1.1
1.5 h at 23 °C + 1.5 h at 35–40 °C	46.6	43.3	8.3	1.8
1.5 h at 23 °C + 3.5 h at 35–40 °C	24.3	52.7	21.3	1.7
19.5 h at 23 °C + 3.5 h at 35–40 °C	7.8	47.1	43.5	1.6
3 days at 23 °C + 3.5 h at 35–40 °C	1.3	28.4	68.2	2.1
7 days at 23 °C + 3.5 h at 35–40 °C	1.0	25.1	71.1	2.8

Table 8. GC Analysis of the Addition Reaction of s-BuLi with MPECH in the Presence of TEA at Room Temperature in Toluene (TEA/Li = 1)

reaction time	MPECH (%)	monoadduct (%)	diadduct (%)	impurities (%)
20 min	19.5	54.1	23.7	2.7
1 h	2.6	37.4	57.8	2.2
2 h	1.0	28.5	68.0	2.5
3 h	0.9	28.0	69.1	2.0
2 days	0.8	24.3	68.4	6.5

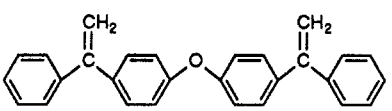
Table 9. GC Analysis of the Addition Reaction of s-BuLi and MPECH in Cyclohexane at 25 °C with a 5% Excess of s-BuLi and the Presence of TEA (TEA/Li = 1)

reaction time	MPECH (%)	monoadduct (%)	diadduct (%)	impurities (%)
20 min	31.3	54.3	11.6	2.8
1 h	2.3	45.1	50.6	2.0
2 h	0.2	24.5	72.3	3.0
3 h	0	15.0	83.3	1.7
4 h	0	9.9	88.2	1.9
6 h	0	6.3	91.8	1.9
22 h	0	3.3	94.8	1.9
2 days	0	3.0	93.7	3.3
3 days	0	3.0	94.0	3.0

A third addition reaction was carried out using cyclohexane instead of toluene as the solvent. A 5% excess of s-BuLi and a 1:1 TEA to s-BuLi ratio were used. The result is given in Table 9.

Apparently the reaction again reached a plateau after 22 h. Since no metallation of toluene was possible, it is puzzling that an equilibrium of the reaction could have existed when one of the products was a precipitate.

Isoprene polymerization was conducted using another DLI solution made with a 3.2% excess of s-BuLi with MPECH and a TEA/Li of 1 in cyclohexane at 25 °C. Analysis of the product after 18 h showed 0% MPECH, 1.1% monoadduct, and 96.3% diadduct. The DLI was then solubilized by seeding with isoprene to give approximately a DP of 8 on each of the reactive sites. It is interesting to note that more diadduct and less monoadduct existed in this DLI than in the DLI at longer reaction times shown in Table 9. If the analysis had adequate precision, the result would indicate that a reverse reaction had taken place. Reversal of the reaction has been reported[13] for the addition of styryllithium to the diolefin bis[4-(1-phenylethenyl)phenyl] ether.



In the polymerization cyclohexane was used as the solvent. After completion of isoprene polymerization, styrene was added to make the triblock SIS. The GPC chromatograms of the samples taken during the polymerization are shown in Figure 3. The two peak chromatograms in the earlier stages and the "melting" of the DLI–adduct peak into the formation of the main peak are similar to the chromatograms shown in Figure 1. The only difference is that, at the later stages, the peaks of the bimodal distribution merged into a single peak. The seeded DLI was equivalent to a DLI–isoprene adduct with 16 units of isoprene attached. The propagation rate of isoprene from it is expected to be faster than the DLI–isoprene adduct produced from a soluble DLI which would have only 2–3 units of isoprene attached to the early stage of polymerization. Consequently, the main peak derived from the seeded DLI from MPECH is closer in molecular weight to the molecular weight of the peak derived from MFI. The merging of the peaks of the bimodal distribution into a single peak at the later stage of the polymerization is therefore expected.

The seeding step used above differed some from that used in the seeding study reported earlier.[6] In the earlier study on PEB-based DLI, seeding was carried out to a DP of about 280 per each site on the DLI. The distribution had evolved past the melting of the adduct peak and the formation of the main peak during the seeding. In the present study, the small amount of isoprene was added mainly to solubilize the DLI. The chromatograms in Figure 3 are those after the seeding step. The essential feature of the polymerization for this non-DDPE-based DLI is identical to that for all the DDPE-based DLI. Therefore, it is likely that the rapid initial formation of a DLI–isoprene adduct which then undergoes slow propagation is a general phenomenon for all DLI-initiated polymerizations.

The final SIS triblock copolymer had a composition of 15.8% styrene and 84.2% isoprene, a number-average molecular weight of 124 000, and a polydispersity index, M_w/M_n, of 1.21. The tensile strength of the SIS was 1140 psi, and the elongation was 1390%. With the diadduct of the DLI at only 96% and the possibility of excess s-BuLi as an additional source of MFI, such a tensile strength for the final SIS was not unreasonably low.

Experimental Methods

Synthesis of PEB. Benzene was acylated by isophthaloyl dichloride 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.

Synthesis of MPEB. The same procedure as in the synthesis of PEB was used except that toluene replaced benzene in the acylation step.

Synthesis of EPEB. The same procedure in PEB synthesis was followed, except that, in the acylation of ethylbenzene, ethylene dichloride was used as the solvent.

Synthesis of TBPEB. Acylation of *tert*-butylbenzene was carried out in the same manner as the acylation of benzene in PEB synthesis. The Wittig reaction was used to convert the resulting diketone to TBPEB.

Synthesis of DMPEB. *m*-Xylene was acylated in the preparation of the corresponding diketone. Repeated crystallization was used to purify the final product to better than 99% pure.

Synthesis of DPEB. Terephthaloyl dichloride was used for acylating *n*-dodecylbenzene, and ethylene dichloride was used as the solvent.

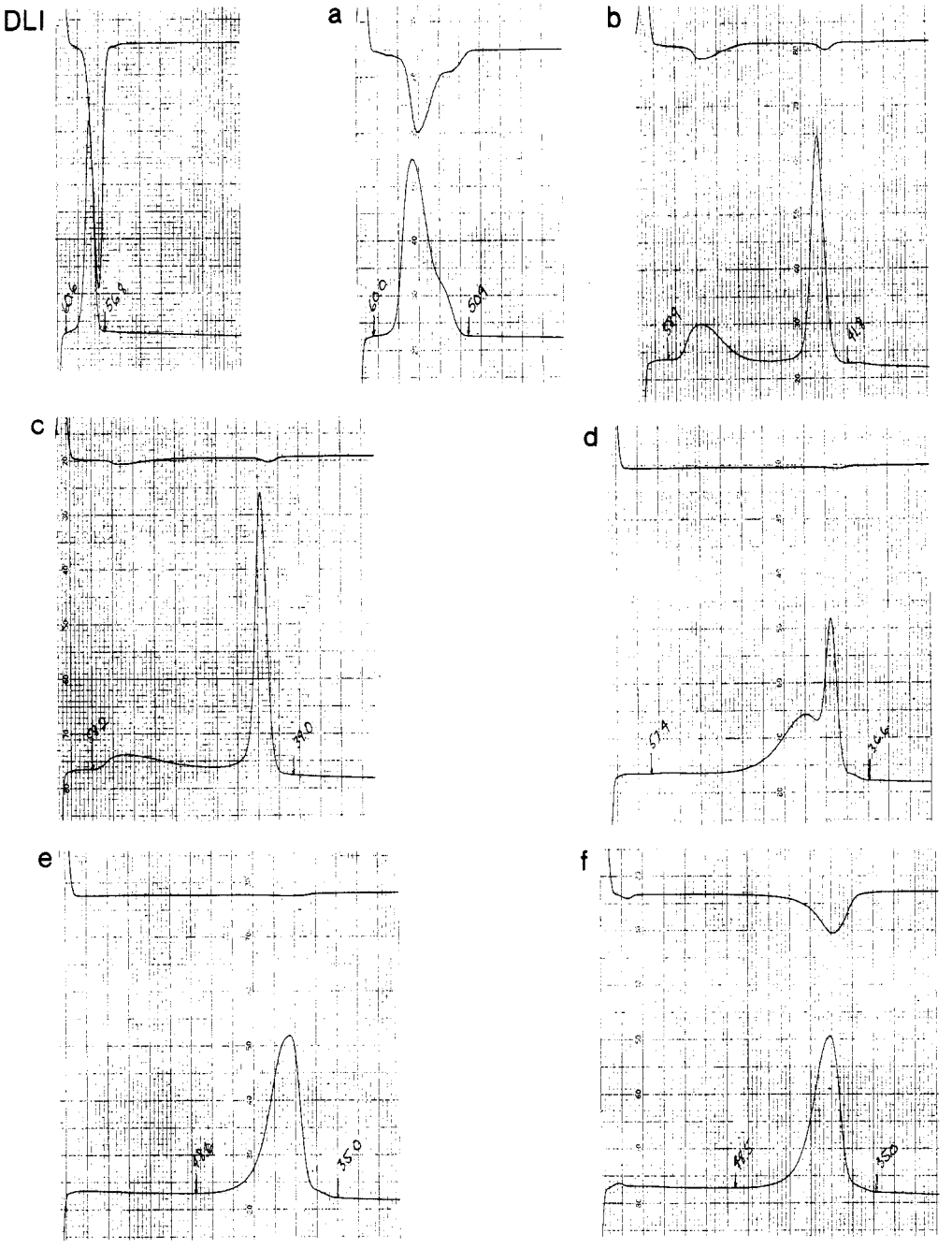


Figure 3. GPC chromatograms of polyisoprene (b–e) and SIS triblock (f) initiated by seeded DLI (a) from MPECH. Mins is the time when the sample was taken; % is the monomer conversion. The upper curve is the chromatogram from the UV detector, and the lower curve is from the differential refractive index detector. (Upper far left) DLI. (a) Seeded DLI. (b) 2.5 min, 5.8%. (c) 5 min, 10.6%. (d) 10 min, 35.5%. (e) 40 min, 98.4%. (f) SIS triblock.

Synthesis of TBMPEB. The dichloride, 3-*tert*-butylisophthaloyl dichloride, for the acylation reaction was prepared by reacting 3-*tert*-butylisophthalic acid (purchased from Amoco) and thionyl chloride in the presence of a phase-transfer catalyst. Methyl Grignard and dehydration reaction were carried out as in the preparation of PEB.

Synthesis of MPECH. Aldrich's 95% *trans*-1,4-cyclohexanedicarboxylic acid was converted to the diacid chloride by reacting with thionyl chloride in ethylene dichloride using benzyltriethylammonium chloride as catalyst. The diacid chloride was then used to acylate toluene with ethylene dichloride as the solvent.

Preparation of DLI. The DLI from PEB and the three MPEB samples were prepared in cyclohexane in 500-mL stainless steel tubes. The procedure has been described earlier.[2]

The DLI from other DDPE compounds were prepared in toluene in a round-bottomed flask. The apparatus and detailed procedures have also been described earlier.[2]

Polymerization. Polymerizations were carried out in a 1.3-L jacketed reactor using similar procedures described earlier.[5]

Analysis. All analyses and properties were done as described earlier.[2,5,6]

Conclusions

Neither the number nor the isomeric position of the methyl groups on the outer aromatic rings of PEB made a significant difference when the derived DLI was used in isoprene polymerization. A similar lack of effect on the polymerization results when the chain length and bulkiness of the alkyl substituents on the aromatic rings are varied. Replacement of the center aromatic ring with a saturated cyclohexane ring also had no effect on the basic nature of the polymerization.

The structural variations made could reasonably be expected to alter the reactivity of the carbon–lithium bond and the state of association of the DLI. Indeed the reactivity of the two double bonds toward s-BuLi was observed to be influenced by the positions of the methyl

group on the phenyl rings of MPEB. Replacement of the center phenyl ring with a saturated one drastically reduced the rate of its reaction with s-BuLi. Unlike the addition of a polar additive or the use of seeding, the basic nature of isoprene polymerization remained unaltered by any of the structural changes of the DLI. This lack of effect is consistent with a polymerization mechanism having a rapid initial formation of a DLI–isoprene adduct that then undergoes slow propagation because of intramolecular association of the isoprenyllithium end groups. It also lends weight to the belief that the mechanism is a general phenomenon for dilithium-initiated polymerization in solvents where organolithium are highly associated.

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