

Synthesis of a Difunctional Organolithium Compound as Initiator for the Polymerization of Styrene-Butadiene/Isoprene-Styrene Triblock Copolymer

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ABSTRACT: A difunctional organolithium compound was prepared by the addition of butyllithium (BuLi) to 1,4-bis(4-methyl-1-phenylethenyl)benzene (MPEB). The effects of the solvent, polar modifier (THF), butyl lithium structure, and reaction time on the formation of the difunctional organolithium compound were studied. Results showed that toluene as solvent was in favor of the addition reaction over cyclohexane, in the absence of the polar modifier. However, cyclohexane was a better option as solvent for the addition reaction, when polar modifier was employed. A small amount of polar modifier could efficiently accelerate the reaction rate and have no significant effect on the structure of the polydiene, which was initiated by the polar modifier containing organolithium compound. Results also showed that isobutyl lithium was more active in the addition reaction than *n*-butyl lithium, because of inductive effect. The optimum molar ratio of THF/Li⁺ was determined

as 4. The THF containing difunctional organolithium cyclohexane solution was sequentially used in the step-wise polymerization of triblock thermoplastic copolymer SIBS. The so-prepared SIBS shared the similar phase separation structure with SBS and exhibited excellent mechanic properties. As the content of the central polyisoprene block increases, the tensile strength of the copolymer is decreased, and the elongation at break is increased. The glass transition temperature T_g of the central block was correlated with its content as $T_g = 0.33 \times -62.81$, where \times is the wt % of the central block, based on the triblock copolymer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1395–1402, 2006

Key words: difunctional organolithium; addition reaction; block copolymers; phase separation; glass transition; anionic polymerization

INTRODUCTION

Over the past decades, great attention had been paid to the synthesis and characterization of the difunctional anionic polymerization initiators, which are advantageous in the polymerization of triblock thermoplastic copolymer, e.g., polystyrene-polybutadiene-polystyrene (SBS).^{1–4} Currently, three-step feeding is used in the monofunctional lithium-initiated polymerization of SBS. The copolymer was made in a sequential manner (PS → PB → PS). Multistep feeding increases the chance of deactivation of the living seeds, resulting in two-block or one-block fragments in the final product. The properties of the thermoplastic copolymer could be negatively affected because of the presence of these fragments. In the difunctional organolithium-initiated polymerization, the central block (PB) was made first, and the PS blocks were

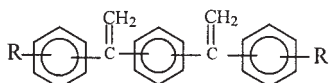
elongated simultaneously, from both living ends of the PB block. Two-step or even one-step feeding can be used instead of three-step feeding. The chance of the resulting two-block or one-block fragments dramatically decreased because of the reduced feeding steps. Moreover, in an effort to improve the strength of the thermoplastic copolymer, it was proposed to introduce polar monomers to the PS blocks to increase the glass transition temperature of the hard block.^{5–9} This proposal is infeasible in the monofunctional initiation, since once the polar monomers are introduced in the first PB block, the polar anionic living seeds are not able to initiate the addition of the diene monomers. Difunctional organolithium initiator may resolve this problem easily by initiating the diene polymerization first. Another advantageous feature of the difunctional organolithium initiator is that specially structured polymers, such as telechelic polymers and stereotriblock homopolymers, could be synthesized.¹⁰

Three methods have been investigated for the synthesis of the difunctional organolithium initiators. One is via the coupling of radical anions.¹¹ Another one is via substitution of dihaloparaffin by lithium.¹² At one time, 1,4-dilithiobutane was considered the most

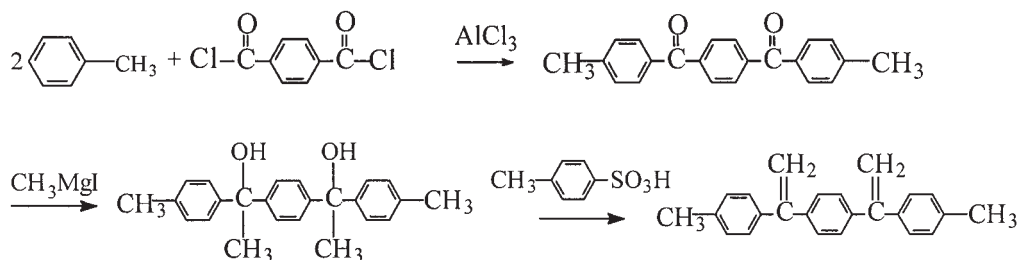
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promising difunctional initiator for industrial application. However, polar solvent is a necessary condition for the dihaloparaffin substitution reaction. When a small amount of polar solvent was introduced into the conjugate diene polymerization system with the difunctional initiator, significant pendent content resulted, which is an undesirable feature as far as the mechanic properties of the polymer are concerned. Lately, research attention is attracted towards the addition of lithium to a type of nonconjugated diene.^{4,13} The type of structure of the nonconjugated diene is shown as follows:



In almost all the repeated research, aromatic solvents, such as toluene, were used in the addition reaction to obtain a better solubility of the diene precursors. In the current SBS production process, a non-polar solvent, such as cyclohexane, was used as solvent. If the small amount aromatic solvent was introduced in the SBS production with initiator, the downstream processing, such as solvent recycling will be complicated and the associated operation cost will also increase. One of the challenges in the addition reaction of lithium to the nonconjugated diene is replacing of the aromatic solvent by a nonpolar solvent.



Addition reaction: experimental setup and procedure

Addition reaction was carried out in an experimental setting. All the glassware was well dried before use. After MPEB and a magnetic stirring bar were added to the reactor, a rubber stopper with the nitrogen connecting tube was used to isolate the reactor content from the atmosphere. The reactor was carefully purged with purified and dehydrated nitrogen for 10 min. After the purge, solvent, THF, and BuLi were transferred into the reactor with a syringe and/or stainless steel capillaries in a sequential manner. A water bath was used to keep the reactor at $(30 \pm 2)^\circ\text{C}$.

Polymerization procedures

Polymerization of SIBS was carried out in a 5-L reactor. The reactor and accessories were purged by nitro-

gen and washed by cyclohexane before reaction. A solution of 10 wt % diene (monomer B) in cyclohexane was charged into the reactor and preheated to the polymerization temperature (50°C). A stoichiometric amount of DiLi was added into the reactor to initiate the polymerization. After 4 h, the rest monomer (monomer A, styrene) was added into the reactor to continue the polymerization. Two hours later, the polymerization was then shortstopped by discharging the reaction content from the bottom valve into an ethanol reservoir and stabilized with 1 phm of antioxidant. After evaporating cyclohexanes, the resulting polymer was dried in a vacuum oven at 50°C .

EXPERIMENTAL

Materials

Cyclohexane (Jinzhou Petrochemical, China) was dehydrated by 5-Å molecular sieves. The water content in cyclohexane was kept below $5 \mu\text{g/g}$. The solvent was also purged with highly purified nitrogen (Beijing Pulaikesi Practicality Gas, China) for more than 15 min before use. The oxygen content was maintained below $10 \mu\text{g/g}$. Toluene (Beijing No. 2 Chemical Reagent Factory, China) was treated in similar fashion. THF (Beijing YiLi Fineness Chemical Factory, China) was refluxed over CaH_2 for several days, and then diluted with cyclohexane. Butadiene and Isoprene (polymerization grade, Beijing Yanshan Petrochemical, China), were purified with a small amount of *n*-BuLi and then vaporized to keep the water content below $10 \mu\text{g/g}$. Commercially available *n*-BuLi and isoBuLi (Beijing Yanshan Petrochemical, China) were analyzed by the double-titration method with 1,2-dibromobutane. 1,4-bis(4-methyl-1-phenylethenyl)benzene (MPEB) was synthesized according to the following procedures:

gen and washed by cyclohexane before reaction. A solution of 10 wt % diene (monomer B) in cyclohexane was charged into the reactor and preheated to the polymerization temperature (50°C). A stoichiometric amount of DiLi was added into the reactor to initiate the polymerization. After 4 h, the rest monomer (monomer A, styrene) was added into the reactor to continue the polymerization. Two hours later, the polymerization was then shortstopped by discharging the reaction content from the bottom valve into an ethanol reservoir and stabilized with 1 phm of antioxidant. After evaporating cyclohexanes, the resulting polymer was dried in a vacuum oven at 50°C .

Characterization techniques

SHIMADZU GC-14A and VG TS250 MS were used in tandem to monitor the addition reaction of butyl lith-

ium to MPEB. ^1H NMR spectra of the MPEB and the hydrolysis productions of the initiator were obtained with a Bruker AVANCE-400 and CDCl_3 was used as solvent, ^1H chemical shifts were referred to $(\text{CH}_3)_4\text{Si}$. Waters Maxims 820-GPC column was used to determine the molecular weight of the polymers. Polystyrene standards were used for calibration, and THF was the elution solvent.

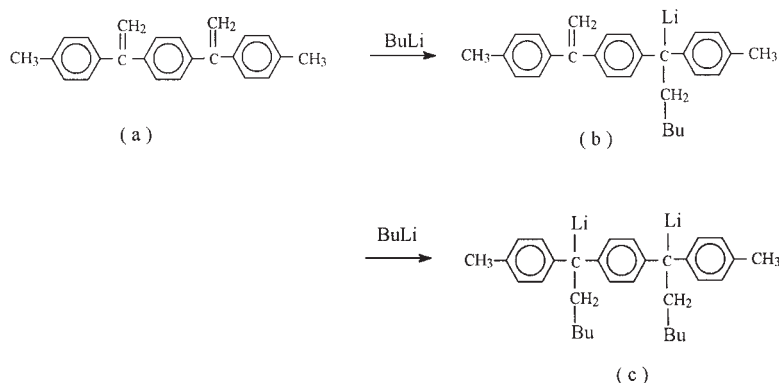
Glass transition temperatures (T_g) and dynamic mechanical analysis (DMA) were carried out on a TA2980 at the frequency of 5 Hz at the heating rate of $5^\circ\text{C}/\text{min}$ from -120 – 150°C . Transmission electron microscopy (TEM) was performed with a FEI TECNAI G220 transmission electron microscope at an acceleration voltage of 100 kV. The specimens were prepared with an ultramicrotome and glass knife, and the thin sections were stained with OsO_4 .

The TEM picture was used to show the microstructure of the triblock polymer.

RESULTS AND DISCUSSION

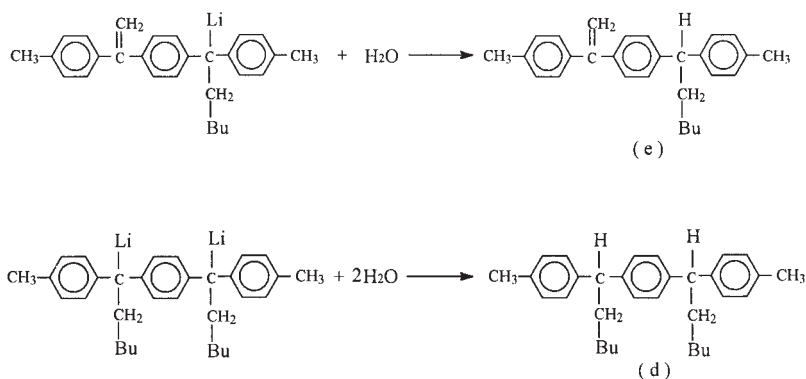
Addition reaction optimization

The addition reaction of BuLi to MPEB is completed by a step-wise fashion. The progress of the reaction is shown in the following procedures. Product (c) is the desired production, since it has two functional Li^+ . Compound (b) is the intermediate of the reaction and it has only one functional Li^+ . Compound (b) is not desired in the final products. The purpose of this optimization research is to investigate the effect of solvents, type of BuLi, and polar additives on the addition reaction kinetics. The criteria of the optimization is the maximum (c) formation and minimum (b) accumulation in the reaction system.



To accurately quantify the two compound, a GC method was used. Before the samples were injected into the GC column, the two compounds were dramatized by hydrolysis. The hydrolysis reactions are

shown in the following procedures. Hydrolysis products (d) and (c) are corresponding to intermediate (b) and product (c).



In the initial stage of the research, an experiment was carried out under the following conditions: BuLi/MPEB = 1.5 (molar ratio), cyclohexane was used as solvent, and no other additives were used. The sample was take after 30 min. Hydrolysis of the sample was followed by ^1H NMR and GC-MS analyses. Figure 1

shows the ^1H NMR spectra of the samples. For comparison purpose, the ^1H NMR spectrum of the starting material MPEB is shown in Figure 2, in which signals at 2.5–3.0, 6.9–7.2, and 5.3–5.5 ppm (versus tetramethylsilane) were the resonances of the benzylic protons, aromatic protons, and $\text{CH}_2 =$ protons, respectively.

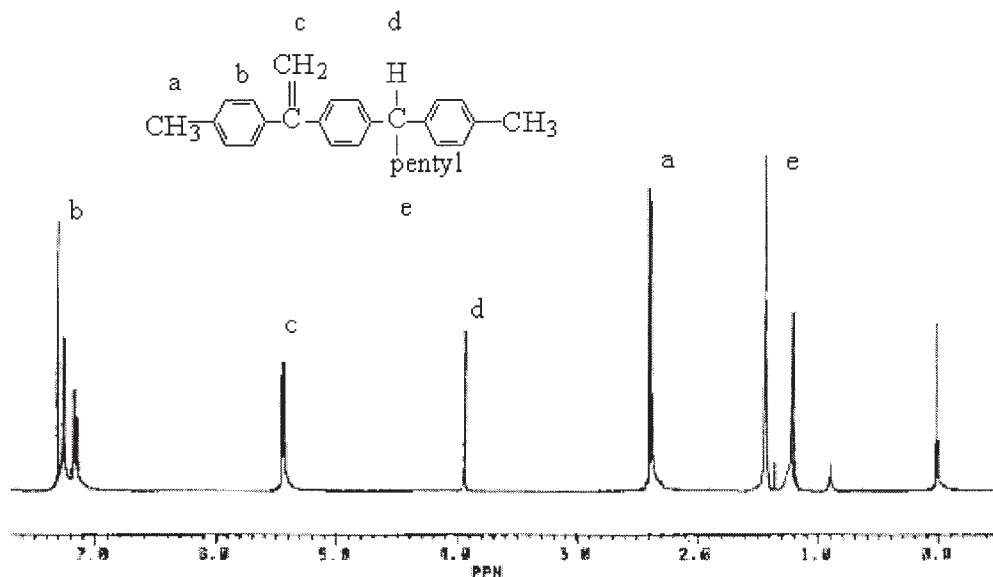


Figure 1 ^1H NMR spectrum of the hydrolysis productions of BuLi to MPEB in 3:2M ratio, without polar additive, in cyclohexane.

The ^1H NMR spectrum of the reaction mixture was more complex. The signal at 3.9 ppm is attributed to $(\text{Ar})_2\text{CH}$ —proton and signal at 0.8–1.6 ppm is attributed to pentyl protons.

A more straightforward qualitative analysis of the reaction mixture was performed by GC-MS. Figure 3 shows the chromatograph of the reaction mixture. Peaks in the chromatograph were identified by MS as cyclohexane (retention time 22 min, $M/e = 80$), hydrolysis product d (retention time 26 min, $M/e = 368$), and hydrolysis product e (retention time 27.5 min, $M/e = 426$). The degree of functionality of the organolithium was designated to measure the progress of the addition reaction. The degree of functionality is defined as:

$$F = 2 - \frac{\text{Area}_d}{\text{Area}_d + \text{Area}_e}$$

where Area_d and Area_e were normalized peak areas of peak d and peak e in the chromatograph.

Kinetics of the addition reaction

Kinetics of the addition reaction was studied to determine the necessary time for an acceptable F under different reaction conditions. The results are summarized in Table I.

A further analysis of the chromatograph showed that in all the cases studied, (in the presence and

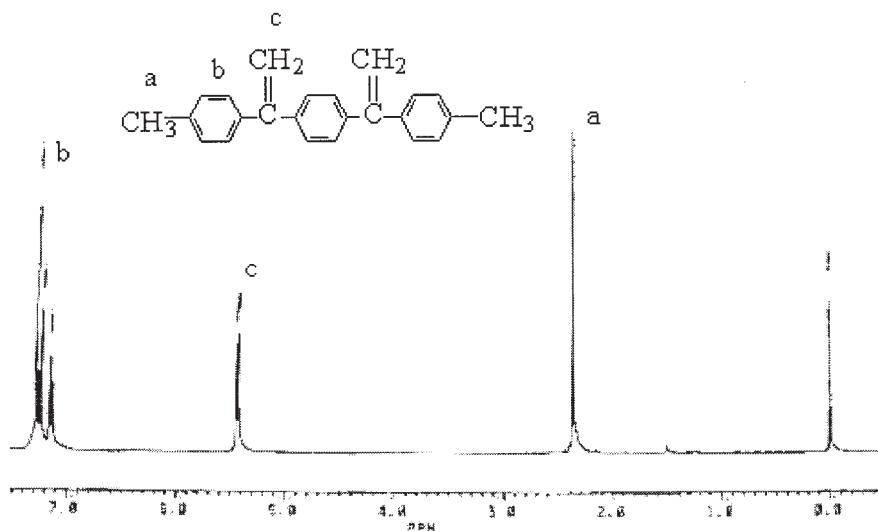


Figure 2 ^1H NMR spectrum of MPEB.

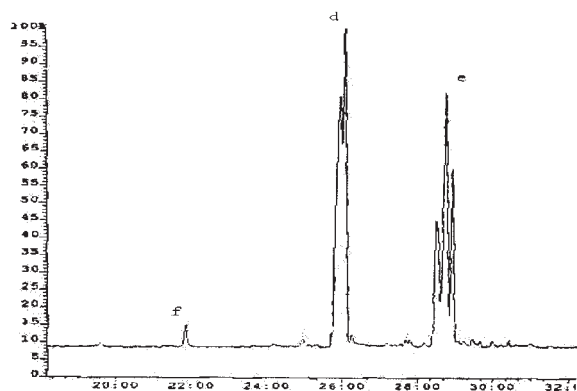


Figure 3 Typical chromatograph of the addition reaction mixture. Peaks (d) and (e) are corresponding compounds (d) and (e) shown in the above hydrolysis reactions, respectively.

absence of the polar additives, toluene, or cyclohexane as solvent), MPEB was consumed completely, at the very beginning of the reaction. There was no MPEB peak shown in the chromatograph. One can conclude that the first addition reaction is very efficient. The second addition reaction is the bottle-neck step. This is not surprising, because as the first step reaction completes, the so-called no-conjugated effect will decrease the activity of the other double bond, making the second addition reaction kinetically less favorable than the first addition reaction. Table I also shows that in most of the case, F started to decrease as the peak F value was achieved. This may be attributed to the chemical equilibrium under different reaction conditions. The best F in all the studied cases was 1.97, which was obtained in just 0.25 h in experiment No. 2. The reaction conditions of experiment No. 2 deserve further study.

Effect of the type of solvent on functionality

Solvents affect the kinetics of the addition reaction because of their difference in polarity. As illustrated in Table I, when toluene was used as solvent, F approached 1.96 after 6 h of reaction in experiment No. 4. F approached 1.52 after 24 h, when cyclohexane was used as solvent and under otherwise identical conditions (experiment No. 1). Based on these data, one can conclude that the more polar the solvent, the faster the reaction.

Effect of polar additive on functionality

It is known that higher polarity is in favor of the addition reaction. However, high polar solvent is not the best option for this particular reaction because when subjected to the polymerization reaction, the polar solvent would significantly affect the polymer structure. A solution to this dilemma is to employ a

small amount of polar additive into the addition reaction system. The small amount of additive would be strong enough to adjust the addition reaction environment to such a point that it would result in a high degree of functionality, at the same time, it would not affect the polymer structure in the sequential polymerization reaction. THF was tested as a polar additive candidate. Experiment Nos. 4 and 6 in Table I shows that when a small amount of THF was applied (molar ratio of THF/Li⁺ = 4) F reached 1.94 in 0.5 h. The same F needed a 5-h reaction time, when no THF was applied under otherwise identical conditions. Other reaction results showed in Table I also suggest that a small amount of THF could profoundly accelerate the reaction rate.

Effect of BuLi structure on degree of functionality

Both *n*-BuLi and *iso*BuLi are widely used in the anion polymerization processes. However, *iso*-butyl lithium is more active than *n*-butyl lithium because of the so-called inductive effect. In this addition reaction, *n*- and *iso*butyl lithium were tested for their effect on the degree of functionality of the product mixture. Our hypothesis is that *iso*butyl lithium could result in higher degree of functionality in this addition reaction than *n*-butyl lithium could, under otherwise identical conditions. Results in Table I show that the hypothesis is true in all the comparable cases, and even more profound in the case that toluene served as solvent. The difference in the degree of functionality caused solely by the butyl lithium structure does not look

TABLE I
Time Course of the Addition Product
at Different Conditions^a

Sample no.	Solvent/BuLi	THF/Li	Reaction time (h)	F
1	Cyclohexane/ <i>iso</i> -BuLi	0	0.5	1.34
			24	1.52
2	Cyclohexane/ <i>iso</i> -BuLi	4	0.25	1.97
			0.5	1.96
			0.5	1.93
			2.5	1.94
3	Cyclohexane/ <i>n</i> -BuLi	4	4.5	1.93
			6.5	—
			7.5	—
			0.5	1.35
			2	1.72
4	Toluene/ <i>iso</i> -BuLi	0	4	1.87
			5	1.93
			6	1.96
			0.5	1.89
5	Toluene/ <i>n</i> -BuLi	4	1	1.89
			3	1.92
			6	1.93
6	Toluene/ <i>iso</i> -BuLi	4	0.25	1.94
			0.5	1.93

^a In all cases, the molar ratio of butyl lithium/MPEB is 2.0.

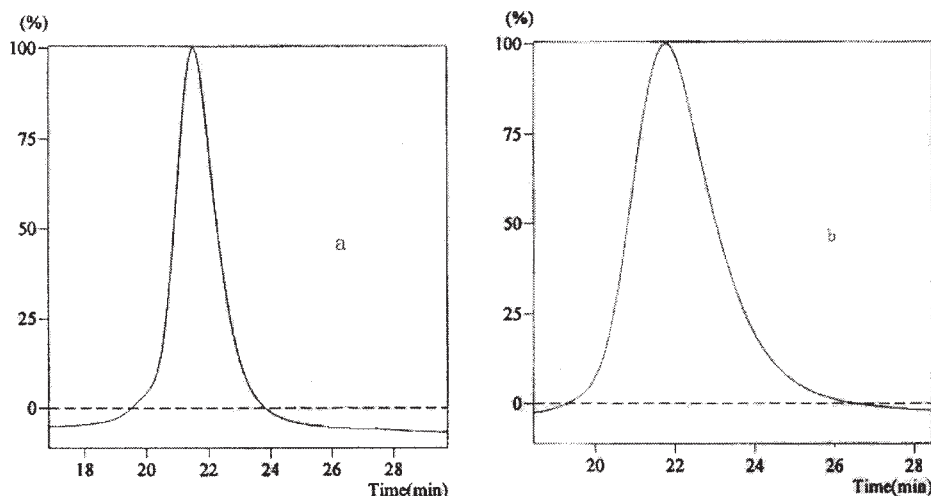


Figure 4 GPC traces of SIBS picked out before styrene addition (a) and the final copolymer (b) (sample No. 1 in Table II).

profound (2–3%); however, these differences could result in significant difference in polymer structure, when they are employed in the polymerization of the triblock SBS copolymer.

The optimization study concluded that the degree of functionality could reach its highest value under the following conditions: molar ratio of isobutyl lithium/MPEB = 2, THF as polar modifier at molar ratio of THF/Li = 4, cyclohexane as solvent, 30°C and 0.5 h of reaction.

Behavior of the difunctional initiator and its use in triblock copolymers

Identification of the difunctionality and particularly the Li content of the dilithium was not sufficient to guarantee the efficiency for the living polydienes, having two equireactive living end groups. If the two end living groups were of different reactivity when synthesizing the ABA triblock copolymers, the initiation of the second monomer might be incomplete and AB diblock copolymers might be formed consequently. The efficiency of the dilithium for the synthesis of ABA triblock copolymers could be tested by two methods: degradation of the central block and/or evaluation of the physicomechanical properties. The latter method had high efficiency and was easy to operate in practice. If the dilithium behaved as an efficient difunctional initiator for the polymerization of butadiene and styrene, the resulting polystyrene-*b*-polydiene-*b*-polystyrene(SDS) triblock copolymers should exhibit good properties, and have a narrow molecular weight distribution. In this report, we did not focus on how to guarantee the efficiency of the dilithium having two equireactive living end species, we just concentrated on the copolymers that we had got by the dilithium synthesized by the procedures described above. A sequential polymerization of diene

and styrene had accordingly been initiated by the dilithium described above. After the stoichiometric butadiene and isoprene monomer mixture was charged into the reactor, a weakly polar additive Et₂O (Et₂O/Li = 5, molar ratio) was added. When the solution was preheated to the polymerization temperature (50°C), a stoichiometric amount of DiLi was added into the reactor to initiate the polymerization. Four hours later, styrene was added and polymerized for 2 h. The final polymer was a block copolymer, having a structure represented by a general formula: SIBS. GPC traces of a sample picked out before styrene addition and of the final copolymer are shown in Figure 4. Both the central block and the final copolymer had a symmetrical, monomodal, and narrow MWD, and the molecular weights were close to what were the expected values. Detailed mechanical properties are illustrated in Table II. Expected M_n for all samples was 10×10^4 , in fact experimental M_n obtained from GPC for all samples was about 10×10^4 , and M_w/M_n was about 1.20 (see Table III). Microstructure of the central block yielded was almost constant. The sample contained 1,2-vinyl bonds in a butadiene segment in a proportion of 15.4 wt % and 3,4-vinyl

TABLE II
Typical Mechanical Properties of SIBS
Prepared by the DiLi

Sample no.	Composition of copolymer (wt %)		Tensile strength (MPa)	Elongation at break (%)
	S	B:I (In central block)		
1	30	30:70	15.1	1280
2	30	50:50	19.2	1150
3	30	70:30	19.6	1120
4	20	70:30	14.7	1200
5	40	70:30	23.6	800

TABLE III
Characterization of Central Block/Copolymers Prepared by the DiLi

Sample no.	M_n				MWD	
	Expected		Experimental		Central block	Copolymer
	Central block	Copolymer	Central block	Copolymer		
1	70,000	100,000	70,000	105,000	1.07	1.18
2	70,000	100,000	72,000	104,000	1.07	1.17
3	70,000	100,000	72,000	110,000	1.07	1.20
4	80,000	100,000	79,000	110,000	1.06	1.22
5	60,000	100,000	63,000	106,000	1.07	1.20

bonds in an isoprene segment in a proportion of 16.0 wt % (obtained by ^1H NMR).

From Table II it is interesting to note that when styrene content was same, the increase of the butadiene content in the central block, increased the tensile strength of the copolymer and decreased the elongation at break gradually. Although the reason was not clear, it might arise from the increase of the entanglement point.^{14,15} The strength of the SDS came from two parts, first one was from the polystyrene microdomains, which acted as the reinforcement fillers and the crosslink nodes; the second one was from the entanglement of the macromolecular chains, and the density of the entanglement points in polybutadiene was more than that in polyisoprene. When styrene content was same, the increase of the butadiene content increased the entanglement points and the strength.

It is well-known that SBS had a character of a two microdomain structure, which could be proved by TEM directly and concluded by DMA curve indirectly. Figure 5 is the TEM micrograph of SIBS synthesized by DiLi, described above. It is very clear that white polystyrene microdomains are equally dis-

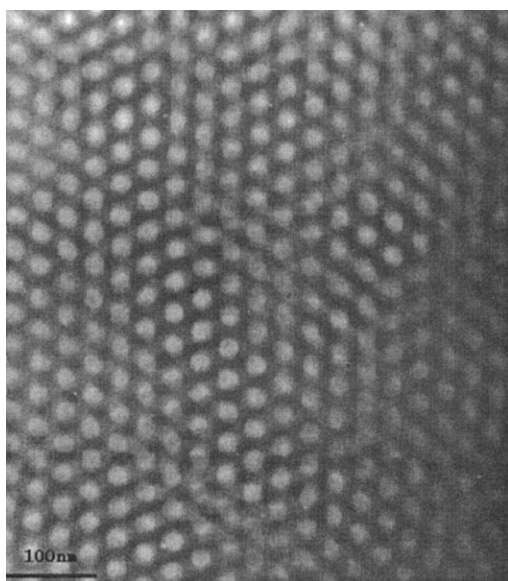


Figure 5 TEM micrograph of SIBS, PS content was 40%, B/I = 70/30 (w/w) (sample No.5 in Table II).

bursed in black polydiene areas, like islands in sea. Figure 6 shows the DMA curves of some samples of SIBS. It is a typical DMA curve of SDS, with peaks at lower and higher temperature that came from the dynamic loss of polydiene and polystyrene microdomains at their glass transition temperature (T_g), respectively. It was interesting that the peaks of the polydiene were monomodal and narrow, which indicated that butadiene and isoprene might be random in the central block chain. In fact from the kinetic research of the butadiene and isoprene copolymerization, the reactivity ratios of the butadiene and the isoprene were nearly same at our polymerization condition. T_g of the polydiene had some relationship with the isoprene content and the detailed relationship is seen in Figure 7, from which the relationship could be described as a line equation as follows:

$$T_g = 0.33x - 62.81$$

where x is the wt % of the central block based on the triblock copolymer.

CONCLUSIONS

From the above discussion, comparable to the cyclohexane, toluene employed as solvent was in favor of

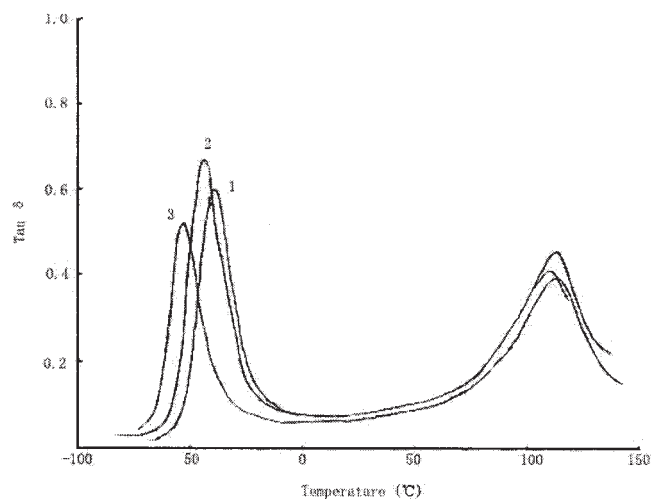


Figure 6 DMA curves of some SIBS samples (sample Nos. 1, 2, 3 in Table II).

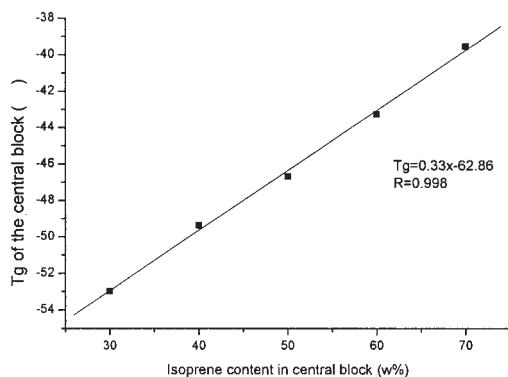


Figure 7 Relationship between T_g of the central block in SIBS and content of isoprene.

the addition reaction of BuLi to MPEB, when there was no polar modifier added. But when polar modifier was employed, even a small quantity as THF/Li = 4, which nearly had no effect on the structure of the polydiene, cyclohexane had some advantages over toluene. Although the advantage was not obvious, it had enough practical meaning in the manufacture of triblock SBS. Compared with toluene, cyclohexane was nontoxic and in accordance with the solvent, which was used in the manufacture of SBS. The employment of polar additive could accelerate the addition reaction and reduce the addition reaction time. isoBuLi was more suitable to the addition reaction than *n*-BuLi. A sequential polymerization of diene and styrene had accordingly been initiated by the dilithium described above to synthesize a triblock copol-

mer SIBS, which were phase separated similar to the novel SBS triblock copolymer and exhibited excellent mechanical properties. With the increase of the isoprene content in the central block, the tensile strength of the copolymer decreased and the elongation at break increased gradually. It was interesting to note that the T_g of the central block was in direct proportion to the isoprene content in the central block, which can be depicted as the following equation: $T_g = 0.33 \times -62.81$, where \times is the wt % of the central block, based on the triblock copolymer.

References

1. Soum, A.; Fontanille, M.; Aboudalle, A. *Polymer* 1988, 29, 1528.
2. Halasa, A. F.; Hsu, N. L. U.S. Pat. 6,518,214 (2003).
3. Shin, H. C.; Lee, C. H. U.S. Pat. 6,221,975 (2001).
4. Tung, L. H.; Lo, G. Y.-S. *Macromolecules* 1994, 27, 2219.
5. Krass, G.; Rollmann, W. J. *Polym Sci Polym Phys Ed* 1976, 14, 1133.
6. Matsumoto, A.; Mizuta, K.; Otsu, T. *Macromolecules* 1993, 26, 1659.
7. Deporter, C. D.; McGrath, J. E. *Polym Int* 1994, 33, 205.
8. Tung, L. H.; Lo, G. Y.-S. *Macromolecules* 1994, 27, 1680.
9. Quirk, R. P.; Ma, J. J. *Polym Int* 1991, 24, 197.
10. Wang, Y. R.; Li, G. H.; Leng, Y. *J Appl Polym Sci* 2003, 88, 1049.
11. Han, G. Y.; Zhang, X. Y.; Jin, G. T. Chinese Pat. 01136233 (2003).
12. Sufcak, M.; Pleska, A.; Seycek, O.; Tureckova, O.; Trekoval, J. German Democratic Republic Pat. 154609 (1982).
13. Lo, G. Y. S.; Otterbacher, E. W.; Walther, B. W.; Bezoari, M. D. EP Pat. 316857 (1987).
14. Gyor, M.; Fodor, Zs.; Wang, H.-C.; Faust, R. *J Macromol Sci Pure Appl Chem* 1993, 30, 349.
15. Gyor, M.; Balogh, L.; Wang, H.-C. *Polym Prepr Am Chem Soc Div Polym Chem* 1992, 33, 158.