

# Formation of SBS Thermoplastic Block Copolymer Using Hexamethyleneimine Alkenyl Lithium (N-Li) Initiator

Qiang Wang,<sup>1</sup> Yurong Wang,<sup>1</sup> Mingyi Liao,<sup>2</sup> Chunqing Zhang<sup>1</sup>

<sup>1</sup>Department of Polymer Materials, College of Chemical Engineering, Dalian University of Technology, Dalian 116012, People's Republic of China

<sup>2</sup>Institute of Materials Technology, Dalian Maritime University, Dalian 116026, People's Republic of China

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**ABSTRACT:** Styrene and butadiene block copolymers (SBS) end functionalized with amino group at the initiating chain ends were synthesized using hexamethyleneimine alkenyl lithium (N-Li) as initiator, tetrahydrofuran (THF) as polar modifier, and cyclohexane as solvent. By attaching a few number of butadiene molecules to *N*-lithium hexamethyleneimine, a new N-Li initiator that can effectively initiate the polymerization of SBS was obtained. <sup>1</sup>H NMR spectrums of the N-Li initiator terminated by ethanol, end functionalized polystyrene, and SBS block copolymer proved the structure of N-Li and its ability to initiate the polymerization of styrene and SBS block copolymer. Kinetics studies suggested that the polymerization rate of styrene in the first block reached the maximum when the ratio of THF/Li was

increased to 5, while further increase of the ratio of THF/Li could not improve the polymerization rate. The molecular weight distribution (MWD) of SBS initiated by N-Li varied with the ratio of THF/Li. The vinyl content of polybutadiene block increased by improving the ratio of THF/Li, while the content of *cis*-1,4 and *trans*-1,4 structures decreased. The vinyl content of end functionalized SBS was somewhat higher than that of SBS initiated by classical *n*-butyllithium when other condition was the same. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 81–88, 2006

**Key words:** anionic polymerization; functionalization of polymers; microstructure; molecular weight distribution; thermoplastics

## INTRODUCTION

End functionalized polymers are a valuable class of materials. Owing to the ability of the functional groups to participate in a variety of physical (e.g., reversible ionic association) and chemical (e.g., chain extension, crosslinking) reactions, these materials are of both academic and commercial interest.<sup>1</sup> These polymers have also been used as precursors for the synthesis of rod-coil block copolymers, specially shaped polymers, branched polymers, cyclic polymers, and regular and asymmetric star-branched polymers.<sup>2</sup> Recently there has been a special demand for block copolymers that are compatible with polar fillers and polar polymers. To meet this demand, a modified polymer having an end-functional group capable of interacting with other polar materials has attracted interests of many.<sup>3–6</sup>

Anionic polymerization is a key technique for the synthesis of end-functional polymers. In fact, in addition to the predictable molecular weight and narrow molecule weight distribution, well defined end group can be quasi-quantitatively attached to the chains by appropriate choice of either the functionalized initiator or the termination agent or both of them.<sup>7–9</sup> In the

case of functionalized initiator, the influence of functionalized group on the polydispersity and microstructure of the resulting polymers should be considered.<sup>10</sup>

Lithium dihydrocarbon amides have been known as alternative initiators for anionic polymerization of dienes.<sup>10–11</sup> However, the products obtained from polymerization in hydrocarbon solvents are typified by low conversions and broad polydispersities because most of the traditional N-Li initiator is insoluble in hydrocarbon solvent, giving rise to heterogeneous initiation. Solubilities of many lithium amide initiators have been studied by D.F. Lawson and it was found that *N*-lithium hexamethyleneimine (LHMI) and *N*-lithium pyrrolidinide (LPY) had a good solubility in hydrocarbon solvent and produced well defined styrene-butadiene rubber (SBR) of narrow molecular weight distribution (MWD).<sup>12–14</sup>

Styrene-butadiene block copolymers (SBS) have traditionally been made by using organolithium compound such as *n*-butyllithium and *sec*-butyllithium. However, this kind of SBS block copolymer is difficult to interact with other materials through physical or chemical interaction. SBR with tertiary amine group at the end of the chain has been synthesized by using LHMI and LPI as functionalized initiators, and the corresponding vulcanized SBR rubber is found to enhance hysteresis reduction by the interaction of amine group and carbon black.<sup>12–14</sup>

In this article, we present a study of the formation of SBS using N-Li initiator. The influence of the ratio of

Correspondence to: Q. Wang (wangqdlut@yahoo.com.cn).

THF/Li on the polymerization kinetics of styrene, the polydispersity and microstructure of SBS is investigated.

## EXPERIMENTAL

### Materials

Butadiene, styrene, cyclohexane, and *n*-butyllithium used in this work were obtained from Beijing Yanshan Petrochemical Corp., China. Styrene and cyclohexane were dried by molecular sieves to keep water content below 5  $\mu\text{g/g}$  and were purged with highly purified nitrogen for more than 15 min before use to keep oxygen content below 10  $\mu\text{g/g}$ . Hexamethyleneimine (HMI) and tetrahydrofuran (THF) were refluxed over calcium hydride for more than 4 h and then distilled under the protection of purified  $\text{N}_2$ . The purity of HMI and THF was checked with gas chromatography. The concentration of *n*-BuLi was calibrated by Gilman double titration method.<sup>15</sup>

### Synthesis and analysis of N-Li initiator

A 50 mL pressure resistant glass flask that was dried and purged with purified nitrogen was filled with cyclohexane and hexamethyleneimine (HMI). To the solution, 0.5M cyclohexane solution of *n*-butyllithium (*n*-BuLi) with a ratio of 1:1 to HMI was added dropwise with stirring for 10 min at room temperature to obtain LHMI. A little amount of pure liquid butadiene were added to the solution of LHMI and the reaction was proceeded for 30 min at 40°C. The number of butadiene molecules attached to LHMI could be controlled by the addition of liquid butadiene and the actual amount of butadiene attached to the initiator chain could be determined by  $^1\text{H}$  NMR of the terminated N-Li initiator. In our studies, the number of butadiene molecules was controlled to be 5–8.

Initiator concentration was determined by two methods of analysis. In the first, a known amount of purified styrene was polymerized using a known amount of N-Li initiator, and the active concentration was calculated by the following equation<sup>10</sup>

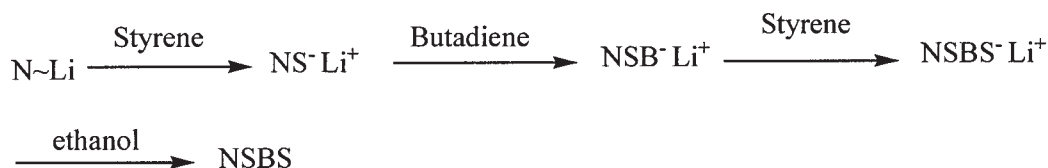
$$\text{Moles of initiator} = \text{grams of monomers} / \overline{M}_n$$

where  $\overline{M}_n$  is the number-average molecular weight of polystyrene formed, determined by GPC.

In the second method, the active concentration was calculated directly by the moles of LHMI (equal to HMI) and the measured volume of the ultimate initiator system. Good agreement between the two methods was observed.

### Polymerization procedures

A 5 L stainless reactor that was dried and purged with nitrogen was charged with cyclohexane and styrene, and the temperature was maintained at 50°C using water bath. THF and N-Li was added using a syringe to first polymerize styrene monomer. About 1.5 h after the addition of N-Li, the temperature of water bath was increased to 70°C, and butadiene monomer was added to the reactor. After the copolymerization of styrene and butadiene monomers for 1 h at 70°C, a known amount of styrene was added to the reactor and polymerization proceeded for 1 h. The total monomer ratio of styrene to butadiene was 30 : 70. A small amount of degassed methanol was added to terminate the living polymers, at which point the color of the solution changed from red to colorless. An aging-resistant agent was added to 1% of the dry rubber and the reactor temperature was then lowered to 20°C. The solution was precipitated by the addition of an excess amount of ethanol and the precipitated polymer was dried in a vacuum oven at 40°C to a constant weight. The overall polymerization was represented as follows:



Where N= hexamethyleneimine alkenyl

S = polystyrene block

B= polybutadiene block

Experiments on the polymerization kinetics of styrene were conducted in an improved capillary tube dilatometer manufactured at the glasswork in our university.<sup>16</sup> The mechanism of dilatometer was based on the decrease of solution volume during the polymer-

ization of styrene. A 70 mL dilatometer that was dried and purged with nitrogen was filled with cyclohexane and styrene. After the dilatometer was heated to the designed temperature, THF and N-Li were added by syringe. After styrene was initiated, the height of po-

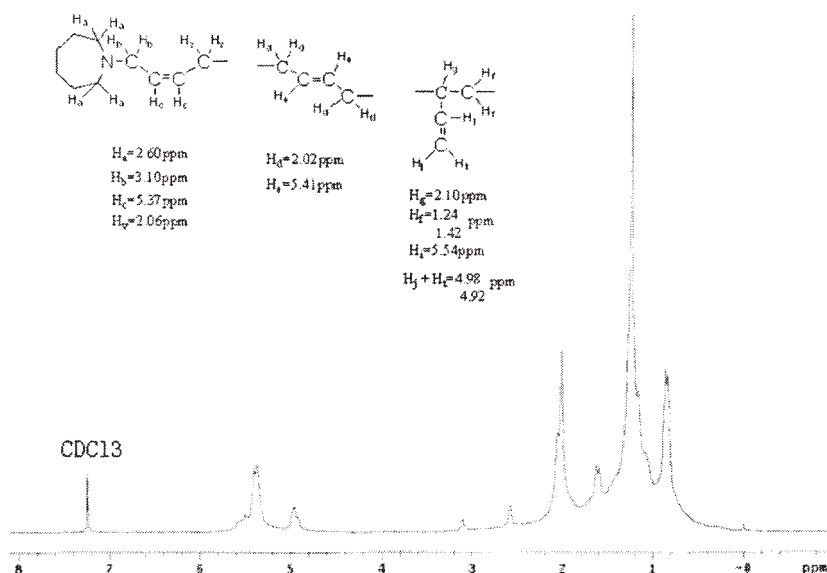


Figure 1  $^1\text{H}$  NMR spectrum of terminated N-Li initiator.

lymerization solution ( $h$ ) in the dilatometer decreased and the relationship between conversion ( $x$ ) and  $h$  was as follows

$$x = (h_0 - h) \times 100\% / (h_0 - h_1)$$

where,  $h_0$  is the original height of polymerization solution in the dilatometer before styrene begin to react;  $h_1$  is the terminal height of polymerization solution after styrene have reacted thoroughly;  $h$  is the height of polymerization solution at different time of polymerization;  $x$  is the corresponding conversion of styrene.

### Characterization

The molecular weight was determined by GPC (Waters, Maxims820) using three Waters u-Styragel Columns ( $10^3$ ,  $10^4$ ,  $10^5$ ) at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent. The GPC instrument was calibrated using monodisperse polystyrene standards.

The composition of polymers was analyzed by  $^1\text{H}$  NMR (Bruker AM-400) spectroscopy at room temperature. The sample was dissolved in deuteriochloroform ( $\text{CDCl}_3$ ) to prepare the solution with a concentration of 150 mg/mL.  $^1\text{H}$  NMR spectra was used to calculate the content of vinyl and 1,4-microstructures of SBS.<sup>17</sup> The percentage of block styrene and the microstructure of the butadiene portion were calculated from the areas ( $A$ ) under the peaks, which correlated with the number of protons contributing to them. The following equations were used.<sup>17</sup>

$$\begin{aligned} 5M_1 + 3M_2 &= A_A \\ 2M_2 &= A_B \\ 2M_3 &= A_T \end{aligned}$$

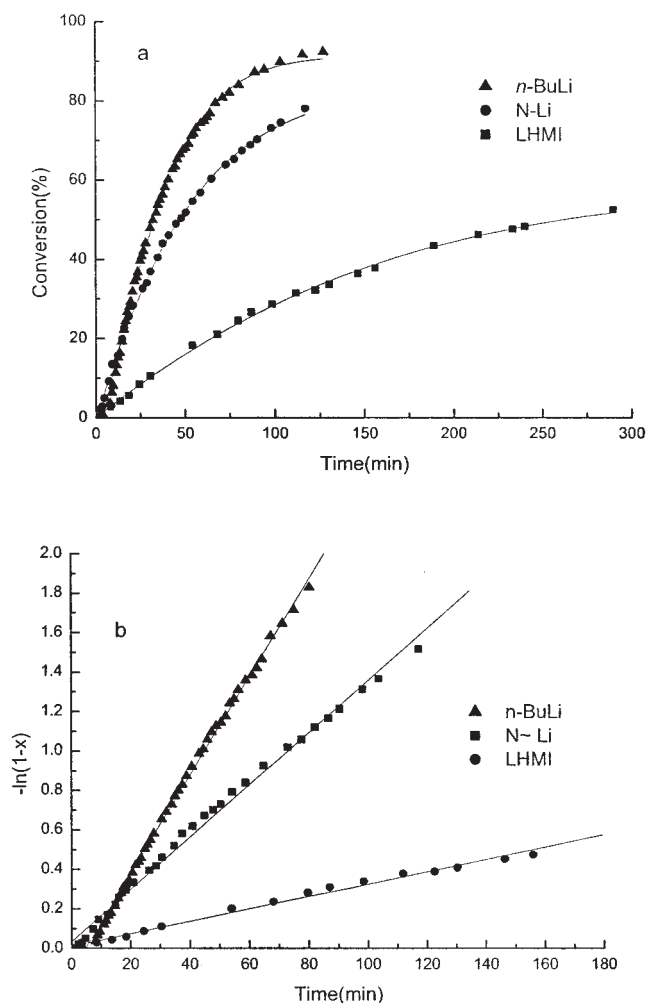


Figure 2 Plot of (a) conversion ( $x$ ) and (b)  $-\ln(1-x)$  versus time ( $t$ ) for styrene polymerization initiated by different initiators, initiator concentration  $[C] = 1.25 \text{ mmol}/100 \text{ g}$  styrene,  $T = 50^\circ\text{C}$ .

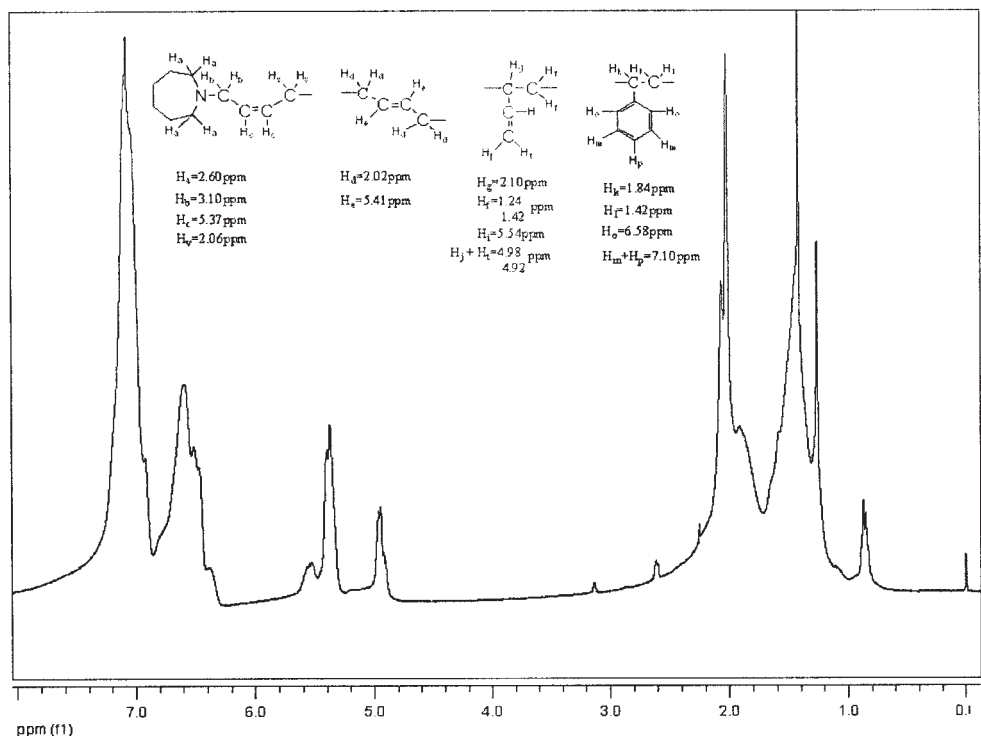


Figure 3  $^1\text{H}$  NMR Spectrum of end functionalized polystyrene initiated by N-Li.

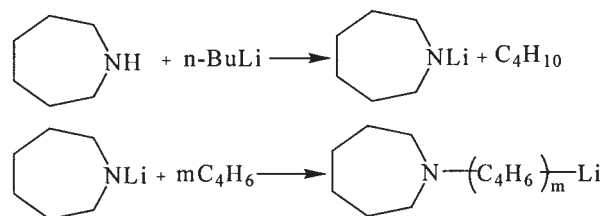
$$2M_4 + M_3 = A_N$$

where  $M_1$  = relative number of moles of nonblock styrene,  $M_2$  = relative number of moles of block styrene,  $M_3$  = relative number of moles of 1,2-butadiene,  $M_4$  = relative number of moles of 1,4-butadiene,  $M_1 + M_2$  = the relative number of moles of styrene.  $A_A$ ,  $A_B$ ,  $A_T$ , and  $A_N$  were the relative areas under peaks A, B, T, N respectively, (Fig. 6). *Cis*-1,4 and *trans*-1,4 structures were obtained from the expanded olefinic regions by electronic integration of the areas under the peaks from 2.02 to 2.06 ppm. The equations of the calculation of *cis*-1,4 and *trans*-1,4 content of polybutadiene block were described in ref. 17.

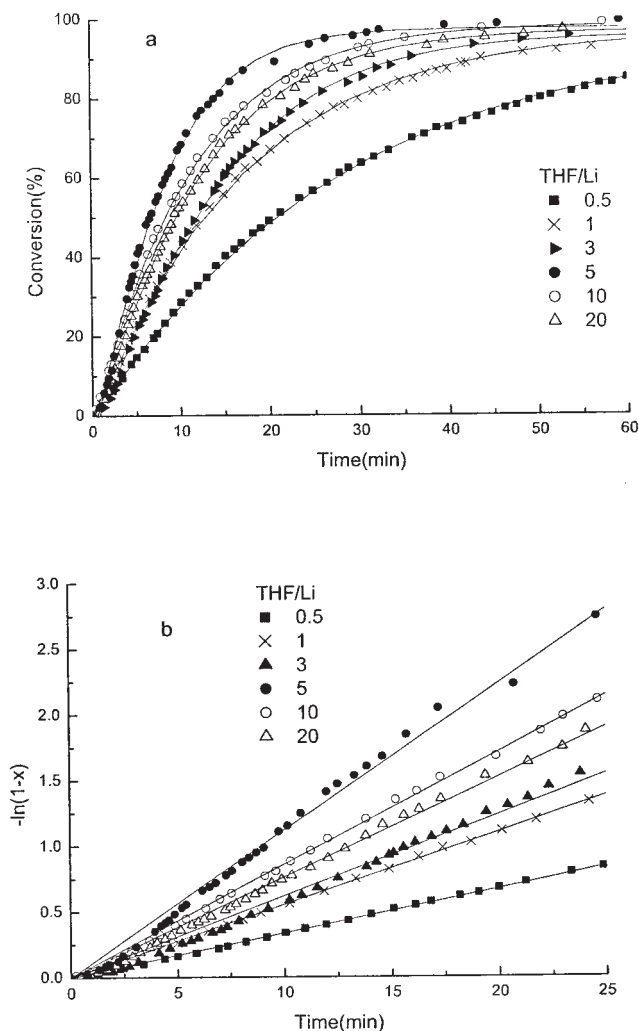
## RESULTS AND DISCUSSION

### Mechanism of initiator synthesis

LHMI is soluble in hydrocarbon solvent and can initiate diene efficiently.<sup>14</sup> However, in our study, we find the polymerization rate of styrene initiated by LHMI is very slow when compared with *n*-BuLi. In an attempt to improve the initiating activity of LHMI, we try to attach a few number of butadiene molecules to LHMI to obtain a novel N-Li initiator. Synthesis of N-Li initiator can be illustrated as follows:



The produced N-Li initiator is soluble in hydrocarbon solution. The reaction of LHMI with *n*-BuLi can be finished in 10 min at room temperature.<sup>18</sup> The characterization of N-Li and the average number of butadiene molecules attached to LHMI is investigated through the  $^1\text{H}$  NMR spectrum of terminated N-Li initiator, which is obtained by the reaction of N-Li and ethanol. In Figure 1 the proton ( $H_b$ ) appearing at 3.1 ppm is the characteristic of methylene hydrogen bonded to the carbon at the polybutadiene chain that is adjacent to nitrogen. The proton ( $H_a$ ) appearing at 2.6 ppm is the characteristic of methylene hydrogen bonded to the carbon at HMI moiety that is adjacent to nitrogen. The ratio of the areas of  $H_b$  to  $H_a$  is 2.00 : 4.20, which is close to 2.00 : 4.00. So it can be concluded that LHMI could react with butadiene effectively. Butadiene can be incorporated in the initiator chain in two structures: vinyl structure ( $H_j$  and  $H_k$  appears from 4.92 to 4.98 ppm) and 1,4-structure ( $H_c$  and  $H_e$  appears from 5.37 to 5.41 ppm). The ratio of the areas of  $H_b$ , ( $H_j + H_k$ ), and ( $H_c + H_e$ ) is 2.00 : 4.00 :

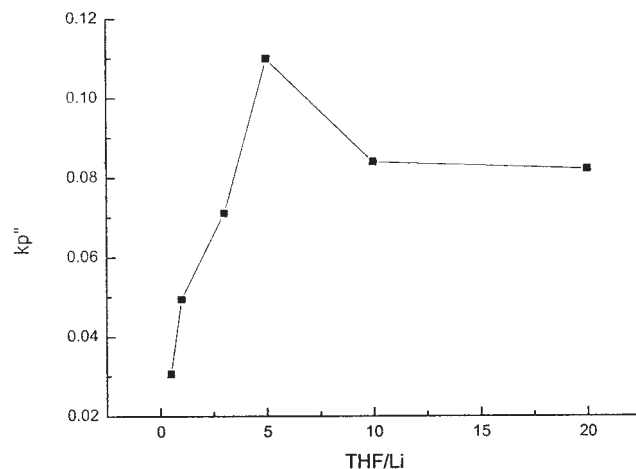


**Figure 4** Plot of (a) conversion ( $x$ ) and (b)  $-\ln(1-x)$  versus time ( $t$ ) for styrene polymerization initiated by N-Li at different ratios of THF/Li, initiator concentration  $[C] = 1.25$  mmol/100 g styrene,  $T = 50$  °C.

12.10. So there exist two butadiene molecules with vinyl structure and 6.05 butadiene molecules with 1,4-structure on the initiator chain. The total number of butadiene molecules attached to LHMI is about 8.

The polymerization rate of styrene initiated by  $n$ -BuLi, LHMI, and N-Li is discussed in Figure 2(a) on the basis of conversion ( $x$ ) versus time ( $t$ ) plot. The initiating activity of LHMI decreased marked when compared with  $n$ -BuLi. However, the activity of N-Li is improved to some extent after 8 butadiene molecules are attached to LHMI.

The  $^1\text{H}$  NMR spectrum of end functionalized polystyrene is shown in Figure 3. The peak at 2.6 ppm is assigned to the methylene hydrogen bonded to the carbon at HMI moiety that is adjacent to nitrogen. The peak at 3.1 ppm is assigned to the methylene hydrogen bonded to the carbon at the polymer chain that is adjacent to nitrogen.  $^1\text{H}$  NMR results illustrate that N-Li initiated the polymerization of styrene effectively.



**Figure 5** False first-order rate constant ( $k_p''$ ) for polymerization of styrene at 50°C with various amount of THF, using N-Li as initiator.

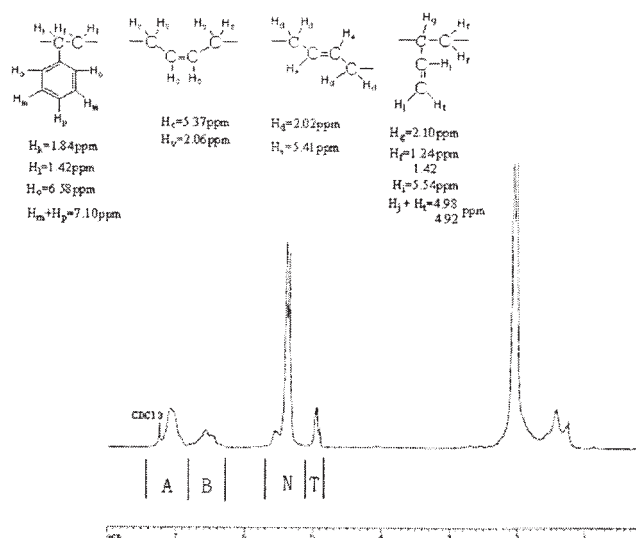
### Styrene polymerization kinetics

It is reported that the polymerization of styrene in the first block of SBS play an important role in the structure and property of synthesized SBS. First, we investigate the polymerization kinetics of styrene initiated by novel N-Li initiator.

Kinetic behavior of styrene is studied by establishing the relationships between conversion ( $x$ ) and time ( $t$ ) using different initiators, as plotted in Figure 2(a). According to the kinetics equation of anionic polymerization,

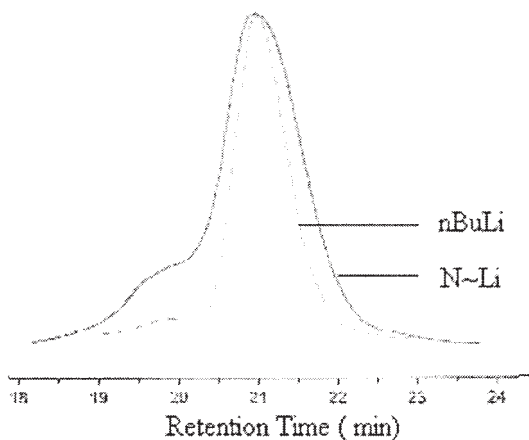
$$-d[M]/dt = k_p[C]^{\alpha}[M]^{\beta} \quad (1)$$

where  $[M]$  is the concentration of monomer,  $t$  is the polymerization time, and  $k_p$  is the apparent rate con-



**Figure 6**  $^1\text{H}$  NMR spectrum of SBS initiated by N-Li. The ratio of THF/Li = 1.0,  $[C] = 1.00$  mmol/100 g monomer.





**Figure 7** GPC spectrum of SBS initiated by N-Li and *n*-BuLi, respectively. The ratio of THF/Li = 20, [C] = 1.00 mmol/100 g monomer.

stant of the propagating reaction. Assuming the reaction rate is first-order in monomer concentration, e.g.,  $\beta = 1$  and let  $k_p'' = k_p[C]^\alpha$ , then  $k_p''$  is the false first-order rate constant of propagating reaction, on condition that the concentration of propagating active center remains constant.

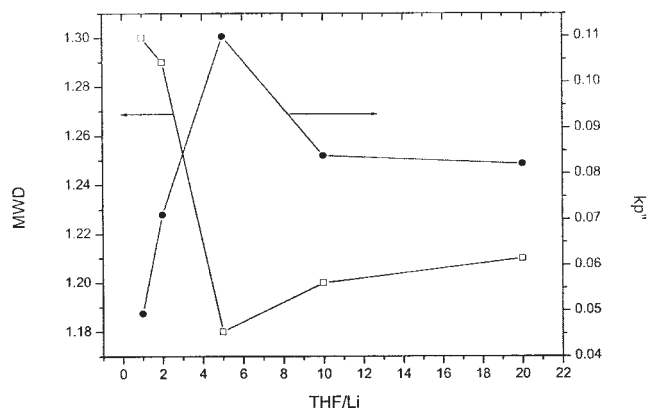
$$-d[M]/dt = k_p''[M] \quad (2)$$

by rewriting eq. (2) and then integrating it, we get

$$-\ln(1 - x) = k_p''t \quad (3)$$

According to eq. (3), conversion  $x$  is plotted against time  $t$  (Fig. 2(b)), taking  $-\ln(1 - x)$  as the  $y$ -axis. The linear relationship between  $t$  and  $-\ln(1 - x)$  proves that the assumption of  $\beta = 1$  is correct. The false first-order rate constant of propagating reaction ( $k_p''$ ) of styrene was  $0.0029 \text{ min}^{-1}$  (initiated by LHMI),  $0.0231 \text{ min}^{-1}$  (initiated by N-Li), and  $0.1049 \text{ min}^{-1}$  (initiated by *n*-BuLi). Through kinetic studies we find that the polymerization rate of styrene initiated by N-Li is about ten times faster than that of LHMI.

In general, the living styryllithium chain ends are associated in nonpolar hydrocarbon solvent.<sup>7</sup> This association phenomenon alters the kinetic mechanism. Although this association does not occur in polar sol-



**Figure 8** Plot of the molecular weight distribution (MWD) of SBS and styrene polymerization rate ( $k_p''$ ) to the ratio of THF/Li using N-Li as initiator.

vent because of the strong solvating power, the living chain end can exist in the form of a contact ion pair, loose ion pair, or free ions having different reaction rates. We employ THF as polar modifier to increase the rate of initiation. The experimental data of polymerization of styrene at  $50^\circ\text{C}$  with various amounts of THF as polar modifier and cyclohexane as solution are represented in Figure 4. The rate increased as the ratio of THF/Li increased from 1 to 5. Nevertheless, a further increase of the ratio of THF/Li resulted in a slight rate decrease. The corresponding  $k_p''$  was plotted in Figure 5. This change in the polymerization rate with different amount of THF addition was similar to the previous results of styrene polymerization kinetics by using *n*-BuLi as initiator.<sup>19</sup>

### Formation of SBS

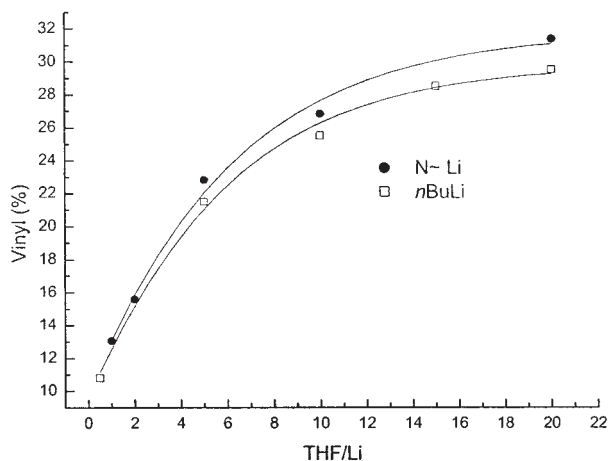
In the sequential SBS synthesis process, the polystyrene block was made first, followed by the addition of butadiene to the living polystyryllithium chain end. The preparation of SBS was completed by the further addition of a second quantity of styrene in an equal amount to that of the first styrene usage. The typical  $^1\text{H}$  NMR spectrum of synthesized SBS are listed in Figure 6. Usually, the resonance peak of the *ortho*-proton ( $\text{H}_o$ ) at 6.58 ppm, which is the characteristic of

**TABLE I**  
Molecular Characteristics of SBS Copolymers Prepared by N-Li

THF/Li	$\overline{M}_w (10^{-4})$	$\overline{M}_n (10^{-4})$	MWD
1	11.37	8.74	1.3
2	12.44	9.59	1.29
5	13.07	11.1	1.18
10	10.56	8.8	1.2
20	7.95	6.57	1.21

**TABLE II**  
Microstructure of SBS Polymers, Initiator Concentration [C] = 1.25 mmol/100 g Monomer

THF/Li	Styrene (%)	Vinyl-1,2 (%)	<i>cis</i> -1,4 (%)	<i>trans</i> -1,4 (%)
1	27.7	13.05	26.85	60.00
2	27.9	15.57	26.72	57.61
5	27.8	22.82	24.00	53.18
40	28.5	26.83	23.18	49.98
20	28.4	31.37	22.07	46.53



**Figure 9** Comparison of vinyl content of SBS initiated by N-Li and *n*BuLi.

block polystyrene sequences, suggests that styrene in the sample incorporates in block way.

The GPC spectrum of SBS initiated by N-Li is shown in Figure 7. The corresponding molecular weight characterization is summarized in Table I. Apparently the MWD is somewhat higher when compared with that of *n*-BuLi polymerization. As mentioned before, the molecular weight and its distribution are always influenced by the polymerization rate. Through kinetics study of polystyrene, we find the initiating rate of N-Li is relatively slower than that of *n*-BuLi. It is likely that the broad MWD of end functionalized SBS is due to the slow initiating rate of N-Li when compared with that of *n*-BuLi. The MWD decreases from 1.30 to 1.18 when the ratio of THF/Li increased from 1 to 5, nevertheless, MWD became slightly broad when the ratio of THF/Li increased from 5 to 20. This change correlates somewhat to the rate of styrene polymerization. Plot of polymerization rate constant ( $k_p''$ ) of polystyrene and MWD of SBS to the ratio of THF/Li is shown in Figure 8. As we can see, the value of MWD decreases with the increase of  $k_p''$ , while MWD increases with the decrease of  $k_p''$ . It may be concluded that the styrene polymerization rate in the first block of SBS is responsible for the change of MWD.

It is reported that THF could alter the microstructure of polybutadiene from high 1,4-content to a high 1,2-content even in a nonpolar hydrocarbon solvent containing a very small amount of THF. In our study, we use  $^1\text{H}$  NMR to identify the various isomeric units of polybutadiene block initiated by N-Li. The influence of the ratio of THF/Li on the microstructure of polybutadiene portion is shown in Table II. The vinyl content increases from 13.05 to 31.37% with the increasing of the ratio of THF/Li from 1 to 20, while the contents of *cis*-1,4 and *trans*-1,4 units decreases. To investigate the influence of functionalized group in

the initiator on the microstructure of polybutadiene block, plot of the vinyl content of SBS to the ratio of THF/Li using N-Li and *n*-BuLi as initiators is shown in Figure 9. The vinyl content of polybutadiene portion is higher than those obtained with the classical initiator *n*-BuLi with the same initiator concentration. The same results are also obtained when 3-dimethylaminopropylolithium is used as functionalized initiator for the polymerization of butadiene.<sup>10</sup>

## CONCLUSIONS

The initiator activities of *n*-BuLi, LHMI, and N-Li in the polymerization of styrene (formation of the first block of SBS) were studied by kinetics method. LHMI could not initiate the polymerization of styrene effectively. However, by attaching a few number of butadiene molecules to LHMI, the obtained new N-Li was an effective initiator for the synthesis of styrene and the corresponding SBS.  $^1\text{H}$  NMR spectrum suggested that butadiene could attach to LHMI effectively and the average number of butadiene molecules attached to LHMI in our studies was about 8. The polymerization rate of styrene initiated by N-Li in the first block was increased by increasing the ratio of THF/Li from 1 to 5, and the corresponding MWD of SBS became lower. However, further increase of the ratio of THF/Li from 5 to 20 could not improve the polymerization rate of styrene, neither did it decrease the MWD of SBS. It could be concluded that the styrene polymerization rate in the first block of SBS was responsible for the change of MWD. With the increase of the ratio of THF/Li, the vinyl content of SBS increased and content of *cis*-1,4 and *trans*-1,4 decreased. At the same ratio of THF/Li, polymerization temperature, and initiator concentration, the vinyl content of end functionalized SBS initiated by N-Li was slightly higher than SBS initiated by the classical initiator *n*-BuLi.

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