

# Synthesis and Kinetic Behavior of Stereotriblock Polybutadiene Using Dilithium as Initiator

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**ABSTRACT:** Anionic polymerization of butadiene was conducted in cyclohexane using 1,1,4,4-tetraphenyl-1,4-dilithium butane (TPB-DiLi) as initiator and dipiperidinoethane (DPE) as modifier. The polymer design effects of DPE/TPB-DiLi (simplified as DPE/Li) and polymerization temperature on the 1,2 content of polybutadiene (PB) were examined and 1,2-polybutadiene (1,2-PB) with a nearly 100% 1,2 content was obtained. 1,2-1,4-1,2-Stereotriblock polybutadiene (STPB) can be synthesized easily by means of one feed reaction. DSC and DMA analyses showed that STPB with the designed molecular structure (molecular weight, block ratio, and 1,2 content in 1,2 blocks) has two  $T_g$ 's and two loss moduli and exhibits microphase

separation. Studies on reaction kinetics established the polymerization kinetics equation of 1,4-PB as  $-d[M]/dt = 0.356[C]^{0.5}[M]$ , indicating the first-order relationship between polymerization rate and monomer concentration. At 50°C, the addition of the strong polar modifier DPE into the system increased the reaction rate. The apparent propagating activating energies before and after DPE addition were also determined in this study. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1049–1054, 2003

**Key words:** stereospecific polymers; polybutadiene; kinetics (polym.); structure; anionic polymerization

## INTRODUCTION

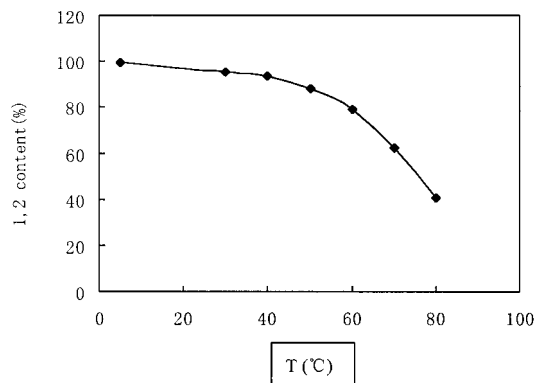
By means of polymer design, Halasa, Cohen, Bates, and Yang<sup>1–7</sup> all synthesized 1,2–1,4-stereodiblock polybutadiene using *n*-BuLi as initiator and dipiperidinoethane (DPE) as modifier in hexane or benzene. They reported in detail the polymerization kinetics and relationships among polymer structure, morphology, properties, and reaction conditions concerning monolithium-initiated anionic polymerization of butadiene to prepare stereodiblock or stereotriblock polybutadiene. Tung (Dow Co.) and Zelinsk<sup>8–12</sup> have been dedicated to the synthesis of dilithium initiators and explored their applications in synthesizing BAB-type triblock copolymers from two kinds of monomers. In their reports, lithium naphthalene, an electronic complex, and dilithium isoprene were used, respectively, to initiate anionic polymerization of butadiene and styrene to obtain triblock copolymers. Furthermore, a blend of monolithium and dilithium initiators, prepared by mixing monosubstituted and disubstituted alkane at a certain ratio then reacting with lithium, was attempted for the same purpose. An oligomer of dilithium butadiene disubstituted by alkyl halogen was the initiator that Li et al.<sup>13–15</sup> chose to synthesize symmetrical two-head-transition butadiene/styrene block copolymer S-(S/B-B-(B/S)-S) in cyclohexane in

one feed. They also determined the polymerization rate constants of each block and the apparent reactivity ratio of this copolymerization reaction.

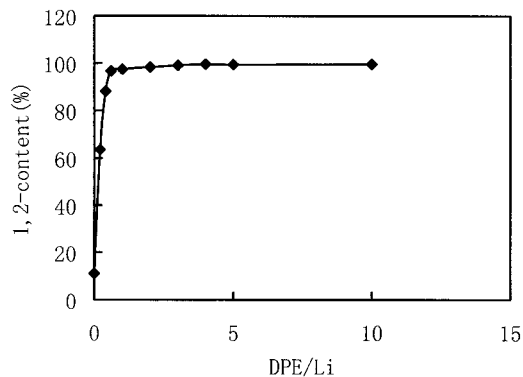
Xie et al.<sup>16</sup> synthesized stereotriblock polybutadiene by the initiation of  $\alpha$ -toluene lithium naphthalene in the presence of diethylene glycol dimethyl ether; determined its solution properties, absolute molecular weight, and the second-dimension coefficient; and calculated the solubility parameter  $\delta$  and the Flory interaction parameter  $\chi$  as well. On the basis of Xie's work, Li et al.<sup>17,18</sup> added the strong polar modifier DPE into the initiator and obtained 1,2–1,4–1,2-stereotriblock polybutadiene (STPB) whose 1,2 content was nearly 100%. They also probed the relationships among molecular structure, morphology, and properties and conducted research on kinetic behaviors.

In this report, we describe the synthesis of 1,2–1,4–1,2-STPB by means of a one-step reaction. The polymerization system consisted of self-made 1,1,4,4-tetraphenyl-1,4-dilithium butane (TPB-DiLi) as initiator, DPE as modifier, cyclohexane as solvent, and butadiene, the only monomer employed. 1,2–1,4–1,2-STPB produced in this way had a nearly 100% 1,2 content in 1,2-blocks. Our research on this TPB-DiLi/DPE/cyclohexane/butadiene polymerization system covered effects of polymerization conditions on polymer microstructures, relationships between polymer structure and morphology, and, most important, the polymerization kinetic behaviors of 1,4-polybutadiene (1,4-PB) and 1,2-polybutadiene (1,2-PB).

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**Figure 1** Effect of temperature on 1,2 content at DPE/Li = 5.0.



**Figure 2** Effect of DPE/Li on 1,2 content at 50°C.

## EXPERIMENTAL

### Materials

TPB-DiLi was prepared by the following procedures. First,  $\text{CH}_3\text{MgI}$  was reacted with  $(\text{C}_6\text{H}_5)_2\text{CO}$  to form  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_3$  and 1,1-diphenyl ethylene was obtained in the presence of sulfuric acid. Then, under the protection of purified nitrogen, the refined 1,1-diphenyl ethylene reacted with Li filament at 20°C for 50 h, producing lithium diphenyl ethylene free-radical anion, which coupled to produce deep red TPB-DiLi. The concentration of TPB-DiLi was analyzed by use of the Gillman double-titration method before use. Butadiene (Beijing Yanshan Petrochemical Corp., China) was purified with a small amount of BuLi and then vaporized to keep water content below 10  $\mu\text{g/g}$ . Cyclohexane, as received (Liaoyang Petrochemical Co., China), was dried by 5-Å molecular sieves to keep water content below 5  $\mu\text{g/g}$  and was purged with highly purified nitrogen for more than 15 min before use to keep oxygen content below 10  $\mu\text{g/g}$ . The preparation of DPE followed the procedures described by Wang et al.<sup>18</sup>

### Polymerization procedures

#### 1,4-PB

A solution of 10 wt % butadiene in cyclohexane was introduced into a polymerization flask filled with purified  $\text{N}_2$  and preheated to the polymerization temperature ( $T$ ). A stoichiometric amount of TPB-DiLi was added into the flask to initiate the polymerization.

After 100% monomer conversion, an aging-resistant agent, the mass of which was 1% that of dry rubber, was added to the flask. The reaction was terminated with isopropanol and products were dried in a vacuum oven at 40°C to a constant weight.

#### 1,2-PB

Into the preheated polymerizing solution, the same as that in 1,4-PB polymerization, was added a stoichiometric amount of DPE before TPB-DiLi was introduced, resulting in 1,2-PB products of various 1,2 content.

#### 1,2-1,4-1,2-STPB

According to the conversion ( $x$ ) versus time ( $t$ ) plot obtained in 1,4-PB polymerization, at the designed conversion  $x$ , by regulating temperature to 5°C, adding a stoichiometric amount of DPE into the flask, and waiting until 100% conversion was reached, we were able to obtain 1,2-1,4-1,2-STPB products of different block ratios.

Experiments on polymerization kinetics were conducted in an improved capillary tube dilatometer manufactured in the glasswork at our university.

### Characterization

Microstructure analyses were carried out on a Shimadzu IR-408 (Shimadzu, Kyoto, Japan) spectrophotometer and a JEOL FX-90Q  $^1\text{H-NMR}$  spectrometer (JEOL, Tokyo, Japan). Glass-transition temperatures

**TABLE I**  
Comparison Between Designed and Measured Values of Block Ratios of 1,2-1,4-1,2-STPB

$\overline{M}_n \times 10^4$	10	10	10	15	15	15
1,2/1,4/1,2 (molar ratio)						
Designed value	35/30/35	25/50/25	15/70/15	35/30/35	25/50/25	15/70/15
Measured value	34/32/34	25/50/25	15.5/69/15.5	35/30/35	26/48/26	16.5/69/16.5

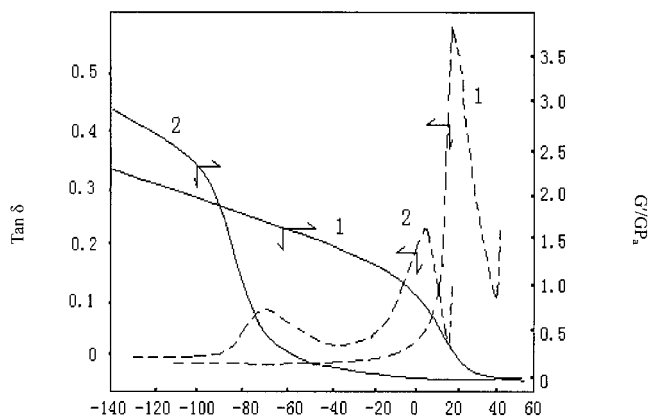


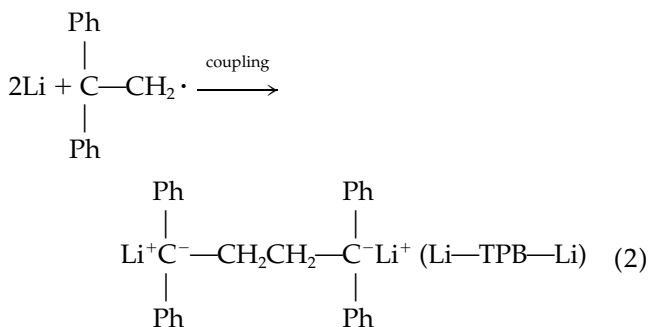
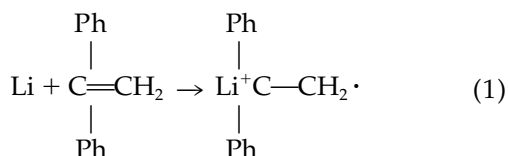
Figure 3 DMA graph of stereotriblock PB.

were measured according to a Japanese scientific standard DSC-TDA at a heating rate of 20°C/min. Dynamic mechanical tests were made on a Dupont 990 viscoelastometer (Dupont, Boston, MA) between -150 and 50°C, 3.5–150 Hz, at a heating rate of 5°C/min, a fixed amplitude of 0.2 mm, and a measuring range of 0–10<sup>6</sup> N/cm<sup>2</sup>.

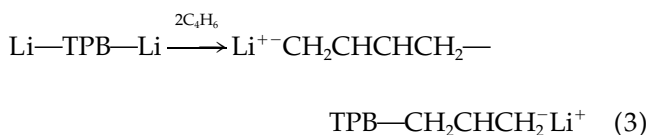
## RESULTS AND DISCUSSION

### Mechanism of 1,2-1,4-1,2-STPB synthesis

#### 1. Synthesis of dilithium initiator

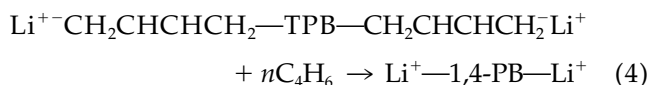


#### 2. Initiation

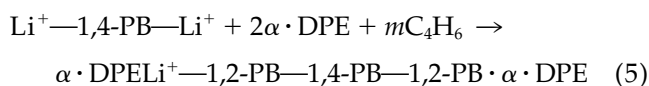


#### 3. Propagation

##### First step



##### Second step



Reactions (4) and (5) contribute to regulating the block ratios of 1,4-PB and 1,2-PB blocks. The amount of DPE added in reaction (5) affected the 1,2 content in 1,2 blocks and the molecular weight of triblock PB can be adjusted by the amount of initiator used.

#### Effects of temperature and DPE amount on 1,2 content

Results of characterization of 1,2-1,4-1,2-STPB by IR and <sup>1</sup>H-NMR are shown in Figures 1 and 2, respectively. When DPE/Li = 5.0, the 1,2 content declined rapidly with increasing temperature, as illustrated in Figure 1. When the temperature was increased from 5

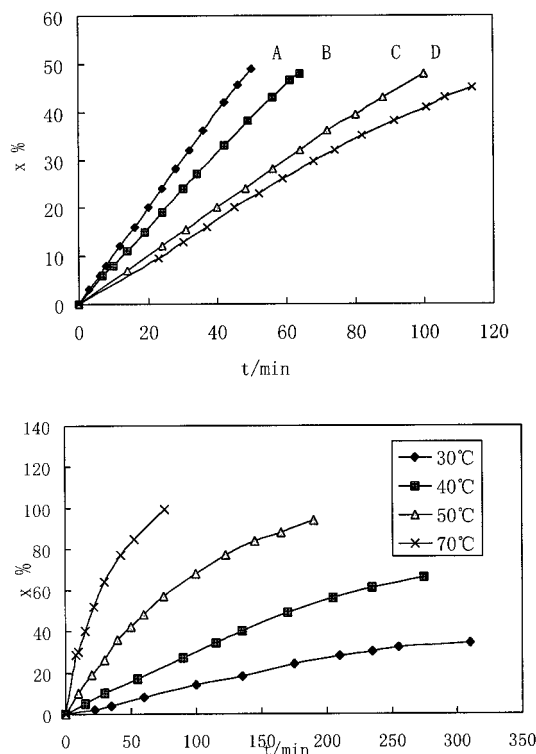
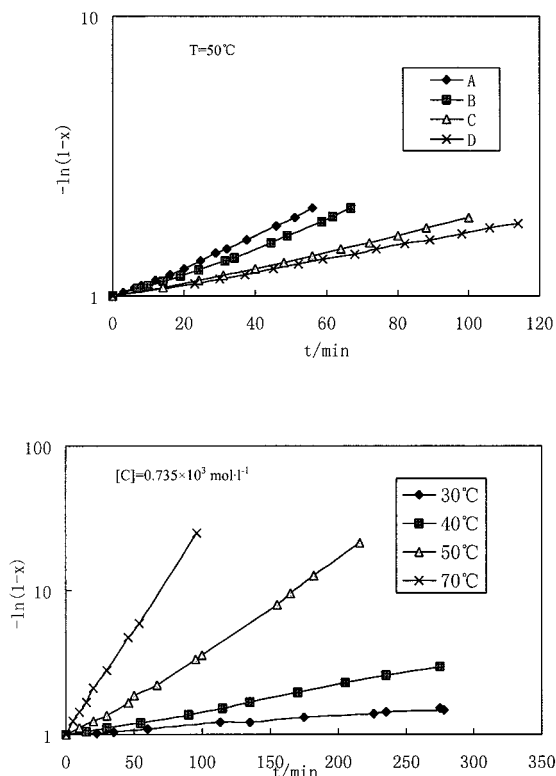


Figure 4 Plot of conversion ( $x$ ) versus time ( $t$ ) for 1,4-PB polymerization at different initiator concentrations  $[C]$  and temperatures  $T$ . A = 0.735; B = 0.525; C = 0.200; D = 0.1055 ( $\times 10^3$  mol/L).



**Figure 5** Plot of  $-\ln(1-x)$  versus  $t$  plot at different  $[C]$  and  $T$  for 1,4-PB polymerization. A = 0.735; B = 0.525; C = 0.200; D = 0.1055 ( $\times 10^3$  mol/L).

to 80°C, the 1,2 content decreased from 99 to 40%. At 50°C and DPE/Li > 3.0, the 1,2 content approached 100% after a 5-h reaction. These data indicate that temperature and the amount of DPE are sensitive in regulating polymer microstructures.

### 1,2-1,4-1,2-STPB with desired block ratios

On the basis of the time ( $t$ ) versus conversion ( $x$ ) plot of 1,4-PB polymerization, it is possible to design and synthesize triblock copolymers with desired block ratios by determining  $x$  from the desired block ratio and determining the time needed to produce 1,4-PB block at this conversion before adding DPE. Values of measured block ratios listed in Table I are calculated from the following equations:

$$\begin{cases} \text{overall 1,2 content in STPB} = S_{1,4}V_{1,4} + S_{1,2}V_{1,2} \\ S_{1,2} = (1 - S_{1,4})/2 \end{cases}$$

(6) By integrating eq. (9), we obtain

or

$$\begin{cases} \text{overall 1,2 content in STPB} = 0.11S_{1,4} + 0.99S_{1,2} \\ S_{1,2} = (1 - S_{1,4})/2 \end{cases} \quad (7)$$

where  $S_{1,2}$  and  $S_{1,4}$  are molar percentages of 1,2 and 1,4 blocks, respectively, and  $V_{1,4}$  and  $V_{1,2}$  are molar percentages of 1,2 content in 1,4 and 1,2 blocks, respectively.

Data in Table I indicate that the measured block ratios are in close agreement with values calculated from the equations described above, which suggests the realization of polymer design by applying this kind of dilithium initiator.

STPB with molecular weight  $15 \times 10^4$  and block ratio 30/40/30 was characterized by DSC and DMA. In the DSC test two distinct glass-transition temperatures ( $T_g$ ) were observed at  $-87$  and  $0^\circ\text{C}$ . Figure 3 is the DMA graph of this triblock polymer in which two dynamic loss peaks appeared, indicative of the possibility of synthesizing microphase-separated polymers from only one monomer, butadiene.

### 1,4-PB polymerization kinetics

Kinetic behaviors of 1,4-PB were studied by establishing relationships between conversion ( $x$ ) and time ( $t$ ) at different initiator concentrations and temperatures, as plotted in Figure 4.

According to the kinetics equation of polymerization,

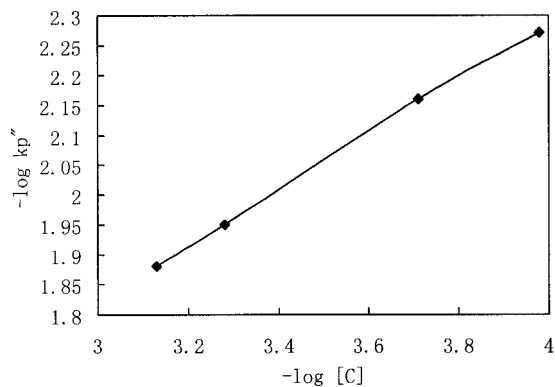
$$-d[M]/dt = k_p[C]^a[M]^b \quad (8)$$

where  $[M]$  is the concentration of monomers,  $t$  is the polymerizing time, and  $k_p$  is the apparent rate constant of the propagating reaction. If the polymerization rate is first order in  $[M]$ ,  $k_p[C]^a$  can be replaced by  $k_p''$ , the false first-order rate constant of propagating reaction, on condition that the concentration of propagating active centers remains constant. Then eq. (8) changes to

$$-d[M]/dt = k_p'' dt \quad (9)$$

**TABLE II**  
Values of  $k_p''$  at Different Initiator Concentrations  $[C]$  and Temperatures  $(T)$

$[C] \times 10^3$ (mol/L)	0.735	0.525	0.200	0.1055	0.735	0.735	0.735
$T$ ( $^\circ\text{C}$ )	50	50	50	50	30	40	70
$k_p'' \times 10^3$ ( $\text{min}^{-1}$ )	13.3	11.7	6.85	5.53	1.55	4.89	115



**Figure 6** Plot of  $-\log k_p''$  versus  $-\log [C]$  at  $T = 50^\circ\text{C}$  for 1,4-PB polymerization.

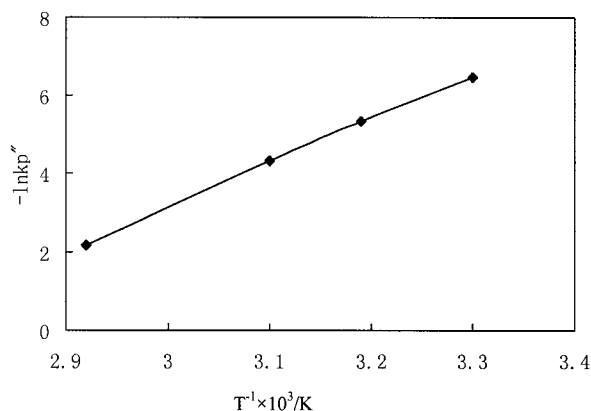
$$-\ln(1-x) = k_p''t \quad (10)$$

According to eq. (10), conversion  $x$  is replotted against time  $t$  (Fig. 5), taking  $-\ln(1-x)$  as the  $y$ -axis. The linear relationship between  $t$  and  $-\ln(1-x)$  proves that the assumption of  $b = 1$  is correct. The slopes of these lines represent  $k_p''$  at different  $[C]$  and  $T$ , the values of which are listed in Table II.

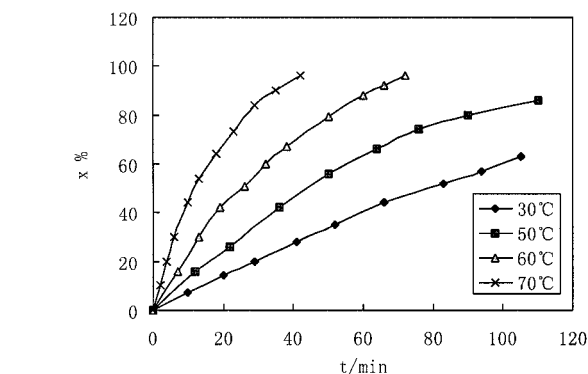
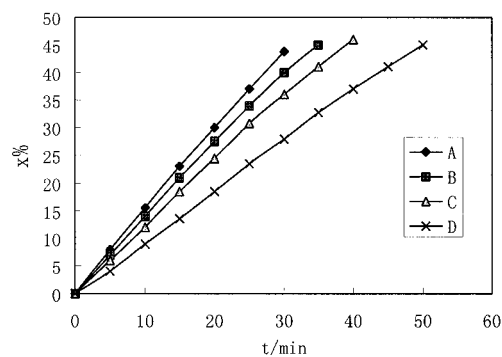
Data in Table II indicate that polymerization rates increase when  $[C]$  and  $T$  increase: one can take the logarithm of the equation  $k_p'' = k_p[C]^a$  when  $T = 50^\circ\text{C}$  and plot  $-\log k_p''$  versus  $-\log [C]$ , as shown in Figure 6.

From the line slope,  $\log a$ , and the intercept,  $\log k_p$ , we obtained the reaction order  $a = 0.481 \approx 0.5$  and the apparent rate constant of the propagating reaction  $k_p = 0.356$ . Thus the kinetics equation is specified as  $-d[M]/dt = 0.356[C]^{0.5}[M]$ .

By taking the logarithm of the Arrhenius equation,  $k_p'' = Ae^{Ep'/RT}$ , and plotting  $-\ln k_p''$  against  $T^{-1}$  (Fig. 7), we obtained  $Ep' = 90.6$  KJ/mol from the line slope, where  $Ep'$  is the apparent activating energy of the propagating reaction.



**Figure 7** Plot of  $-\ln k_p''$  versus  $T^{-1}$  at  $[C] = 0.735 \times 10^3$  mol/L.



**Figure 8** Plot of conversion ( $x$ ) versus time ( $t$ ) at different DPE/Li ratios and temperatures for 1,2-PB polymerization. DEP/Li ratios: A = 10.0, B = 5.0, C = 2.0, D = 0.

### 1,2-PB polymerization kinetics

Figure 8 is a plot of  $x$  against  $t$  at different DPE/Li ratios and temperatures concerning 1,2-PB polymerization. It shows that the addition of more DPE into the system and increasing temperature both result in an increase in the polymerization rate. Like 1,4-PB, the polymerization rate of 1,2-PB is first order in  $[M]$ .  $k_p''$  obtained at different DPE/Li ratios and  $T$  are listed in Table III, which shows that  $k_p''$  is slightly affected by DPE but is considerably affected by temperature.

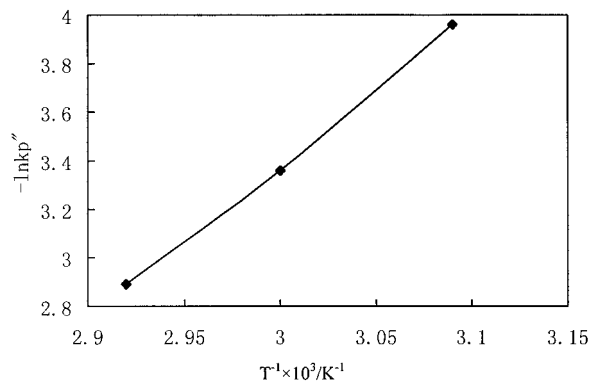
Figure 9 is a plot of  $-\ln k_p''$  against  $T^{-1}$  at DPE/Li = 5.0, based on data in Table III. In this case  $Ep'$  is calculated to be 32.10 KJ/mol when DPE/Li = 5.0, which is much less than the value obtained in the system without DPE.

### CONCLUSIONS

By adopting the polymer design method in a TPB-DiLi/DPE/cyclohexane system, a new type of stereo-

**TABLE III**  
Values of  $k_p''$  at Different DPE/Li Ratios and Temperatures

DPE/Li (mol ratio)	0	2.5	5.0	10	5.0	5.0	5.0
$T$ ( $^\circ\text{C}$ )	50	50	50	50	30	60	70
$k_p'' \times 10^3$ ( $\text{min}^{-1}$ )	13.3	18.3	19.0	19.5	9.25	36.5	55.3



**Figure 9** Plot of  $-\ln k_p''$  versus  $T^{-1}$  at DPE/Li = 5.0 for 1,2-PB polymerization.

triblock polybutadiene of various molecular weights and block ratios can be synthesized easily from only one monomer, butadiene. The strong polar modifier DPE promotes an increase of the 1,2 content in 1,2-PB blocks to more than 99%. This triblock copolymer exhibits microphase separation. Results of polymerization kinetics indicate that the polymerization rate is first order in monomer concentration in both TPB-DiLi and TPB-DiLi/DPE systems, and that the activity of  $\sim pLi \cdot \alpha$  DPE is higher than that of  $\sim pLi$ , whereas the changing trend of apparent propagating activating energy is similar for both systems.

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