

# Microstructure and Glass-Transition Temperature of Novel Star *N*-SIBR

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**ABSTRACT:** In this study, a polymeric *N*-functionalized multilithium (*N*-M-Li) compound was prepared from commercial divinylbenzene (DVB) and lithiohexamethylenimine (LHMI), and star-shaped copoly(styrene-butadiene-isoprene) was obtained by anionic polymerization using preformed *N*-M-Li as initiator, tetramethylethylenediamine (TMEDA) as polar modifier, and cyclohexane as solvent. The microstructure and the glass-transition temperature ( $T_g$ ) of copolymers were characterized by <sup>1</sup>H NMR and differential scanning calorimetry (DSC), respectively. It showed that the non-1,4-structure content and the  $T_g$  of copolymers increased with the increase of TMEDA dosage or the decrease of polymerization temperature; however, the effects of the initiator concentration and DVB dosage

on them were not obvious. We also obtained the relationships between the non-1,4-structure content of copolymers and the  $T_g$  of copolymers respectively, and between the  $\ln(T/Li)$  (TMEDA/*N*-M-Li, mole ratio) and the non-1,4-structure content of copolymers, as follows:  $T_g$  (°C) =  $0.6258C_{\text{non } 1,4} - 55.93$  and  $C_{\text{non } 1,4} = 20.79 \ln K + 59.11$ , where  $K$  is  $T/Li$  value. Therefore on the basis of experimental results, we realize polymer design according to our practical requirements. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5848–5853, 2006

**Key words:** functionalized multilithium initiator; integral rubber; anionic polymerization; structure; glass transition temperature

## INTRODUCTION

The interest in anionic polymerization has grown tremendously in recent years because it can be employed to tailor-make polymers of controlled properties. Because of the demands on tire skid resistance, elastomers with a high glass transition temperature or high vinyl content are of particular interest to the tire industry because of their inherently better grip properties.<sup>1</sup> The synthesis of polymers with a variety of functional groups at one or both ends has also been reported.<sup>2–9</sup> The microstructures of homopolymers or copolymers of butadiene or isoprene are the non 1,4-structures that include 1,2-structures of polybutadiene and 3,4-structures of polyisoprene in the soft segments. The change of non-1,4-structure content of polymers will induce the change of their mechanical behaviors. Commonly considering the increase of non-1,4-structure content conduces the plastic characteristics. But some investigators' experimental results indicated that rubber with higher non-1,4-structure content has the better rebound elasticity, lower calorification, lower hysteresis loss, and lower rolling resistance in the high application temperature. Therefore, the industrial production is trend to improve the non-1,4-structure content of rub-

bers.<sup>10–14</sup> For rubbers, the glass transition temperature ( $T_g$ ) will affect their low temperature properties, wear performance, and rebound elasticity. In addition,  $T_g$  is the unique important parameter to balance the traction properties and wear resistance properties.<sup>15</sup> Herewith, several previous reports have been published concerning the microstructures and the  $T_g$  of rubbers.<sup>16,17</sup>

In this research, a type of novel star-shaped azo-functionalized integral rubber (Star *N*-SIBR), which was used as tire tread, was synthesized by using preformed azofunctionalized multilithium as initiator. This rubber has advantages over other rubbers, such as NR, BR, SBR, and so on. Besides, the star *N*-SIBR contains cyclic amine group to the core that can improve the rubber's mechanical behaviors and the combination power between the matrix and fillers.

## EXPERIMENTAL

### Materials

Cyclohexane (Jinzhou Petrochemical, China) was dehydrated by 5 Å molecular sieves for 2 weeks. The water content in cyclohexane was kept below 5 µg/g. The solvent was also purged with highly purified nitrogen (Beijing Pulaikesi Practicality Gas, China) for more than 15 min before use so as to keep oxygen content below 10 µg/g. Butadiene and Styrene (Bd and St, polymerization grade, Beijing Yanshan Petrochemical, China) were purified with a

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small amount of *n*-BuLi and then vaporized to keep water content below 10 µg/g. Isoprene (Ip, Shanghai Jinshan Petrochemical, China) was treated with similar fashion. Commercially available *n*-BuLi (Beijing Yanshan Petrochemical, China) was analyzed by the double titration method with 1,2-dibromoethane. Divinylbenzene (DVB) (mixture of 1,3- and 1,4-isomers and 49% ethylstyrene, Shanghai Chemical Reagent Factory, China) was marinated over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for several weeks and then decompressed distilled over CaH<sub>2</sub>. Hexamethyleneimine (HMI, Jiangsu Sheyang County Chemical Factory, China) was first refluxed and then distilled over CaH<sub>2</sub>. Tetrahydrofuran (THF, Beijing YiLi Fineness Chemical Factory, China) was refluxed over CaH<sub>2</sub> for several days and then diluted with cyclohexane. *N,N,N',N'*-tetramethylethylenediamine (TMEDA, Beijing Daxing Xingfu Chemical Graduate School, China) was purified with similar fashion with HMI and then dehydrated by 5 Å molecular sieves for more than 2 weeks.

### Polymerization procedures

#### Synthesis of *N*-functionalized initiator

Addition reaction was carried out in an experimental setting. All the glassware was well-dried before use. A magnetic stirring bar was added to the reactor, and 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, and then filled with purified nitrogen. The stoichiometric amount of THF, Bd (Bd for improving solubility and THF for improving reaction velocity), DVB, and lithiohexamethyleneimine (LHMI), which was preformed from equal amount *n*-BuLi and HMI, were transferred into the reactor with syringes or stainless steel capillaries in a sequential manner. A water bath was used to keep the reactor's temperature at about 30°C. After 1.5 h the *N*-functionalized multilithium initiator was obtained.

#### Synthesis of star *N*-SIBR

The polymerization of SIBR was carried out in a 5 L stainless steel kettle. The reactor and accessories were purged by purified nitrogen and washed by cyclohexane before the reaction. A solution of 10 wt % styrene/isoprene/butadiene (monomers St/Ip/Bd, 30/35/35) in cyclohexane and a quantitative TMEDA

were successively charged into the reactor and preheated to the polymerization temperature (50°C). A stoichiometric amount of *N*-M-Li performed was added into the reactor to initiate the polymerization. After 3 h, the polymerization was completed, the reaction content was from the bottom valve into an ethanol reservoir, and stabilized with 1 phm of antioxidant. After evaporating cyclohexanes, the resulting copolymer was dried in a vacuum oven at 50°C. By means of the anionic polymerization technique, using self-made *N*-M-Li as initiator and TMEDA as polar modifier, a *N*-functionalized integral rubber (*N*-SIBR) was obtained that could be introduced cyclic amine group to the polymer chain. And elastomers prepared with this initiator exhibit improved properties such as decreased hysteresis loss.

### Characterization

The microstructure of the copolymers was analyzed by <sup>1</sup>H NMR spectroscopy and the glass transition temperature of the copolymers was determined by differential scanning calorimetry (DSC). The <sup>1</sup>H NMR spectroscopy was a Bruker ARX-400 MHz using CDCl<sub>3</sub> as solvent and TMS as inner mark. The sampling time and the pulsing interval time were 0.445 s and 6 s, respectively. The DSC used a DuPont MDSC-2910 at the modulation periods 60 s, modulation swing ±1.5°C, and at the heating rate of 10°C/min from -120 to 120°C, which was protected by nitrogen at the flowing rate of 50 mL/min.

### Testing techniques

The <sup>1</sup>H NMR spectra of the copolymers were like the Figure 1, which was composed of three apexes groups. The phenyl peaks, double bond peaks, and saturable bond peaks respectively, appeared at 6.05–7.50, 4.0–6.0, and 1.0–3.0 ppm. The integral areas that correspond to the peaks were marked as a, b, and c, respectively. Peaks b would be accurately divided into three group peaks (b<sub>1</sub>, b<sub>2</sub>, and b<sub>3</sub>). b<sub>1</sub> (5.15–5.85 ppm) corresponded to the proton peaks of =CH— of 1,4-polybutadiene (1,4-PB) and 1,2-polybutadiene (1,2-PB); b<sub>2</sub> (4.85–5.15 ppm), was attributed to the proton peaks of =CH— of 1,4-polyisoprene (1,4-PI) and =CH<sub>2</sub> of 1,2-PB; b<sub>3</sub> (4.25–4.85 ppm), was due to the proton peaks of =CH<sub>2</sub> of 3,4-polyisoprene (3,4-PI). The composition of the copolymers would be calculated according to the following equation groups:

$$\begin{cases} 5S = a \\ 3S + 4B_{1,4} + 3B_{1,2} + 7I_{1,4} + 6I_{3,4} = c \\ 2B_{1,4} + B_{1,2} = b_1 \\ 2B_{1,2} + I_{1,4} = b_2 \\ 2I_{3,4} = b_3 \end{cases} \begin{cases} \text{PS} : 0.2a/A \\ 3,4 - \text{PI} : 0.5b_3/A \\ 1,4 - \text{PI} : [(-1.2a - 4b_1 - b_2 - 6b_3 + 2c)/13]/A \\ 1,2 - \text{PB} : [(0.6a + 2b_1 + 7b_2 + 3b_3 - c)/13]/A \\ 1,4 - \text{PB} : [(-0.6a + 11b_1 - 7b_2 - 3b_3 + c)/13]/A \end{cases}$$

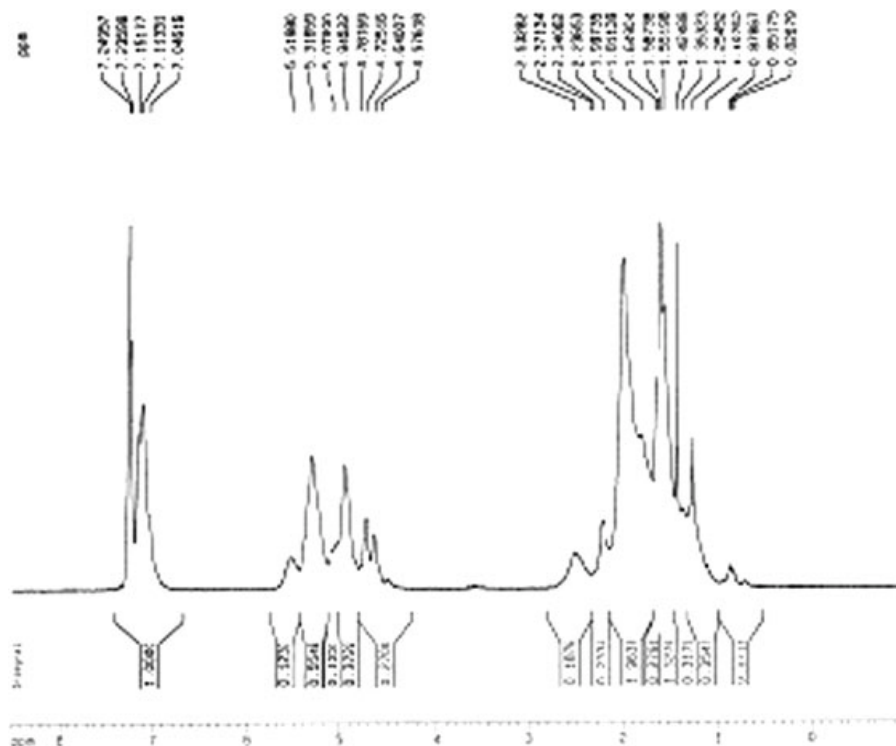


Figure 1 The  $^1\text{H}$  NMR spectrum of *N*-SIBR.

where S is styrene, B is butadiene, I is isoprene, PS is polystyrene, and A is  $(3.4a + 7b_1 + 5b_2 + 4b_3 + 3c)/26$ , respectively.

## RESULTS AND DISCUSSION

### Effects of TMEDA dosage on microstructure

The copoly (styrene–butadiene–isoprene), *N*-SIBR, were obtained using self-made initiator at different T/Li ratio values and analyzed by  $^1\text{H}$  NMR spectroscopy. The characterizations of microstructure are shown in Table I. The 3,4-structure of Ip units and 1,2-structure of Bd units content increased sharply with increasing the ratio values of T/Li as revealed in Table I. In contrary, the 1,4-structure content of copolymers rapidly decreased in the polymerization

system. These data indicated that the amount of TMEDA was sensitive in regulating polymer microstructures. Jin and Li<sup>18</sup> have improved Morton  $\sigma$ ,  $\pi$ -allyl polymerization mechanism, that is  $\sigma$ -allyllithium mainly promote non-1,4-structure and  $\pi$ -allyllithium mainly promote 1,4-structure units, and according to this we can explain the test results. In this polymerization system the polar modifier easily integrate with the *N*-M-Li initiator and the adduct product amount increases with the increase of TMEDA dosage, and so the  $\pi$ -allyllithium amount also increased.

We also investigated the relationship between the TMEDA dosage and the non-1,4-structure (the sum of 3,4-structure content of Ip units and 1,2-structure content of Bd units) of copolymers, Figure 2. We obtained the quantificational equation between the

TABLE I  
The Microstructure of *N*-SIBR at different T/Li

T/Li	I <sup>a</sup>			II <sup>a</sup>			III <sup>a</sup>		
	St <sup>b</sup> (%)	1,2-PB	3,4-PI	St <sup>b</sup> (%)	1,2-PB	3,4-PI	St <sup>b</sup> (%)	1,2-PB	3,4-PI
0	20.4	8.5	11.6	21.0	8.1	12.1	20.6	8.7	12.1
0.2	22.0	25.6	22.1	20.9	24.0	24.0	20.4	26.2	22.4
0.5	21.2	43.0	50.3	22.1	44.0	50.2	21.0	43.4	51.0
1.0	20.9	50.4	71.4	21.6	51.2	69.9	20.9	51.6	71.2
1.5	21.2	52.4	75.8	20.9	53.9	76.2	22.0	54.0	77.9

<sup>a</sup> Relative content of various monomer.

<sup>b</sup> The mass contents of reaction system.

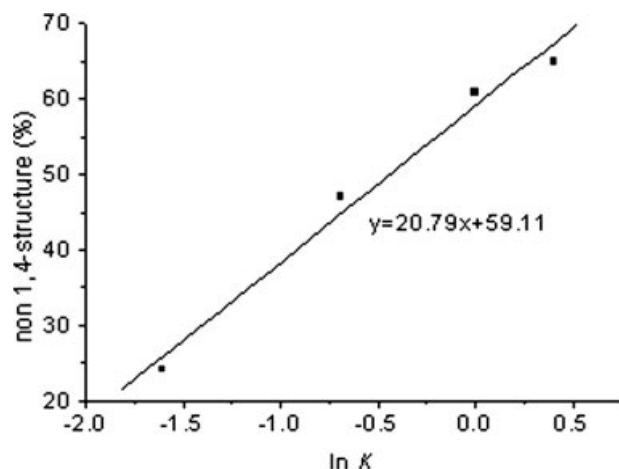


Figure 2 Relationship between the  $\ln(T/Li)$  values and the non-1,4-structure content of N-SIBR.

$\ln(T/Li)$  and the average non-1,4-structure content via plotting based on Table I. The linear correlation equation (the correlation coefficient is 0.9915 and the equation is similar with ref. 19) is

$$C_{\text{non } 1,4} = 20.79 \ln K + 59.11. \quad (1)$$

where  $C_{\text{non } 1,4}$  is the non-1,4-structure content of copolymers and  $K$  is the ratio values of  $T/Li$  of the polymerization system. We can calculate the non-1,4-structure content of polymers at random  $K$  values using the eq. (1) in the range of experiment. Apparently in the case of this polymerization system while keeping the polymerization temperature and  $DVB/N-M-Li$  ( $D/Li$ , mole ratio) as constant, we may optionally modulate the 3,4-structure and vinyl content of polymers via designing various  $K$  values. Consequently, we get to the goal to control the microstructure of novel integral rubber N-SIBR by controlling the TMEDA dosage and satisfy the requirement of polymer molecular design by applying this kind of  $N$ -functionalized mullithium initiator to initiate monomers.

#### Effects of polymerization temperature on microstructure

The N-SIBR obtained at different polymerization temperature was measured by  $^1H$  NMR spectroscopy and the analytic results of microstructure are listed in Table II. From the data we knew the effect of polymerization temperature was much pronounced in the change of microstructure. The non-1,4-structure content of copolymers increased with the polymerization temperature decreasing in this reaction system.<sup>20</sup> The main reason leads to the above described results is the presence of polar modifier TMEDA, which easily integrates with the active seeds in anionic polymerization system and the integration

TABLE II  
The Microstructure of N-SIBR<sup>a</sup> at Different Polymerization Temperature

$T$ (°C)	St (%)	Bd <sub>(1,2-)</sub> (%)	Bd <sub>(1,4-)</sub> (%)	Ip <sub>(1,4-)</sub> (%)	Ip <sub>(3,4)</sub> (%)
60	22.2	19.8	31.9	9	17.1
50	22.9	25.4	25.0	6.2	20.5
40	22.7	31.1	23.2	0	23.0

<sup>a</sup> Polymerization conditions:  $T/Li = 1$ ;  $D/Li = 0.8$ .

reaction is exothermic. Consequently, decreasing the polymerization temperature is propitious to form adduct compound. We know that the combinative compound is propitious to create non 1,4-structure. In preceding reasons we ideally control the non-1,4-structure of copolymers via changing the polymerization temperature of this system with other reaction conditions unchanged, i.e., realizing polymer design by using the  $N-M-Li$  initiator.

#### Effects of the concentration of initiator and the ratio values of D/Li on microstructure

Several polymers were obtained using  $N-M-Li$  as initiator at different concentration of initiator or at different ratio values of  $D/Li$  at 50°C. The copolymers were tested by  $^1H$  NMR spectroscopy and the microstructures of N-SIBR are given in Table III. However, the effects of the concentration of initiator and the ratio values of  $D/Li$  on microstructure were not obvious. This study further elucidated the microstructure of copolymers, which was mainly determined by the kind and dosage of polar modifier (i.e., the kind and amount of combinative active seeds) and polymerization temperature. The other influence was very little. We get the same test conclusion as in ref. 20.

#### Effects of TMEDA dosage on $T_g$

Generally in the case of homopolydiene, the amount of 1,2-structure content or 3,4-structure content directly affects the thermocharacteristics of polymers, and especially the effects on  $T_g$  are pronounced.<sup>21-23</sup>

TABLE III  
The Microstructure of N-SIBR at Different Initiator Concentrations and D/Li Values

Microstructure	St (%)	Bd <sub>(1,2-)</sub> (%)	Bd <sub>(1,4-)</sub> (%)	Ip <sub>(1,4-)</sub> (%)	Ip <sub>(3,4)</sub> (%)
$[C_0] \times 10^4$ (mol L <sup>-1</sup> )					
9.26	23.0	31.1	24.5	0	21.4
7.69	23.1	30.3	24.6	0	22.0
6.41	23.1	30.3	24.0	0	22.6
$D/Li$					
0.6	20.6	31.5	26.4	0	21.5
0.8	20.9	25.4	25.0	8.2	20.5
1.0	19.1	24.9	34.1	9.6	12.3

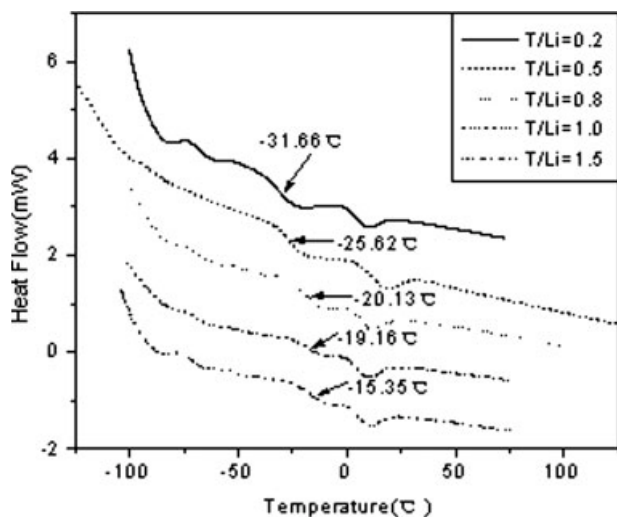


Figure 3 The DSC spectra of *N*-SIBR at different T/Li.

This work centrally investigated the effects of T/Li values on the  $T_g$  of copolymers, T/Li from 0.2 to 1.5. The  $T_g$  of copolymers gradually increased with the increase of T/Li values as visualized in Figure 3. This was mainly due to the rigidity of polymer chains strengthened with the increase of non-1,4-structure content.

The relationship between non-1,4-structure content and the  $T_g$  was studied by plotting non-1,4-structure versus  $T_g$  at different TMEDA dosage, as plotted in Figure 4. Based on Figure 4, there is commendably linear between non-1,4-structure and  $T_g$  of copolymers as Yan et al.,<sup>24</sup> got the same result. Then we obtain the experiential expressions (the linear correlation coefficient is 0.9971):

$$T_g (\text{°C}) = 0.6258C_{\text{non-1,4}} - 55.93. \quad (2)$$

where  $C_{\text{non-1,4}}$  is non-1,4-structure content of copolymers. Thus we can synthesize our needed integral

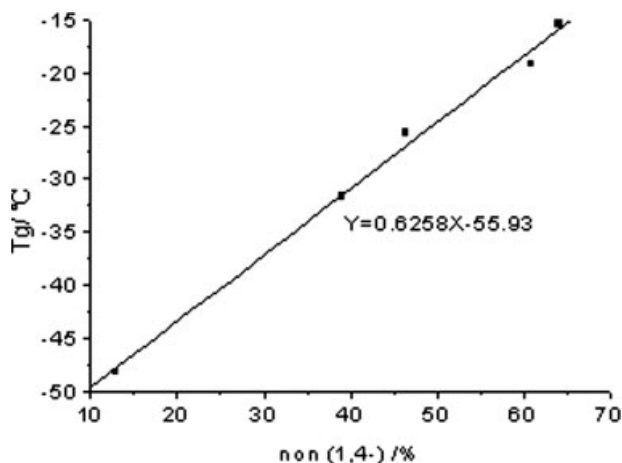


Figure 4 The plotting of  $T_g$  versus non-1,4-structure content.

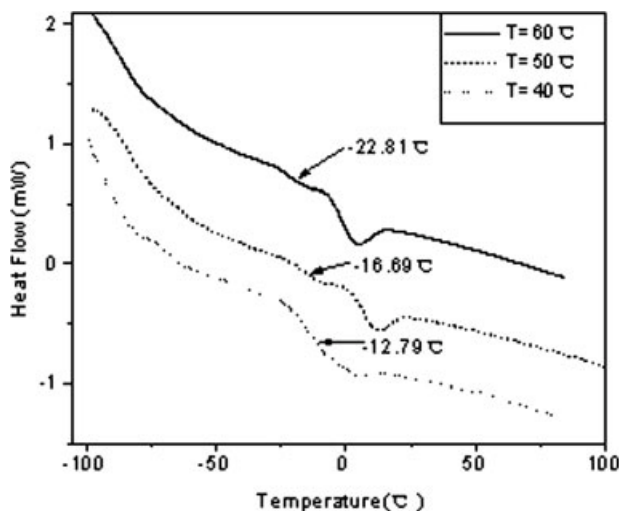


Figure 5 The DSC spectra of *N*-SIBR obtained with different polymerization temperature.

rubber with perfect combination properties via polymer design by using the approach, which alter the T/Li values of this TMEDA/*N*-M-Li system.

#### Effects of polymerization temperature on $T_g$

The glass transition temperatures of copolymers, which was obtained using this *N*-M-Li as initiator at different polymerization temperature with the concentration of initiator and DVB dosage unchanged, were determined by DSC measurement. Figure 5 was the DSC curves of the copolymers in which  $T_g$  decreased with the increase of polymerization temperature. The changing rule was similar with that and was exhibited by the effects of polymerization temperature on non-1,4-structure of copolymers.

#### Effects of the concentration of initiator and D/Li values on $T_g$

The copolymers obtained at the different concentration of initiator and the different ratio values of D/Li were measured by DSC method and the analytic results were shown in Table IV. The data listed in

TABLE IV  
The  $T_g$  of *N*-SIBR Obtained with Different Initiator Concentrations and D/Li Values

	$T_g$ (°C)
$[C_0] \times 10^4$ (mol L <sup>-1</sup> )	
9.26	-19.47
7.69	-17.32
6.41	-18.56
D/Li	
0.6	-17.55
0.8	-16.69
1.0	-18.68

Table IV indicate that by only changing the concentration of initiator or D/Li values, the change of  $T_g$  of copolymers was not inerratic under the determinate TMEDA dosage and polymerization temperature conditions.

### CONCLUSIONS

Several copolymers were obtained in the presence of cyclohexane, using self-made N-M-Li as initiator and TMEDA as polar modifier from monomers, Bd/Ip/St. The microstructure and  $T_g$  of copolymers were measured by  $^1\text{H}$  NMR and DSC, respectively. From the analytic results we drew conclusions that (1) the non-1,4-structure content and  $T_g$  of copolymers increased with the increase of TMEDA dosage, and decreased with the increase of polymerization temperature; (2) it was interesting that just changing the concentration of initiator or the ratio values of D/Li, the change trend was not regular.

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