

EFFECTS OF CHAIN MICROSTRUCTURE OF BUTADIENE-ISOPRENE COPOLYMERS ON THEIR GLASS TRANSITION AND CRYSTALLIZATION*

Jiang-wei Zhao, Han Zhu, Yi-xian Wu**, Wei-wei Zhou, Guan-ying Wu and Ri-wei Xu

State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

Abstract A series of butadiene-isoprene copolymers (BIR) with various compositions were synthesized with a neodymium-based catalyst system. The microstructure, composition and sequence of copolymers were characterized by FTIR and ^{13}C -NMR spectroscopy. The crystallization behavior of the BIR copolymers was investigated by DSC analysis. The results demonstrate that the content of *cis*-1,4 configuration in both butadiene (Bd) and isoprene (Ip) units are around 98% when Bd content in feed (f_{Bd}) covering the range from 55.7 mol% to 96.0 mol%. The reactivity ratios of Bd and Ip were determined to be 1.40 and 0.48 respectively. The random copolymers of Bd and Ip show only one glass transition temperature (T_g) from -107.4°C to -80.5°C , which is dependent on the composition and fits nicely with Fox equation. The sequence distribution followed the first-order Markov statistical model. It is found that the copolymer chains with higher Bd content contain longer polybutadiene (PBd) segments, and the sequence length of PBd segments (N_{Bd}) exhibits great influence on the crystallization behavior of the copolymer. The copolymers with $N_{\text{Bd}} \geq 11.8$ could crystallize at low temperatures (-71°C to -43°C). The crystallization temperature and enthalpy values decreased gradually with decreasing N_{Bd} . The copolymers with $N_{\text{Bd}} \leq 7.9$ are amorphous even at very low temperatures (0°C to -150°C) due to the short PBd segments.

Keywords: Butadiene; Isoprene; Sequence length; Crystallization.

INTRODUCTION

High *cis*-1,4 polybutadiene (PBd) is one of the most important elastomers used for tires and other elastic materials. The glass transition temperature (T_g) of PBd is around -109°C , but its elasticity will be decreased at low temperatures of around -35°C caused by its crystallization behavior^[1, 2]. In order to improve its low temperature property, isoprene (Ip) structural units were introduced into the PBd macromolecular chain and thus the random copolymers of Bd and Ip (BIR) could be synthesized^[3, 4]. Ip units are regarded as point defects inserted in the PBd chains, and this incorporation results in short Bd sequences, which are in favor of the formation of amorphous copolymers. It has been reported that the morphology of BIR products was dependent on their copolymer composition. For example, the copolymers with Bd content (F_{Bd}) of less than 83.4 mol% in the copolymer were amorphous at -42°C by dynamic mechanical thermal analysis^[5] or -65°C by wide angle X-ray diffraction analysis^[6]. It was also reported that the copolymers with F_{Bd} of less than 86.9 mol% were amorphous at -30°C by linear dilatometer^[7]. Therefore, there is some discrepancy in the critical values of copolymer composition between crystalline and amorphous for BIR reported in the literatures. Furthermore, the crystallization behavior of copolymers could be affected by the composition and sequence length of PBd

* This work was financially supported by the National 863 program (No. 2006AA03Z552), China Petroleum Chemical Corp. (SINOPEC) and Program for Changjiang Scholars and Innovative Research Teams in Universities (IRT0706).

** Corresponding author: Yi-xian Wu (吴一弦), E-mail: wuyx@mail.buct.edu.cn

Received April 13, 2009; Revised May 21, 2009; Accepted May 26, 2009

doi: 10.1007/s10118-010-9053-6

segments as well. However, the influence of sequence length of PBd segments on crystallization behavior of BIR has not been reported.

In our previous publications^[8–10], the neodymium-based catalyst was found to exhibit both high catalytic activity and stereoselectivity for the polymerizations of Bd and styrene. In this article, butadiene-isoprene copolymers with compositions ranging from 34.8 mol% to 96.8 mol% were prepared with the neodymium-based catalyst according to our previous work. The microstructure, composition and sequence length were characterized by FTIR and ¹³C-NMR respectively. The effect of sequence length of PBd segments in the BIR macromolecular chain on the crystallization behavior of copolymers will be discussed in detail according to differential scanning calorimetry (DSC) analysis.

EXPERIMENTAL

Materials

Butadiene (Bd), triisobutyl aluminum in hexane ($[Al(i-Bu)_3] = 0.74 \text{ mol}\cdot\text{L}^{-1}$) and 2,6-di-*tert*-butyl-4-methylphenol from Beijing Yansan Petrochemical Company were used as received. Both hexane and isoprene (Ip) from Beijing Yansan Petrochemical Company were distilled from calcium hydride before use, respectively. Ethanol and hydrochloric acid were purchased from Beijing Chemical Company and used without further purification.

Polymerization

All polymerizations were carried out under an atmosphere of dry nitrogen. The monomer solutions of butadiene and isoprene in hexane ($[Bd + Ip] = 1.9 \text{ mol}\cdot\text{L}^{-1}$) were introduced into a round-bottomed flask and the neodymium-based catalyst solution was added by a syringe to start polymerization at a definite temperature for a given time. The polymerization was terminated by injecting ethanol solution containing hydrochloric acid (*ca.* $1 \text{ mmol}\cdot\text{L}^{-1}$) and 2,6-di-*tert*-butyl-4-methylphenol (*ca.* 1 wt%). The resultant copolymer was washed by ethanol and then water until neutral and finally dried under vacuum at 45°C to constant weight.

Characterization

The microstructure and composition of copolymers were characterized by FTIR and ¹³C-NMR^[3, 11]. The FTIR spectra of copolymers were recorded using films on KBr plate by a Nicolet 6700 spectrophotometer as the average of 64 acquisitions over the spectral ranges of 400–2000 cm^{-1} with an instrument resolution of 4 cm^{-1} . ¹³C-NMR spectra were acquired on a Bruker AV600 MHz spectrometer in CDCl_3 ($40 \text{ mg}\cdot\text{mL}^{-1}$) at 25°C with tetramethylsilane (TMS) as internal standard. The parameters were used as follows: relaxation time = 2 s; acquisition time = 0.54 s; flip angle = $\pi/4$; number of transients = 22 K. The thermal properties were analyzed by DSC. The DSC curves were recorded on a TA Q200 instrument equipped with a liquid subambient device under helium flow ($25 \text{ mL}\cdot\text{min}^{-1}$). Temperature calibration was carried out with indium as a standard. The copolymer (*ca.* 8 mg) was weighed into an aluminum pan and cooled from 40°C to -150°C and then heated up to 40°C at a rate of $10 \text{ K}\cdot\text{min}^{-1}$.

RESULTS AND DISCUSSION

The Microstructure, Composition and Sequence Length of the BIR Copolymers

A series of butadiene-isoprene copolymers with different compositions of Bd units (F_{Bd}) were synthesized at different butadiene (Bd) contents in the monomer feed (f_{Bd}) at 50°C. A representative FTIR spectrum of the copolymer BIR is given in Fig. 1. The absorption peaks at 736, 911 and 967 cm^{-1} are assigned to *cis*-1,4, 1,2- and *trans*-1,4 configuration of Bd units, respectively. The absorption peaks at 834 and 889 cm^{-1} are assigned to *cis*-1,4 and 3,4-configurations of isoprene (Ip) units. No absorption peak at 1385 cm^{-1} indicates the absence of *trans*-1,4 configuration in Ip units. The strong absorptions at 736 and 834 cm^{-1} indicate that there exist primarily *cis*-1,4 configurations in both Bd and Ip units. The *cis*-1,4 contents of both Bd and Ip units in copolymers could be calculated on the basis of the FTIR spectra^[3, 11]. As shown in Fig. 2, it can be seen that the *cis*-1,4 content of

Bd units in the copolymer was around 98% when F_{Bd} changed from 34.8 mol% to 96.8 mol%, and the *cis*-1,4 content of Ip units in the copolymers was more than 98% when F_{Bd} was in the range of 64.3 mol% to 96.8 mol% while was around 97% at F_{Bd} of 34.8 mol%.

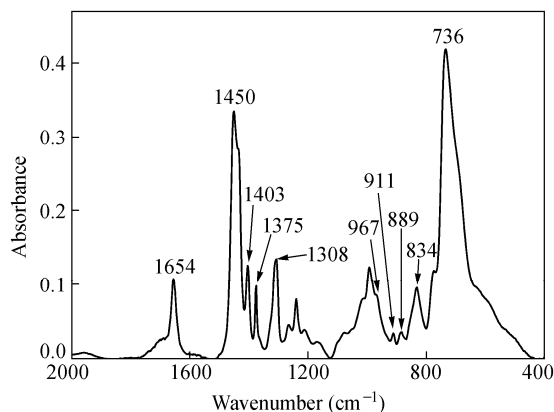


Fig. 1 The representative FTIR spectrum of the butadiene-isoprene copolymer ($F_{\text{Bd}} = 85.5$ mol%)

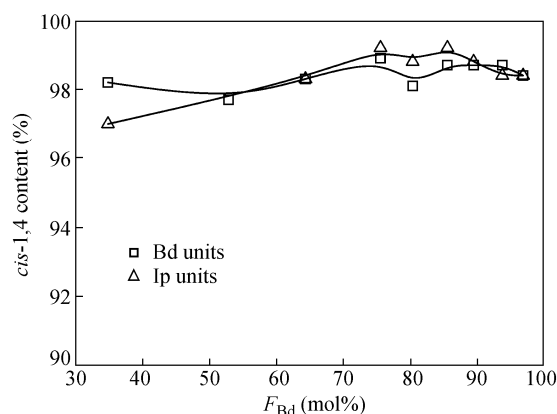


Fig. 2 The *cis*-1,4 content in copolymers with different Bd molar fractions (F_{Bd})

The relationship between copolymer compositions (expressed by molar fraction of Bd in the copolymer, F_{Bd}) and Bd content in feed (expressed by molar fraction of Bd, f_{Bd}) is given in Fig. 3. The Bd content in copolymers (F_{Bd}) is almost in accordance with f_{Bd} ranging from 83.4 mol% to 96.0 mol%, while F_{Bd} is slightly higher than f_{Bd} when $f_{\text{Bd}} = 23.9$ mol%–74.6 mol%. From the copolymer composition data, the monomer reactivity ratios of Bd (r_{Bd}) and Ip (r_{Ip}) could be readily determined according to the extended Kelen-Tüdös (K-T) method for high conversion levels^[12]. The K-T equation is described as following:

$$\eta = (r_{\text{Bd}} + r_{\text{Ip}}/\alpha)\xi - r_{\text{Ip}}/\alpha \quad (1)$$

where $\eta = G/(\alpha + F)$, $\xi = F/(\alpha + F)$, $G = (Y-1)/Z$, $F = Y/Z^2$, $\alpha = (F_{\text{min}} \times F_{\text{max}})^{0.5}$, $Z = \lg(1 - \zeta_1)/\lg(1 - \zeta_2)$, $\zeta_2 = W(\mu + X)/(\mu + Y)$, $\zeta_1 = (Y/X)\zeta_2$, $X = f_{\text{Bd}}/(1 - f_{\text{Bd}})$, $Y = F_{\text{Bd}}/(1 - F_{\text{Bd}})$, where W is the total monomer conversion of copolymerization; μ is the ratio of molecular weight of Ip to that of Bd; F_{min} and F_{max} are the minimum and maximum values of F respectively; X is the molar ratio of Bd to Ip in the monomer feed; Y is the molar ratio of Bd units to Ip units in the copolymer.

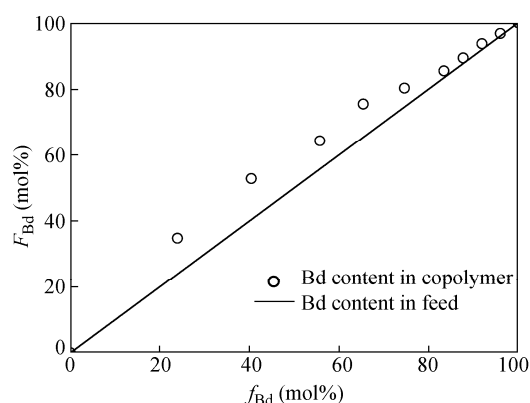


Fig. 3 The Bd content in copolymer (F_{Bd}) versus the Bd content in feed (f_{Bd})

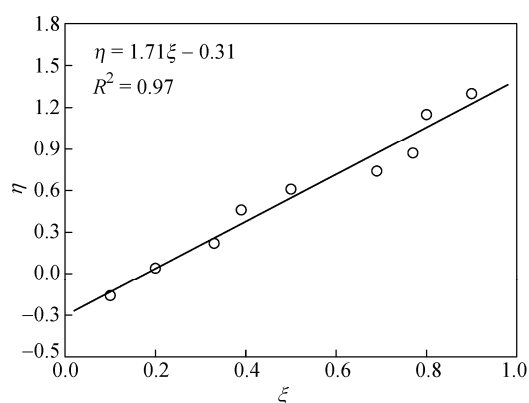


Fig. 4 Kelen-Tüdös plot for copolymerization of Bd with Ip
 $T_p = 50^\circ\text{C}$; $F_{\text{min}} = 0.18$, $F_{\text{max}} = 13.46$; $\alpha = 1.56$

It can be observed from Fig. 4 that η versus ζ plot is linear. The $r_{\text{Bd}} + r_{\text{Ip}}/\alpha$ and $-r_{\text{Ip}}/\alpha$ were obtained to be 1.71 and 0.31 from the slope and intercept of linear plot respectively. F_{min} and F_{max} are 0.18 and 13.46 respectively from the series of measurements and then α was calculated to be 1.56. Thus, r_{Bd} and r_{Ip} could be determined to be 1.40 and 0.48 respectively. It indicates that the rate of Bd homopolymerization is higher than that of copolymerization of Bd with Ip while Ip is more tendent to copolymerization with Bd, resulting in the formation of random copolymers of Bd with Ip.

The copolymers with different Bd contents, PBd and polyisoprene (PIp) were characterized by DSC, and the corresponding DSC curves are shown in Fig. 5. The glass transition temperature (T_g) of PBd and PIp were determined to be -109°C and -66.1°C . All the copolymers with F_{Bd} ranging from 34.8 mol% to 96.8 mol% presented only one glass transition, which indicated that the products were random copolymers. As shown in Fig. 6, the T_g of the copolymers depended on the copolymer composition and decreased from -80.5°C to -107.4°C with increasing F_{Bd} from 34.8 mol% to 96.8 mol%. According to Fox equation shown in Eq. (2)^[13], T_g could also be calculated and the results are also given in Fig. 6. The excellent agreement between experimental data and Fox equation line for all copolymers with different F_{Bd} indicates that the copolymer products were indeed in random sequence.

$$1/T_g = w_{\text{Bd}}/T_{g, \text{Bd}} + w_{\text{Ip}}/T_{g, \text{Ip}} \quad (2)$$

where w_{Bd} and w_{Ip} are the weight percent of Bd and Ip in copolymers, respectively, $T_{g, \text{Bd}}$ and $T_{g, \text{Ip}}$ are T_g of homopolymer of Bd and Ip, respectively.

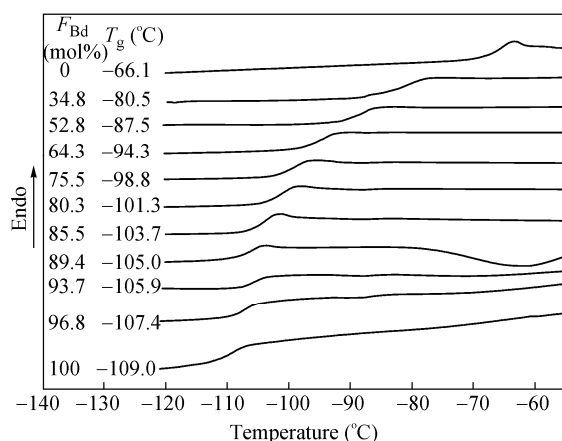


Fig. 5 The glass transition of copolymers with various compositions

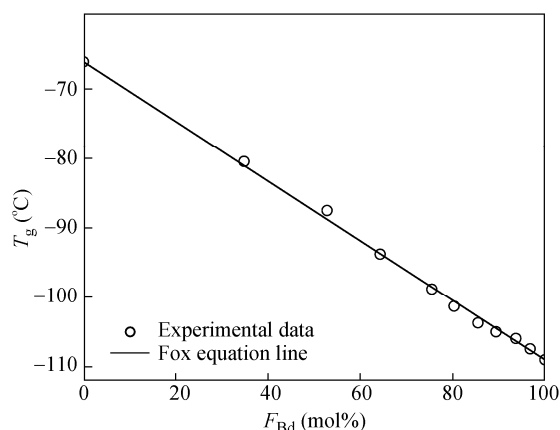


Fig. 6 Effect of Bd content (F_{Bd}) on T_g of copolymers

For further investigation, the ^{13}C -NMR spectroscopy was employed to evaluate the detailed microstructure and sequence of the BIR copolymers. A representative spectrum is shown in Fig. 7. The microstructures of the BIR copolymer are presented by 6 configurations, namely, *cis*-1,4 (C_B), *trans*-1,4 (T_B), 1,2- (V_B) in Bd units, and *cis*-1,4 (C_I), *trans*-1,4 (T_I), 3,4- (V_I) in Ip units. The assignments of the chemical shifts of different monomer triad and diad carbons are listed in Table 1. The strong resonance signals at 27.39 (peak 5), 26.68 (peak 6) and 32.23 (peak 1) are assigned to C_B - $C_{B,1}$ - C_B , $C_{I,4}$ - C_I and C_I - $C_{I,1}$ carbons respectively, suggesting the presence of the primary *cis*-1,4 configuration in both Bd and Ip units. The apparent signals at 25.82 (peak 7), 27.97 (peak 3), 27.74 (peak 4) and 31.87 (peak 2) are assigned to $C_{B,4}$ - C_B , C_B - $C_{I,4}$, C_I - $C_{B,1}$ and $C_{I,1}$ - C_B carbons respectively. It indicates that Bd and Ip units connected in the BIR copolymer. The weak signals at 47.12 (peak a), 43.74 (peak b), 38.12 (peak c), 32.69 (peak d), 25.17 (peak e) and 18.40 (peak f), attributed to $V_{I,3}$, $V_{B,2}$, $V_{B,1}$, $T_{B,1}$, $C_{B,1}$ - V_B and $V_{I,5}$ carbons respectively, indicate that a small fraction of V_B , T_B and V_I units distributed in the copolymer chain. The signal of $T_{I,5}$ (15.76) represented for T_I units in Ip units is absent, which is in agreement with the

results obtained from FTIR. In addition, the signals observed at 34.21, 30.29 and 21.17 (peak g) are related to the carbons of a small amount of 2,6-di-*tert*-butyl-4-methylphenol in copolymers.

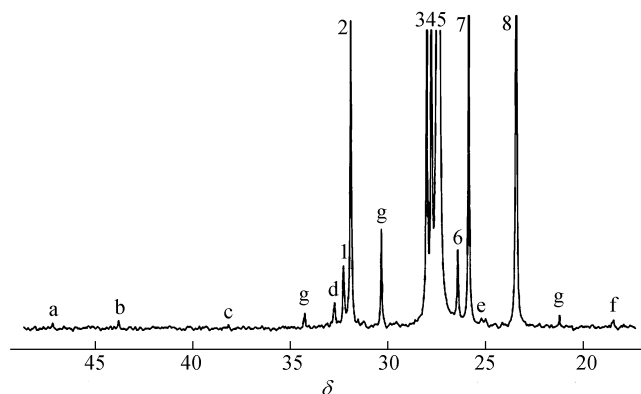


Fig. 7 ^{13}C -NMR spectrum of the copolymer ($F_{\text{Bd}} = 80.3 \text{ mol}\%$)

Table 1. Signal assignment of the aliphatic carbons in the BIR copolymer

Line	Sequence	Exptl. chemical shifts, δ	Ref. [14]	Ref. [15]	Ref. [16]	Ref. [17]	Ref. [10]
1	$\text{C}_1\text{-C}_{1,1}$	32.23	32.20	32.01	32.3	32.08	
2	$\text{C}_B\text{-C}_{1,1}$	31.87	31.88	31.66	31.95		
3	$\text{C}_{1,4}\text{-C}_B$	27.97	27.98	27.76	28.05		
4	$\text{C}_1\text{-C}_{B,1}$	27.74	27.75	27.53	27.8		
5	$\text{C}_B\text{-C}_{B,1}\text{-C}_B$	27.39	27.40	27.18	27.45	27.4	27.43
6	$\text{C}_{1,4}\text{-C}_1$	26.38	26.39	26.12	26.45	26.69	
7	$\text{C}_{B,4}\text{-C}_1$	25.82	25.84	25.62	25.9		
8	$\text{C}_{1,5}$	23.38		23.22	23.4	23.25	
a	$\text{T}_1\text{-V}_{1,3}\text{-C}_1$ $\text{C}_1\text{-V}_{1,3}\text{-V}_1$	47.12				47.07	
b	$\text{V}_{B,2}\text{-C}_B(\text{T}_B)$	43.74				43.5	43.69
c	$\text{C}_B\text{-V}_{B,1}\text{-T}_B$	38.12					38.15
d	$\text{C}_B(\text{T}_B)\text{-T}_{B,1}\text{-C}_B(\text{T}_B)$ $\text{C}_B(\text{T}_B)\text{-T}_{B,4}\text{-C}_B(\text{T}_B)$ $\text{T}_1\text{-T}_{B,1}$	32.69			32.8	32.8	32.71
e	$\text{C}_{B,1}\text{-V}_B$	25.17				24.9	
f	$\text{V}_{1,5}$	18.40				18.74	

Scheme: C_B T_B V_B C_1 T_1 V_1

C_B : $\text{---C}_1\text{---C}_2\text{=C}_3\text{---C}_4\text{---}$
 T_B : $\text{---C}_1\text{---C}_2\text{=C}_3\text{---C}_4\text{---}$
 V_B : $\text{---C}_1\text{---C}_2\text{=C}_3\text{---C}_4\text{---}$
 C_1 : $\text{---C}_1\text{---C}_2\text{=C}_3\text{---C}_4\text{---}$
 T_1 : $\text{---C}_1\text{---C}_2\text{=C}_3\text{---C}_4\text{---}$
 V_1 : $\text{---C}_1\text{---C}_2\text{=C}_3\text{---C}_4\text{---}$

Table 2. Diads content of copolymers determined by ^{13}C -NMR

F_{Bd} (mol%)*	[BB] (mol%)	[II] (mol%)	[BI] (mol%)	[IB] (mol%)	N_{Ip}	N_{Bd}
89.4	83.67	0.84	7.07	8.41	1.1	11.8
85.5	76.50	1.38	11.01	11.12	1.1	7.9
80.3	66.19	3.34	14.16	16.30	1.2	5.3
64.3	46.50	9.76	20.19	23.55	1.4	3.1

* The F_{Bd} was determined by FTIR.

The number-average sequence lengths of PBd (N_{Bd}) and PIp (N_{Ip}) could be calculated according to Eqs. (3) and (4)^[14, 15], and the results are given in Table 2. It can be seen that N_{Bd} increased with increasing F_{Bd} .

indicating that the copolymer chains with higher F_{Bd} contained longer sequences of PBd segments.

$$N_{\text{Bd}} = (2[\text{BB}] + [\text{BI}] + [\text{IB}])/([\text{BI}] + [\text{IB}]) \quad (3)$$

$$N_{\text{Ip}} = (2[\text{II}] + [\text{BI}] + [\text{IB}])/([\text{BI}] + [\text{IB}]) \quad (4)$$

Where $[\text{BB}]$, $[\text{II}]$, $[\text{BI}]$ and $[\text{IB}]$ are diad contents of Bd-Bd, Ip-Ip, Bd-IP and Ip-Bd sequences, respectively. It could be calculated as following:

$$[\text{BB}] = A_5/A, [\text{II}] = (A_1 + A_6)/A, [\text{BI}] = (A_2 + A_7)/A, [\text{IB}] = (A_3 + A_4)/A \quad (5)$$

where, $A = A_1 + A_2 + A_3 + A_4 + A_5 + A_6 + A_7$. $A_1, A_2, A_3, A_4, A_5, A_6$ and A_7 are the integration area of the signals 1–7 in Table 1 respectively.

If the sequence distribution follows the first-order Markov statistical model, N_{Bd} and N_{Ip} could be calculated on the basis of monomer ratios ($[\text{Bd}]/[\text{Ip}]$) in feed and monomer reactivity ratios, as shown in the following^[18]:

$$N_{\text{Bd}} = 1 + r_{\text{Bd}} \times ([\text{Bd}]/[\text{Ip}]) \quad (6)$$

$$N_{\text{Ip}} = 1 + r_{\text{Ip}}/([\text{Bd}]/[\text{Ip}]) \quad (7)$$

It can be seen from Fig. 8 that the results of N_{Bd} or N_{Ip} calculated from Eqs. (6) and (7) are almost in accordance with those determined by ^{13}C -NMR. Evidently, the sequence distribution in the BIR copolymers follows the first-order Markov statistical model. As also shown in Fig. 8, the sequences of PIP segments were short ($N_{\text{Ip}} \leq 2.6$) while N_{Bd} increased from 1.4 to 34.6 when F_{Bd} increased from 34.8 mol% to 96.8 mol%. There exist relatively long sequences of PBd segments in the copolymer chains with high F_{Bd} .

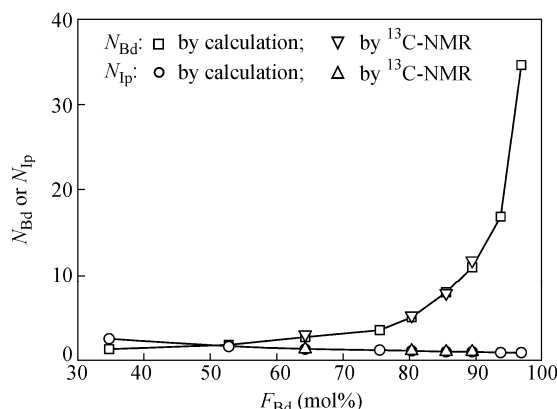


Fig. 8 Effect of copolymer composition on the N_{Bd} and N_{Ip}

The Crystallization Behavior of the BIR Copolymer

In order to further investigate the effect of N_{Bd} on the crystallization behavior of the BIR copolymers, the above copolymers and PBd with high *cis*-1,4 content ($> 98\%$) were analyzed by DSC, as shown in Fig. 9(a). It can be observed that an exothermic peak corresponding to crystallization transition appeared in the cooling DSC curve of polymers with N_{Bd} ranging from 4940 to 11.8 at a scan rate of $10\text{ K}\cdot\text{min}^{-1}$. The crystallization temperature (T_c) decreased gradually from -34.3°C to -71.4°C and the enthalpy values (H_c) decreased gradually from $44.3\text{ J}\cdot\text{g}^{-1}$ to $4.7\text{ J}\cdot\text{g}^{-1}$ with decreasing N_{Bd} from 4940 to 11.8. It indicates that the decrease of N_{Bd} leads to a decrease in crystallization capacity of copolymers. No exothermic peak is observed during cooling process of copolymers with N_{Bd} of less than 11.8 at temperatures in the range from 40°C to -150°C . It shows that the copolymers with short sequences of $N_{\text{Bd}} \leq 7.9$ could not crystallize at low temperatures even at -150°C and could provide excellent low-temperature properties.

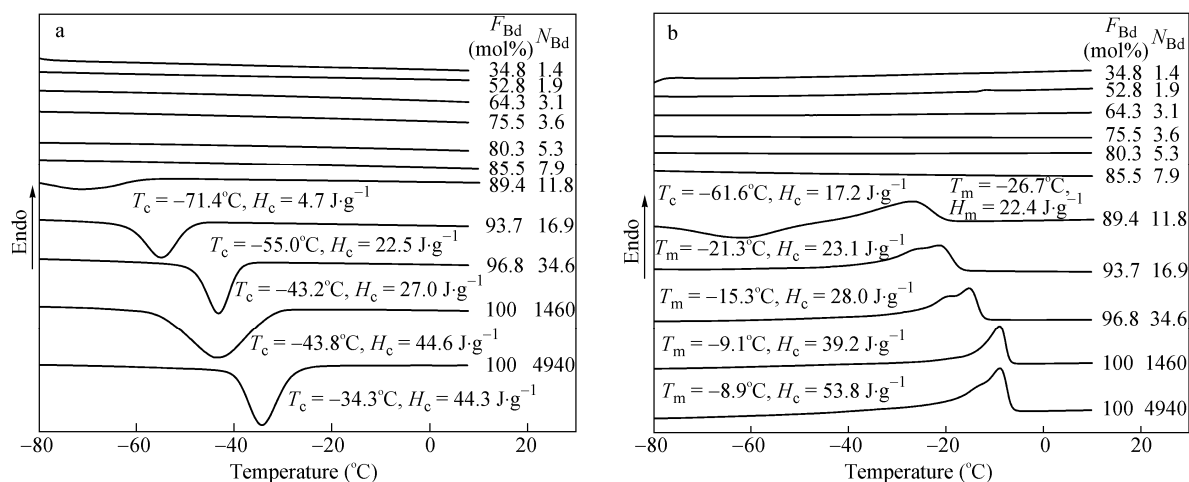


Fig. 9 DSC curves of the copolymer with various compositions
a) Cooling curves; b) Heating curves

After cooling process, these polymers with various N_{Bd} were held at -150°C for 5 min and then heated at a scan rate of $10\text{ K}\cdot\text{min}^{-1}$, as illustrated in Fig. 9(b). An endothermic peak corresponding to melting transition exhibited in the heating curve of polymers with $N_{Bd} \geq 11.8$. The melting point and enthalpy values decrease gradually with decreasing N_{Bd} . It can be clearly seen that no melting peak presented in the heating curves with further decrease of N_{Bd} , which confirms that copolymers with $N_{Bd} \leq 7.9$ are amorphous at low temperatures.

Interestingly, an exothermic peak corresponding to the crystallization behavior presented in heating curves of copolymer with $N_{Bd} = 11.8$. The low crystallization rate of the BIR copolymer resulted in incomplete crystallization during the cooling process at $10\text{ K}\cdot\text{min}^{-1}$ and thus this copolymer further crystallized at appropriate temperatures during the continuative heating process. For further investigation, the cooling scans of the copolymer with $N_{Bd} = 11.8$ were recorded at different rates from $3\text{ K}\cdot\text{min}^{-1}$ to $20\text{ K}\cdot\text{min}^{-1}$ and the corresponding cooling DSC curves at different rates and heating DSC curves at a fixed rate of $10\text{ K}\cdot\text{min}^{-1}$ are shown in Figs. 10(a) and 10(b).

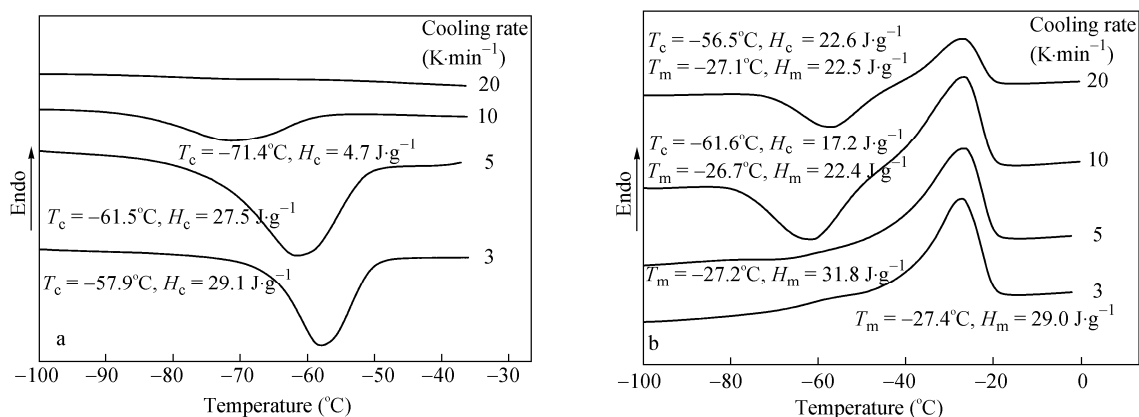


Fig. 10 DSC curves of the copolymer with 89.4 mol% Bd
a) Cooling curves; b) Heating curves

It can be seen that no crystallization peak is observed in the heating thermograms when the copolymer was cooled at a rate of $3\text{ K}\cdot\text{min}^{-1}$ or $5\text{ K}\cdot\text{min}^{-1}$, indicating that the PBd segment crystallized completely during the cooling process at relatively slow rate. The T_c decreased gradually from -54.9°C to -71.4°C and H_c decreased

gradually from $29.1 \text{ J}\cdot\text{g}^{-1}$ to $4.7 \text{ J}\cdot\text{g}^{-1}$ with increasing cooling rate from $3 \text{ K}\cdot\text{min}^{-1}$ to $10 \text{ K}\cdot\text{min}^{-1}$. The crystallization could not occur when the high cooling rate was set as $20 \text{ K}\cdot\text{min}^{-1}$, indicating that the copolymer with $N_{\text{Bd}} = 11.8$ can not crystallize at relatively fast cooling rate due to its low crystallization rate. The non-crystalline PBd segments due to relatively fast cooling rate of $10 \text{ K}\cdot\text{min}^{-1}$ or $20 \text{ K}\cdot\text{min}^{-1}$ did further crystallize at around -60°C during the heating process. Therefore, an exothermic peak corresponding to the crystallization behavior could be observed in heating curves of copolymer with $N_{\text{Bd}} = 11.8$ when the copolymer was cooled at relatively fast cooling rate. Therefore, the critical value of N_{Bd} between crystalline and amorphous for BIR copolymers was 11.8.

CONCLUSIONS

The copolymers of Bd and Ip synthesized by neodymium-based catalyst system possess high *cis*-1,4 content of around 98% in both Bd and Ip units when $F_{\text{Bd}} \geq 64.3 \text{ mol}\%$. The reactivity ratios of Bd and Ip were determined to be 1.40 and 0.48 respectively by Kelen-Tüdös (K-T) method at high monomer conversion. The copolymer chains are mainly composed of $\text{C}_\text{B}\text{-C}_\text{B}$, $\text{C}_\text{B}\text{-C}_\text{I}$, $\text{C}_\text{I}\text{-C}_\text{B}$ and $\text{C}_\text{I}\text{-C}_\text{I}$ sequences. The sequences of PIp segments in the copolymers with $F_{\text{Bd}} = 34.8 \text{ mol}\%$ – $96.8 \text{ mol}\%$ are short ($N_{\text{Ip}} \leq 2.6$), while relatively long sequences of PBd segments exist in the copolymer chains with high F_{Bd} . It is found that the copolymers with $N_{\text{Bd}} = 11.8$ – 34.6 ($F_{\text{Bd}} = 89.4 \text{ mol}\%$ – $96.8 \text{ mol}\%$) crystallize at low temperatures and the crystallization temperature and enthalpy values gradually decrease with decreasing N_{Bd} . The critical value of N_{Bd} between crystalline and amorphous BIR copolymers was 11.8. The copolymers with $N_{\text{Bd}} \leq 7.9$ ($F_{\text{Bd}} \leq 85.5 \text{ mol}\%$) were amorphous at temperatures ranging from -150°C to 40°C .

REFERENCES

- 1 Changchun Institute of Applied Chemistry, "Collection of synthetic rubber catalyzed by rare earth catalysts"(in Chinese), Science Press, Beijing, 1980, p.190
- 2 Song, X.Y., Shen, Y. and Xiao, S.X., *Syn. Rub. Ind.*, 1979, 2(3): 207
- 3 Shen, Z.Q., Song, X.Y., Xiao, S.X., Yang, J.P. and Kan, X.L., *J. Appl. Polym. Sci.*, 1983, 28: 1585
- 4 Kaita, S., Doi, Y., Kaneko, K., Horiuchi, C.A. and Wakatsuki, Y., *Macromolecules*, 2004, 37: 5860
- 5 Yang, Y.H., Yu, F.S. and Xu, G.F., *Chin. J. Appl. Chem.*, 1987, 4(4): 69
- 6 Wei, X.J., Mo, Z.S., Zhang, H.F. and Yan, Y.H., *Chin. J. Appl. Chem.*, 1987, 4(5): 45
- 7 Yu, F.S., Xu, G.Y., Zhang, S.C. and Song, X.Y., *Chin. J. Appl. Chem.*, 1983, 1(1): 58
- 8 Wang, J., Wu, Y.X., Xu, X., Zhu, H. and Wu, G.Y., *Polym. Int.*, 2005, 54: 1320
- 9 Zhao, J.W., Wu, Y.X., Wang, J., Zhu, H., Wu, G.Y. and Yang, W.T., *Acta Polymerica Sinica*(in Chinese), 2007, (3): 240
- 10 Zhu, H., Wu, Y.X., Zhao, J.W., Guo, Q.L., Huang, Q.G. and Wu, G.Y., *J. Appl. Polym. Sci.*, 2007, 106: 103
- 11 Xie, D.M. and Xiao, Y.W., *Syn. Rub. Ind.*, 1982, 5(4): 299
- 12 Tüdös, F., Kelen, T., Földes-Berezsnich, T. and Turcsanyi, B., *J. Macromol. Sci. Chem.*, 1976, A10(8): 1513
- 13 Fox, T.G., *Bull. Am. Phys. Soc.*, 1956, 1: 123
- 14 Guo, C.L., Zhou, Z.N. and Gong, Z., *Acta Polymerica Sinica*(in Chinese), 1991, (1): 77
- 15 Xie, D.M. and Xiao, Y.W., *Acta Polymerica Sinica*(in Chinese), 1982, (3): 202
- 16 Lobach, M.L., Poletayeva, I.A., Khatchaturov, A.S., Druz, N.N. and Kormer, V.A., *Polymer*, 1977, 18: 1196
- 17 Семенович, Г.М. and Храмова, Т.С. (eds), "Handbook of polymer physics and chemistry, Vol. 3", Translated by Yan, J.B. and Zhang, Y.K., China Petrochemical Press, Beijing, 1995, p.513
- 18 Ying, S.K. and Yu, F.N., "Copolymerization principle" (in Chinese), Chemical Industry Press, Beijing, 1984, p.199