

Synthesis and Characterization of *Trans*-1,4-butadiene/Isoprene Copolymers: Determination of Sequence Distribution and Thermal Properties*

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Abstract Two series of *trans*-1,4-poly(butadiene-*co*-isoprene) copolymers (TBIR) were prepared using the catalyst system $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(i\text{-Bu})_3$ at different reaction temperatures. All dyad and triads sequence distributions, the number-average sequence length and the sequence concentration of the copolymers were calculated according to ^{13}C -NMR spectra. The influences of temperature and initial molar ratio of butadiene to isoprene (Bd to Ip) on the distribution of the chain segments in the TBIR copolymers were discussed. The correlation of copolymer compositions and thermal properties were also evaluated, which facilitated the understanding of controlling the degree of crystallinity and the transition temperature by changing Bd content and temperature.

Keywords: *Trans*-1,4-; Isoprene; Butadiene; Copolymer; Thermal properties.

INTRODUCTION

High-*trans*-1,4-configuration diene polymers exhibit distinct dynamic properties including low abrasion loss and excellent anti-fatigue properties, which are necessary for high-performance tire stock^[1–5].

Trans-1,4-polyisoprene (TPI) and *trans*-1,4-polybutadiene (TPB) are both crystalline polymers with high melting temperature, which can be synthesized by Ziegler-Natta catalysts based on Ti ^[6, 7], V ^[8, 9], and rare earth metal based catalysts^[4, 10–13]. Although copolymerization is more complicated than homopolymerization with respect to both process and products, it is important to develop new polymers with desirable properties.

High-*trans*-1,4-poly(butadiene-*co*-isoprene) copolymers (TBIR)^[5, 14, 15] as a new member of *trans*-1,4-configuration polydiene family obviously reduced crystallinity compared with those of TPI and TPB, which showed improved processing and blending properties. Meantime TBIR vulcanizates processed outstanding anti-fatigue properties. In previous work^[16], we reported synthesis of a series of TBIR copolymers at different temperatures using the catalyst system $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(i\text{-Bu})_3$ with bulk polymerization method. Monomers reactivity ratios were calculated with varied feed ratio at a low conversion based on the Kelen-Tüdös (*K-T*) method ($r_{\text{Bd}} = 5.28$, $r_{\text{Ip}} = 0.20$, $T = 35\text{ }^\circ\text{C}$) and the Mao-Huglin (M-H) Method ($r_{\text{Bd}} = 5.72$, $r_{\text{Ip}} = 0.19$, $T = 35\text{ }^\circ\text{C}$). The influence of temperature on copolymer compositions and polymerization rate was discussed in detail^[16]. In the copolymerization, the number-average sequence length of the copolymers and the sequence distribution of

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monomer units in the copolymers can directly affect the physical and mechanical properties of the products. ^{13}C -NMR spectra were sensitive to the skeleton structure of copolymers^[17, 18] and widely applied in analysis of stereoregular polymers^[19]. The dyad sequence distribution of monomer units in the TBIR copolymers obtained from solution polymerization method was analyzed elementarily by ^{13}C -NMR spectra^[20].

In this article, two series of TBIR copolymers were synthesized at different initial molar ratios of Bd to Ip and different polymerization temperatures with bulk polymerization method. Compared to solution polymerization of Bd and Ip, bulk polymerization showed many advantages with low cost, high efficiency and simple polymerization procedures. The chain segment, the sequence distribution and sequence length of monomer units in the TBIR copolymers were analyzed with ^{13}C -NMR in detail. Triads sequence concentration of the copolymer was discussed for the first time, which was seldom analyzed in other articles. The elaborate analysis of the copolymer microstructures will be helpful to know the relationships between the microstructures and the thermal and mechanical properties of the TBIR copolymers, which will supply important instruction for industrial application of TBIR.

EXPERIMENTAL

Samples Preparation

All materials used in this study were synthesized by bulk polymerization method. The polymerization data and the microstructure parameters of the TBIR copolymers are shown in Table 1^[16].

Table 1. The microstructure of the synthetic Bd-IP copolymers

Bd/Ip (mol/mol)	<i>T</i> (°C)	Conv. (wt%)	CE (gP/gTi)	<i>F</i> _{Bd} ^a (%)	Microstructure ^b (mol%)			
					Bd unit		Ip unit	
					<i>trans</i> -1,4	1,2-	<i>trans</i> -1,4	3,4-
0.05	35	2.1	590	20.0	99.5	0.5	98.5	1.5
	55	3.7	1050	18.4	99.0	1.0	98.7	1.3
	75	3.2	890	18.0	99.3	0.7	97.4	2.6
0.20	35	4.8	1300	50.6	99.6	0.4	98.8	1.2
	55	5.0	1370	48.2	99.0	1.0	97.9	2.1
	75	3.7	1010	45.2	97.5	2.5	95.9	4.1

Polymerization conditions: Al/Ti molar ratio = 100; Ti/M molar ratio = 5×10^{-5} ; time = 60 min

^a Determined by ^1H -NMR; ^b Determined by FTIR

Measurements

Differential scanning calorimetry (DSC) analysis was made by a NETZSCH DSC-204 differential scanning calorimeter under N_2 atmosphere. About 5 mg of the sample was sealed in an aluminum sample pan. The sample was heated from -100 °C to 180 °C at a heating rate of 10 K/min to eliminate the thermal history, and then cooled to -100 °C at 10 K/min. Then the samples were heated from -100 °C to 150 °C at 10 K/min, the heat flow versus time were recorded and T_m was determined in the second scan. ^{13}C -NMR (125 MHz) spectra were recorded at 25 °C with a Bruker 500 MHz spectrometer with samples in CDCl_3 containing tetramethylsilane as standard.

RESULTS AND DISCUSSION

Assignments of Signals in TBIR Copolymers

The number I, II, III and IV are defined as the structures of the *trans*-1,4 and 3,4 of the isoprene and *trans*-1,4 and 1,2 of the butadiene, respectively. The carbon atoms in different structures are also given in Fig. 1. Also every structure can give a specific chemical shift in ^{13}C -NMR.

The ^{13}C -NMR spectra of TBIR copolymers are shown in Fig. 2. All the copolymers have no significant difference in chemical shift except the intensity of the peaks. The chemical shift and assignments of aliphatic and olefinic regions of TBIR copolymer (55 °C; Bd/Ip = 0.05 mol/mol) are shown in Fig. 3. All different molar contents of dyad sequences were also evaluated from the ^{13}C -NMR spectra, and are shown in Table 2. For

isoprene triad sequence distribution, the four peaks at $\delta = 124.05, 124.14, 124.26$ and 124.35 were attributed to IIB, BIB, III and BII sequences, respectively. For butadiene triad distribution, the peaks at $\delta = 129.76, 129.91, 130.01$ and 130.16 were assigned to BBI, IBB, both IBI and BBB and IBI, respectively^[5].

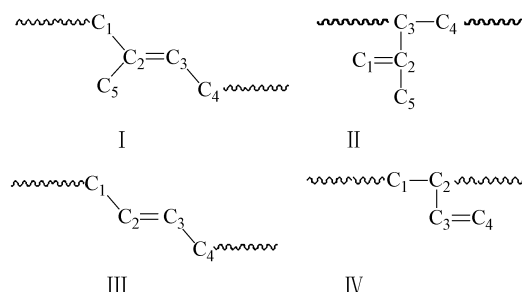


Fig. 1 Main structures of isoprene and butadiene units in TBIR copolymers

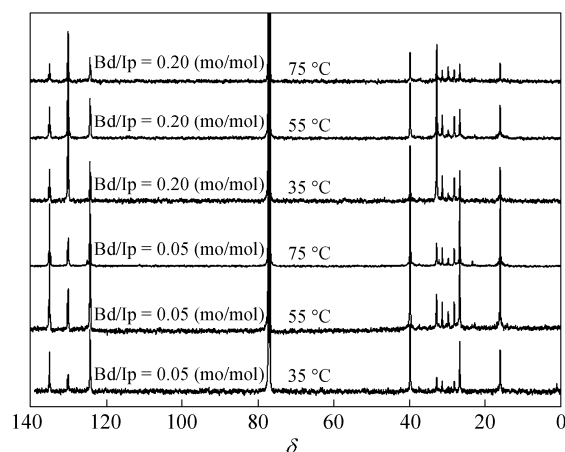


Fig. 2 ¹³C-NMR spectra of the synthetic TBIR copolymers

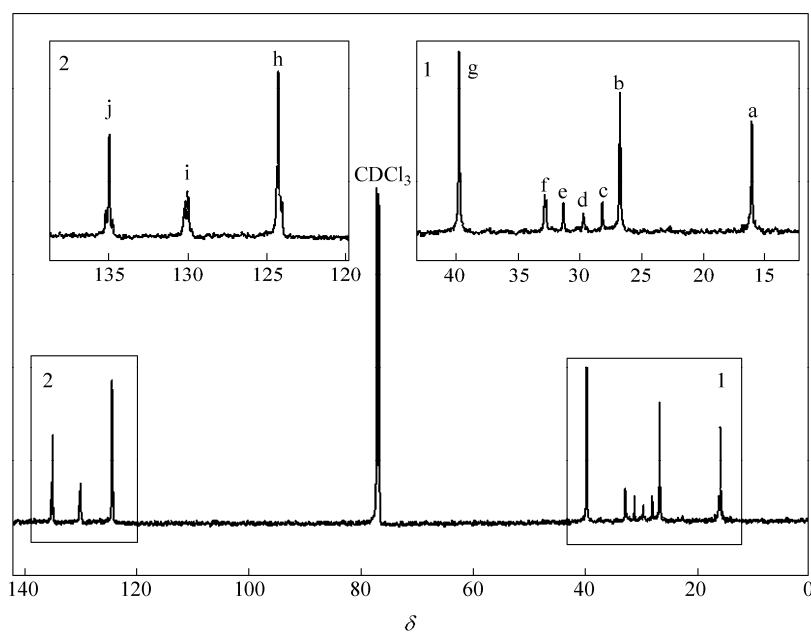


Fig. 3 ¹³C-NMR spectra of dyads and triads sequence distribution of the TBIR copolymer (55 °C; Bd/Ip = 0.05 mol/mol)

Table 2. ^{13}C -NMR chemical shift and assignments of aliphatic region of the TBIR copolymer (55 °C; Bd/Ip = 0.05 mol/mol)

Signals	Position of carbon number	δ		Linkage	Relative strength (%)
		Observed	Reported		
a	C ₅ (Ip)	16.1	16.0 ⁶⁻⁷	I _{trans-1,4} I _{trans-1,4}	21.6
b	C ₁ (Ip)	26.7	26.4 ⁶⁻⁷	I _{trans-1,4} I _{trans-1,4}	25.7
c	C ₄ (Ip-Bd)	28.2	28.0 ¹⁰	I _{trans-1,4} B _{trans-1,4}	4.7
d	Bd _{trans-1,4} -Bd _{1,2}	29.7	29.9 ⁸	B _{trans-1,4} B _{1,2}	3.7
e	C ₄ (Bd-Ip)	31.4	31.9 ⁹	B _{trans-1,4} I _{trans-1,4}	4.7
f	C ₁ (Bd)	32.9	32.9 ⁸	B _{trans-1,4} B _{trans-1,4}	9.9
g	C ₄ (Ip)	39.8	39.8 ⁶⁻⁷	I _{trans-1,4} I _{trans-1,4}	29.7

Sequence Distribution and Sequence Length of Monomer Units in the TBIR Copolymers

Bernoullian model and Markov model were used to analyze and examine the aliphatic sequence distribution of the copolymer, respectively. Dyad sequence concentration ([BB], [II], [BI] and [IB]) of different Bd and Ip molar ratios were calculated based on the ^{13}C -NMR spectra. The measured values were obtained by the formula (1). The number average sequence length of Bernoullian model and Markov model was calculated by the formulae (2) and (3). P_{Bd} and P_{Ip} are the reaction probability of Bd and Ip, respectively. $\overline{n_{\text{Bd}}}$ and $\overline{n_{\text{Ip}}}$ are the number-average sequence length of Bd unit and Ip unit, respectively. The calculated sequence length by two statistical models are listed in Table 3. Triads sequence concentrations named [BII], [III], [BIB], [IIB], [IBI], [BBB], [IBB] and [BBI], were also calculated, and are listed in Table 4.

$$\begin{aligned} n_{\text{Bd}} &= (2[\text{BB}] + [\text{BI}] + [\text{IB}]) / ([\text{BI}] + [\text{IB}]) \\ n_{\text{Ip}} &= (2[\text{II}] + [\text{BI}] + [\text{IB}]) / ([\text{BI}] + [\text{IB}]) \end{aligned} \quad (1)$$

$$[\text{BB}] = (P_{\text{Bd}})^2 \quad [\text{II}] = (P_{\text{Ip}})^2 \quad [\text{BI}] + [\text{IB}] = 2P_{\text{Bd}}P_{\text{Ip}} \quad (2)$$

$$\overline{n_{\text{Bd}}} = \frac{1}{1 - P_{\text{Bd}}} \quad \overline{n_{\text{Ip}}} = \frac{1}{P_{\text{Bd}}}$$

$$\begin{aligned} [\text{BB}] &= P_{\text{IB}}(1 - P_{\text{BI}}) / (P_{\text{BI}} + P_{\text{IB}}) \\ [\text{II}] &= P_{\text{BI}}(1 - P_{\text{IB}}) / (P_{\text{BI}} + P_{\text{IB}}) \\ [\text{BI}] + [\text{IB}] &= 2P_{\text{IB}}P_{\text{BI}} / (P_{\text{BI}} + P_{\text{IB}}) \end{aligned} \quad (3)$$

$$\overline{n_{\text{Bd}}} = \frac{1}{P_{\text{BI}}} \quad \overline{n_{\text{Ip}}} = \frac{1}{P_{\text{IB}}}$$

As shown in Table 3, all the measured data agreed well with those calculated by first-order statistical Markov model. The reason was that the hypothesis of Markov model considers not only the kind of monomer but also the end structure of active centers^[21]. To our knowledge, the Markov first-order chains resulted in micro-block copolymers. At a lower molar ratio of Bd to Ip (0.05), with the increase of temperature, both $\overline{n_{\text{Bd}}}$ and $\overline{n_{\text{Ip}}}$ decreased, indicating the obtained copolymers showed more uniform composition distribution. The results were identical with those of the previous work^[16]. Also with the increase of Bd content in the feed, the number average sequence length $\overline{n_{\text{Bd}}}$ increased, and $\overline{n_{\text{Ip}}}$ decreased relatively.

Table 4 shows the calculation values of the Bd molar concentration in the copolymer (F_{Bd}) from the ^1H -NMR and ^{13}C -NMR were coincident. In the case of low initial molar ratio (Bd/Ip = 0.05), Bd unit distribution MBM showed all the resonances of four triads ([IBI], [BBB], [IBB], [BBI]), but Ip unit distribution MIM only showed two kinds of triads ([III] and [IIB]), which was perhaps due to much higher reactivity of Bd than that of Ip ($r_{\text{Bd}} \gg r_{\text{Ip}}$). With the increase of Bd feed ratio (Bd/Ip = 0.20), all triads including Bd and Ip unit distribution were observed. The peak number and the fact that the intensities of the single peaks varied with comonomer composition were in agreement with a statistical distribution of Bd and Ip monomers along the polymer chain. Also with the increase of Bd feed ratio, all MBM triads increased, and the [III] content decreased.

Table 3. Dyad distribution content and the number-average sequence length of all the copolymers

Bd/Ip (mol/mol)	<i>T</i> (°C)	Measured value					Calculated value										
							Bernoullian model					Frist order Markov model					
		[BB]	[II]	\bar{n}_{Bd}	\bar{n}_{Ip}		[BB]	[II]	P_{Bd}	\bar{n}_{Bd}	\bar{n}_{Ip}		[BB]	[II]	P_{BI}	P_{IB}	\bar{n}_{Bd}
0.05	35	11.8	80.3	4.0	21.3	2.5	71.0	15.8	1.2	6.4	11.8	80.0	0.252	0.0471	4.0	21.2	
	55	13.6	76.9	3.9	17.2	3.4	66.7	18.3	1.2	5.5	13.6	76.9	0.259	0.0580	3.9	17.2	
	75	11.7	77.5	3.2	15.3	2.9	68.7	17.1	1.2	5.8	11.7	77.5	0.316	0.0650	3.2	15.4	
0.20	35	38.8	44.4	5.6	6.3	22.3	27.9	47.2	1.9	2.1	38.8	44.4	0.178	0.159	5.6	6.3	
	55	36.8	45.0	5.0	5.9	21.1	29.3	45.9	1.9	2.2	36.8	44.9	0.199	0.169	5.0	5.9	
	75	37.8	48.2	6.4	7.9	20.1	30.5	44.8	1.8	2.2	37.8	48.2	0.160	0.127	6.4	7.9	

Table 4. Triads sequence concentration of the TBIR copolymers

Bd/Ip (mol/mol)	Temp (°C)	MIM ^a (Triads%)					MBM ^b (Triads%)					F_{Bd}^c	F_{Bd}^d
		[BIB]	[III]	[BII]	[IIB]	[IBI]	[BBB]	[IBB]	[BBI]				
0.05	35	–	63.9	–	17.3	9.0	2.9	3.2	3.8	18.9	20.0		
	55	–	67.3	–	12.8	9.4	3.0	4.0	3.4	19.9	18.4		
	75	–	72.2	–	10.1	10.1	2.5	2.2	2.9	17.7	18.0		
0.20	35	11.2	15.0	10.3	10.6	15.4	15.7	11.4	10.5	52.9	50.6		
	55	10.1	17.1	12.5	10.8	12.0	16.0	10.1	11.6	49.6	48.2		
	75	10.7	19.7	8.9	11.1	11.7	15.7	11.5	10.9	49.7	45.2		

^a Monomeric triads with isoprene as central unit; ^b Monomeric triads with butadiene as central unit; ^c Determined by ¹³C-NMR; ^d Determined by ¹H-NMR

The Distribution of the Chain Segment in the TBIR Copolymers

Probability function, namely $[F_n(M)]$, was used to calculate the distribution of the chain segment of the TBIR copolymers based on the first-order Markov statistic model. The formula of the distribution of the chain segment of the copolymer is described below.

$$F_n(M_{Bd}) = P_{BB}^{n-1} P_{BI} \quad (4)$$

$$F_n(M_{Ip}) = P_{II}^{n-1} P_{IB}$$

P_{BI} and P_{IB} are the reaction probability of monomer Bd and Ip which at the end of the polymer chain, respectively. In the copolymers with different initial molar ratios and reaction temperature, the distribution of Bd and Ip chain segment in the total chain segment is listed in Figs. 4 and 5.

In Fig. 4, when the initial molar ratio of Bd to Ip was 0.05, the distribution of the Ip chain segments was quite wide. The distribution of the Bd chain segment was narrow, which mainly showed 1–3 kinds of Bd unit segment. With the increase of Bd mole content in feed ratio from 0.05 to 0.2 (Fig. 5), the distribution of the Bd chain segment became broader obviously and existed 4–7 kinds of Bd unit segment. The distribution of two monomers chain segment in the copolymers was mainly 1–5 unit length at both Bd/Ip feed ratios (0.05 and 0.20), which showed all the TBIR polymers were micro-block copolymers.

Thermal Behavior of TBIR

DSC was used to characterize the thermal properties of the copolymers. In Fig. 6, all the TBIR copolymers showed only one glass transition temperature T_g and the T_g values of the copolymers were lower than that of TPI. With the increase of Bd content in the initial feed, T_g , the melting temperature $T_{m,I}$ and the crystallization temperature $T_{c,I}$ of the TPI segments of all the TBIR polymers decreased gradually. While the reaction temperature had little effect on the T_g , T_m and T_c of the copolymers. For the TBIR copolymers with high Bd contents (45%–51% in Table 4), a tiny endothermic peak was observed at about 60 °C assigned to the overlap transition temperature ($T_{v/m,B}$) based on hexagonal/monoclinic transition and crystallization of *trans*-1,4-polybutadiene (TPB)^[22]. Also the peak at about 36 °C was assigned to the crystallization temperature ($T_{c,B}$) of *trans*-1,4-polybutadiene. Based on Figs. 4 and 5, tiny TPB crystal was ascribed to over 5 segment length of Bd units.

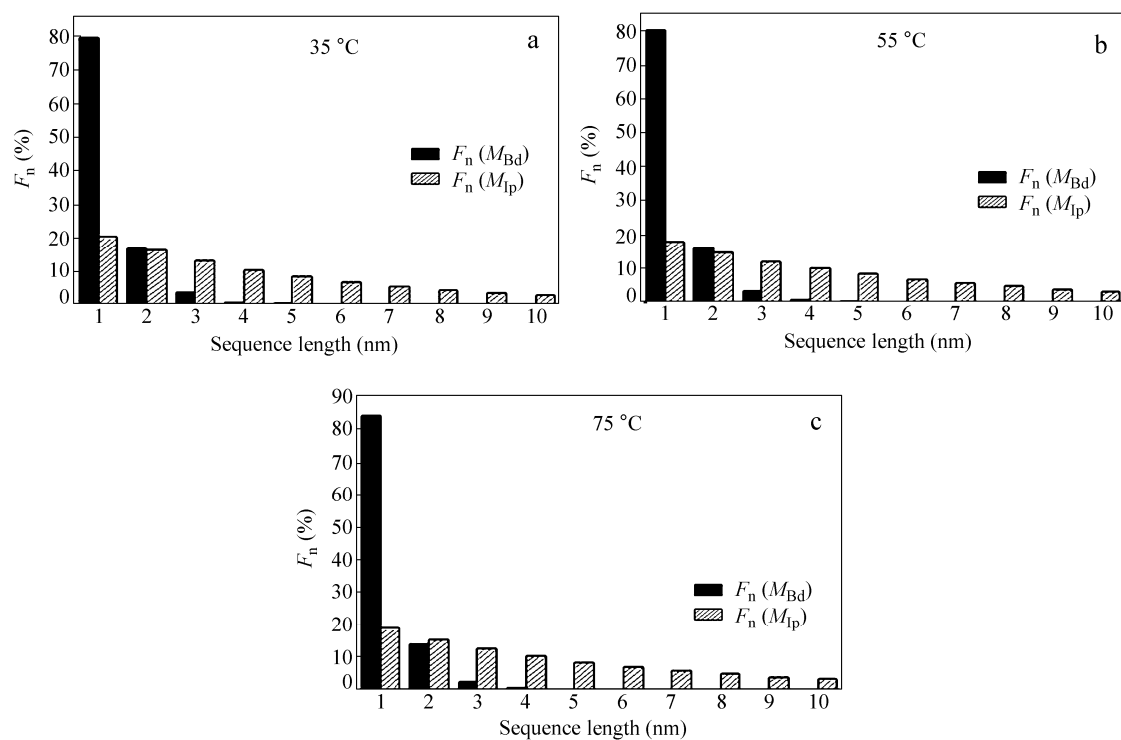


Fig. 4 The distribution of sequence length of TBIR with initial molar ratio of Bd to Ip (0.05) at different temperature

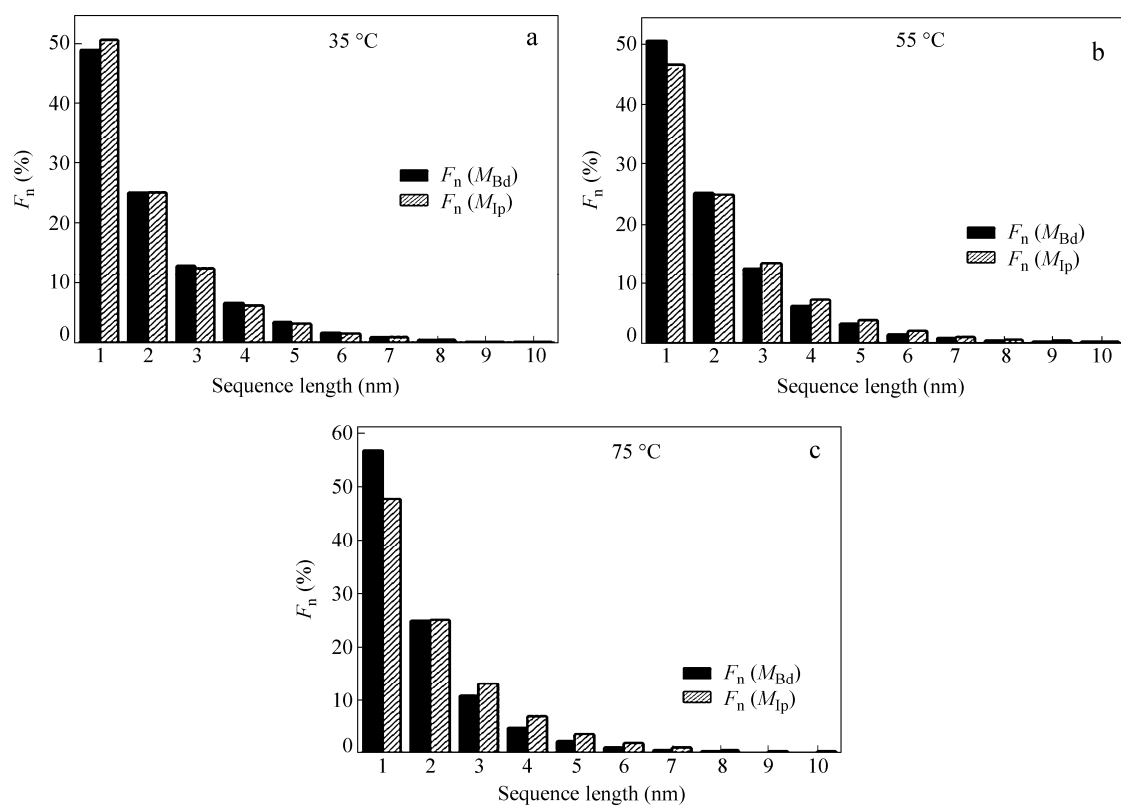


Fig. 5 The distribution of sequence length of TBIR with initial molar ratio of Bd to Ip (0.20) at different temperatures

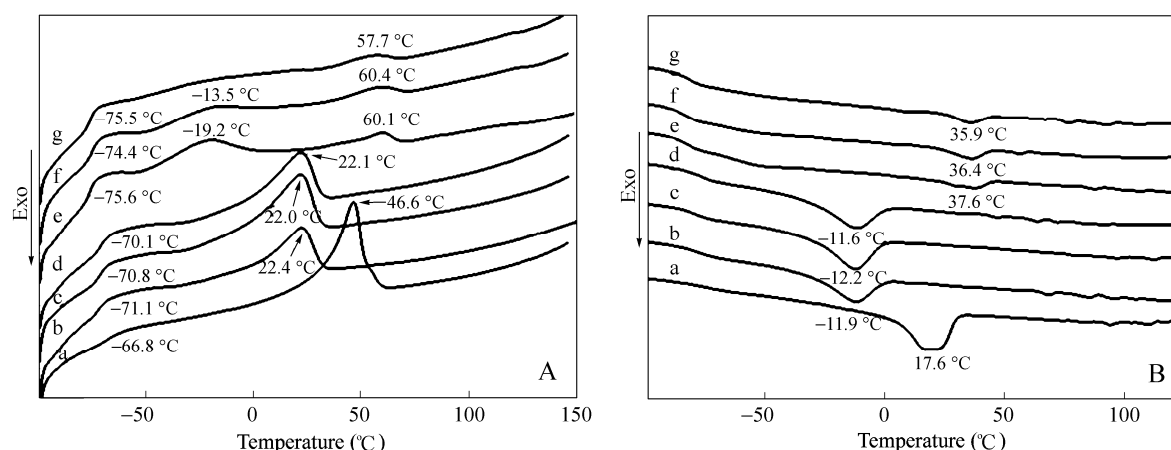


Fig. 6 DSC heating (A) and cooling (B) curves of TBIR copolymers with different initial molar ratios of Bd to Ip and polymerized at different temperatures: (a) 0, 35 °C, (b) 0.05, 35 °C, (c) 0.05, 55 °C, (d) 0.05, 75 °C, (e) 0.20, 35 °C, (f) 0.20, 55 °C and (g) 0.20, 75 °C

The melting enthalpy (ΔH_m) of the copolymer and TPI is listed in Table 5. The melting enthalpy for TPI segments of the copolymer ($\Delta H_{m,i}$) was lower than that of TPI and the values decreased with the increase of Bd content in initial feed, which indicated the insertion of Bd monomers reduced the crystallization degree of *trans*-1,4-polyisoprene chain segments. Also the crystallization enthalpy ($\Delta H_{c,i}$) decreased with the increase of Bd content, which showed similar trend with $\Delta H_{m,i}$.

Table 5. The data of thermal analysis of the TBIR copolymers

T (°C)	Bd/Ip	F_{Bd} (%)	T_g (°C)	$T_{m,i}$ (°C)	$\Delta H_{m,i}$ (J/g)	$T_{u/m,B}$ (°C)	$T_{c,i}$ (°C)	$\Delta H_{c,i}$ (J/g)
35	0.05	20.0	-71.1	22.4	14.2	60.1	-11.9	14.0
	0.20	50.6	-75.6	-19.2	8.1		-	-
55	0.05	18.4	-70.8	22	18.2	60.4	-12.2	18.2
	0.20	48.2	-74.4	-13.5	2.3		-	-
75	0.05	18.0	-70.1	22.1	15.4	57.7	-11.6	15.4
	0.20	45.2	-75.5	-	-		-	-
TPI		0	-68.8	46.6	21.5		17.6	21.5

CONCLUSIONS

The synthetic TBIR copolymers showed low values of T_g , ΔH_m and ΔH_c in comparison with those of TPI. Meantime the increase of the initial molar ratios of Bd to Ip in the feed showed an obvious influence on thermal properties of TBIR copolymers. The initial molar ratios of Bd to Ip influenced the dyad and triads sequence types and concentration. The sequence distribution of the butadiene and isoprene units in all the copolymers followed the first-order Markov statistical model based on the calculation of the dyad and triads sequence concentration. All the TBIR polymers were random copolymers according to the results that the distribution of the two monomers' chain segments in the copolymers was mainly 1–5 unit length at both initial molar ratios of Bd to Ip (0.05 and 0.20).

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