

Synthesis and Characterization of *trans*-1,4-Butadiene/Isoprene Copolymers: Determination of Monomer Reactivity Ratios and Temperature Dependence*

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Abstract A series of *trans*-1,4-butadiene/isoprene copolymers were prepared using the catalyst system $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(i\text{-Bu})_3$ with bulk precipitation technology at different temperatures. Monomers reactivity ratios were calculated based on the Kelen-Tüdös (K-T) method and the Mao-Huglin (M-H) method. The influence of temperature on copolymer composition and polymerization rate was discussed in detail. The increase of reaction temperature brought the decrease of butadiene reactivity ratio r_{Bd} and supplied an effective adjustment on copolymers' composition distribution.

Keywords: *trans*-1,4-; Isoprene; Butadiene; Copolymer; Reactivity ratio.

INTRODUCTION

High-*trans*-1,4-configuration diene polymers have attracted much attention as a high-performance tire stock due to their distinct dynamic properties, including excellent antifatigue properties, low rolling resistance, low heat buildup and low abrasion loss^[1–5]. *Trans*-1,4-polyisoprene (TPI) synthesized by bulk precipitation technology with supported Ti-based catalysts^[6, 7] showed great potential as high-performance tire materials due to low production cost and excellent dynamic properties. TPI and *trans*-polybutadiene (TPB) are crystalline polymers with high crystalline melting temperature especially the crystalline melting temperature of TPB can reach to 145 °C, which makes it impossible for TPB to blend with other elastomer rubbers. The copolymerization of isoprene (Ip) with butadiene (Bd) is an effective way to reduce and further destroy the crystallization of the *trans*-polydienes through adjusting the comonomer content in the copolymers. Meantime, the copolymerization of Ip with Bd can supplement members of high-*trans* 1,4-configuration diene polymers family enormously and supply enough research subjects to figure out the special properties of those compared with high *cis*-polyisoprene. Mechanical properties indicated that the synthetic *trans*-1,4-butadiene/isoprene copolymer (TBIR)^[8, 9] showed relatively high green strength, also the corresponding vulcanizates processed lower heat buildup and outstanding antifatigue properties, when compared with that of NR.

The availability of accurate monomer reactivity ratios in copolymerization is extremely important in order

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to control copolymer composition and monomer feed ratio, which has been calculated widely by different methods^[10–17]. Ricci *et al.* reported the reactivity ratio ($r_{\text{Bd}} = 2.7$, $r_{\text{Ip}} = 0.2$) was obtained for the butadiene-isoprene copolymerization carried out at $-30\text{ }^{\circ}\text{C}$ with the $\text{V}(\text{acac})_3$ -MAO catalytic system based on the Tidwell-Mortimer equation. Cui *et al.*^[18] reported highly *trans*-1,4-selective copolymerization of conjugated dienes proceeded with rare-earth-metal complexes bearing phosphazene ancillary ligands. The kinetics based on their study displayed competitive polymerization rates of $r_{\text{Bd}} = 2.89$, $r_{\text{Ip}} = 0.41$ ^[19]. Zhao *et al.* reported a series of butadiene-isoprene copolymers with various compositions were synthesized with a neodymium-based catalyst system and the reactivity ratios of Bd with Ip were determined to be 1.40 and 0.48, respectively^[20, 21]. Also the copolymerization of Bd with Ip was achieved with cobalt dichloride in combination with methylaluminoxane and triphenylphosphine (Ph_3P), and the reactivity ratios were obtained ($r_{\text{Bd}} = 2.80$, $r_{\text{Ip}} = 0.15$)^[22]. Finally, the effect of temperature on catalytic efficiency of Ip with Bd copolymerization and copolymers composition distribution was first reported here.

In this article, a series of TBIR copolymers were prepared at different temperatures using the catalyst system $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(i\text{-Bu})_3$ which was a highly efficient catalyst system for the synthesis of *trans*-1,4-butadiene/isoprene copolymers. Monomer reactivity ratios were calculated with varied feed ratio at low conversions based on the Kelen-Tüdös (K-T) method and the Mao-Huglin (M-H) method. The influence of temperature on copolymers composition and polymerization rate was discussed in detail.

EXPERIMENTAL

Materials

The supported Z-N catalyst containing 2 wt% Ti content was supplied by Shandong Oriental Hongye Chemical Company, China. Triisobutyl aluminium ($\text{Al}(i\text{-Bu})_3$, > 98%) was purchased from Yanshan Petrochemical Co. China. Isoprene (Ip) (polymerization grade, Jinshan Petrochemical Company, PetroChina) was distilled over molecular sieve before using. Butadiene (Bd) (polymerization grade) was supplied by the Qilu Petrochemical Company, PetroChina.

Polymerization

All polymerization processes were carried out under an atmosphere of dry nitrogen. The copolymerization of Bd with Ip was carried out in a 50 mL round-bottomed flask which was dried thoroughly by the cycle of evacuation and purging with nitrogen several times before use. Then, the monomers (Bd with Ip) in different ratios, $\text{Al}(i\text{-Bu})_3$, and TiCl_4 catalyst were introduced into the round-bottomed flask at the certain temperatures for the copolymerization. The reaction was terminated with ethyl alcohol solution which contains 1% hydrochloric acid. The products were precipitated by ethyl alcohol, and then dried under vacuum for 24 h at $40\text{ }^{\circ}\text{C}$.

Characterization

The microstructures of the copolymers were characterized by the Fourier transform infrared (FTIR) spectra. The FTIR spectra of the copolymers were recorded by a full digital type Bruker-Vertex70 spectrometer (Germany) and the samples were made into films by hot pressing method at $150\text{ }^{\circ}\text{C}$. The FTIR spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans. The calculation to the microstructure of TBIR was according to previous work^[23, 24]. $^1\text{H-NMR}$ measurements were carried out by a Bruker FTPAC280 (Switzerland) instrument. The spectra were acquired with CDCl_3 as the solvent and tetramethylsilane (TMS) as internal standard at room temperature.

RESULTS AND DISCUSSION

The Copolymerization and Microstructure of the Copolymers

A series of copolymerizations between Bd with Ip were proceeded at different Bd feed ratios (f_{Bd}^0 : 4.76%, 9.09%, 13.0%, 16.7% and 20.0%) and different polymerization temperatures ($35\text{ }^{\circ}\text{C}$, $55\text{ }^{\circ}\text{C}$ and $75\text{ }^{\circ}\text{C}$). In order to calculate the reactivity ratios of the Bd and Ip monomers accurately, all the conversions were controlled below 5 wt%. In this case, the catalytic efficiency (CE) was also calculated (Table 1).

Table 1. The polymerization results and microstructures of the TBIR copolymers

Run ^a	<i>T</i> (°C)	<i>f</i> ₁ ⁰ (%)	Conv. (wt%)	CE (gP/gTi)	<i>F</i> _{Bd} ^b (%)	Microstructure ^c (mol%)			
						Bd unit		Ip unit	
						<i>Trans</i> -1,4	1,2-	<i>Trans</i> -1,4	3,4-
1	35	4.76	2.10	590	20.0	99.5	0.5	98.5	1.5
	55	4.76	3.72	1050	18.4	99.0	1.0	98.7	1.3
	75	4.76	3.17	890	18.0	99.3	0.7	97.3	2.6
2	35	9.09	2.26	630	34.8	99.3	0.7	98.6	1.4
	55	9.09	4.35	1210	30.3	99.7	0.3	98.0	2.0
	75	9.09	4.15	1170	30.8	97.0	3.0	96.7	3.3
3	35	13.0	2.98	830	43.0	99.7	0.3	98.6	1.4
	55	13.0	5.03	1390	40.5	99.2	0.8	98.3	1.7
	75	13.0	4.05	1120	38.3	97.6	2.4	96.5	3.5
4	35	16.7	4.75	1300	50.6	99.6	0.4	98.8	1.2
	55	16.7	5.00	1370	48.2	99.0	1.0	97.9	2.1
	75	16.7	3.67	1010	45.2	97.5	2.5	95.9	4.1
5	35	20.0	4.68	1280	56.5	99.9	0.1	98.6	1.4
	55	20.0	3.73	1020	54.0	98.5	1.5	97.9	2.1
	75	20.0	3.16	860	51.9	97.7	2.3	96.6	3.4

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

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

FTIR was used to characterize the microstructure of TBIR copolymers. The characteristic peaks at 911 cm⁻¹ and 966 cm⁻¹ (Fig. 1) represented the 1,2- and *trans*-1,4 configurations of the Bd units, respectively. The peaks at 887 cm⁻¹ and 1382 cm⁻¹ represented the 3,4- and *trans*-1,4 configurations of the Ip units, respectively. The absorption peaks at 740 cm⁻¹ and 834 cm⁻¹ were not observed which indicated that there were no *cis*-1,4 configuration of the Bd or Ip units in the copolymer^[25–27].

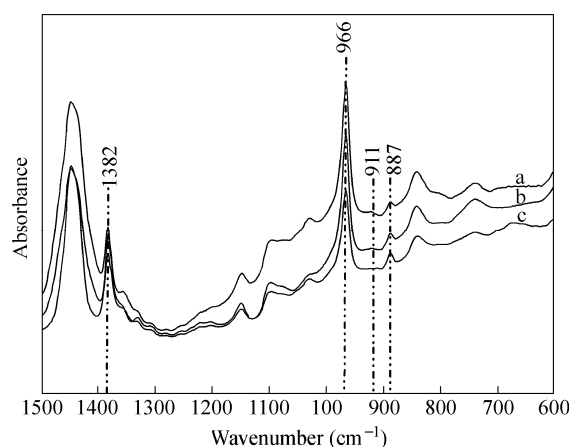


Fig. 1 FTIR spectra of Bd-Ip copolymers with $f_{\text{Bd}}^0 = 4.76\%$ polymerized at different temperatures: (a) 35 °C, (b) 55 °C and (c) 75 °C
Copolymerization conditions: Ti/M molar ratio = 5×10^{-5} , Al/Ti molar ratio = 100, 60 min.

Also ¹H-NMR measurements were carried out, and the results are shown in Fig. 2. The characteristic peak at $\delta = 5.40$ was assigned to the =CH— of *trans*-1,4 Bd unit, and the peak at $\delta = 5.10$ was assigned to the =CH— of *trans*-1,4 Ip unit^[28]. The content of Bd unit was determined by the area ratio between the characteristic peaks **a** and **b** in Fig. 2. All the analysis results of TBIR copolymers are summarized in Table 1. As shown in Table 1, the copolymers synthesized with the supported Ti catalysts showed highly *trans*-1,4-

configuration (Bd: > 97%; Ip: > 96%). f_{Bd}^0 is the initial molar ratio of the Bd/(Bd + Ip). F_{Bd} indicated the content of Bd in the copolymers. With the increase in reaction temperature, the conversion and catalytic efficiency increased to a peak value, and then decreased. F_{Bd} decreased with the increase of temperatures. The values of F_{Bd} were always much larger than f_{Bd}^0 , which indicated the monomer Bd was introduced into the copolymer chain in a much more rapid rate. The results showed Bd had much higher reactivity activity. Meanwhile, F_{Bd} increased with the increase in f_{Bd}^0 .

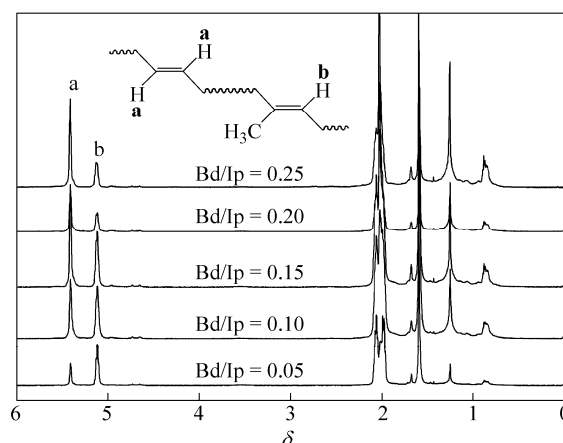


Fig. 2 ^1H -NMR spectra of Bd-Ip copolymers with different initial feed ratios at 75 °C

Determination of Reactivity Ratios

The reactivity ratios of the Bd and Ip monomers with low conversions (< 5%) were calculated by two methods: Kelen-Tüdös (K-T) and Mao-Huglin (M-H) method.

K-T method^[13]

The well-known linearization K-T method is used to measure copolymerization reactivity ratios of the butadiene and isoprene. The K-T equation is given as follows:

$$\eta = \left[r_{\text{Bd}} + \frac{r_{\text{Ip}}}{\alpha} \right] \xi - \frac{r_{\text{Ip}}}{\alpha},$$

where

$$\eta = \frac{G}{\alpha + F}; \xi = \frac{F}{\alpha + F}; X = \frac{[M_{\text{Bd}}]_0}{[M_{\text{Ip}}]_0};$$

$$Y = \frac{d[M_{\text{Bd}}]_0}{d[M_{\text{Ip}}]_0}; G = \frac{X(Y-1)}{Y}; F = \frac{X^2}{Y}; \text{ and } \alpha = \sqrt{F_{\min} \times F_{\max}}$$

r_{Bd} , r_{Ip} are the Bd and Ip reactivity ratio values, respectively; X is the molar ratio of the Bd to Ip in the monomer feed; Y is the molar ratio of the Bd units to Ip units in the copolymer; $F_{\min}$, $F_{\max}$ are the minimum and maximum values of F , respectively. All linear least-square polts for reactivity ratios of the monomers of Bd and Ip with K-T method are listed in Fig. 3. As shown in the Figure, high R^2 values indicated good linear relationship was obtained, which helped to obtain the accurate value of reactivity ratios. The slope and the intercept of the linear plot are the $r_{\text{Bd}} + \frac{r_{\text{Ip}}}{\alpha}$ and $-\frac{r_{\text{Ip}}}{\alpha}$, respectively.

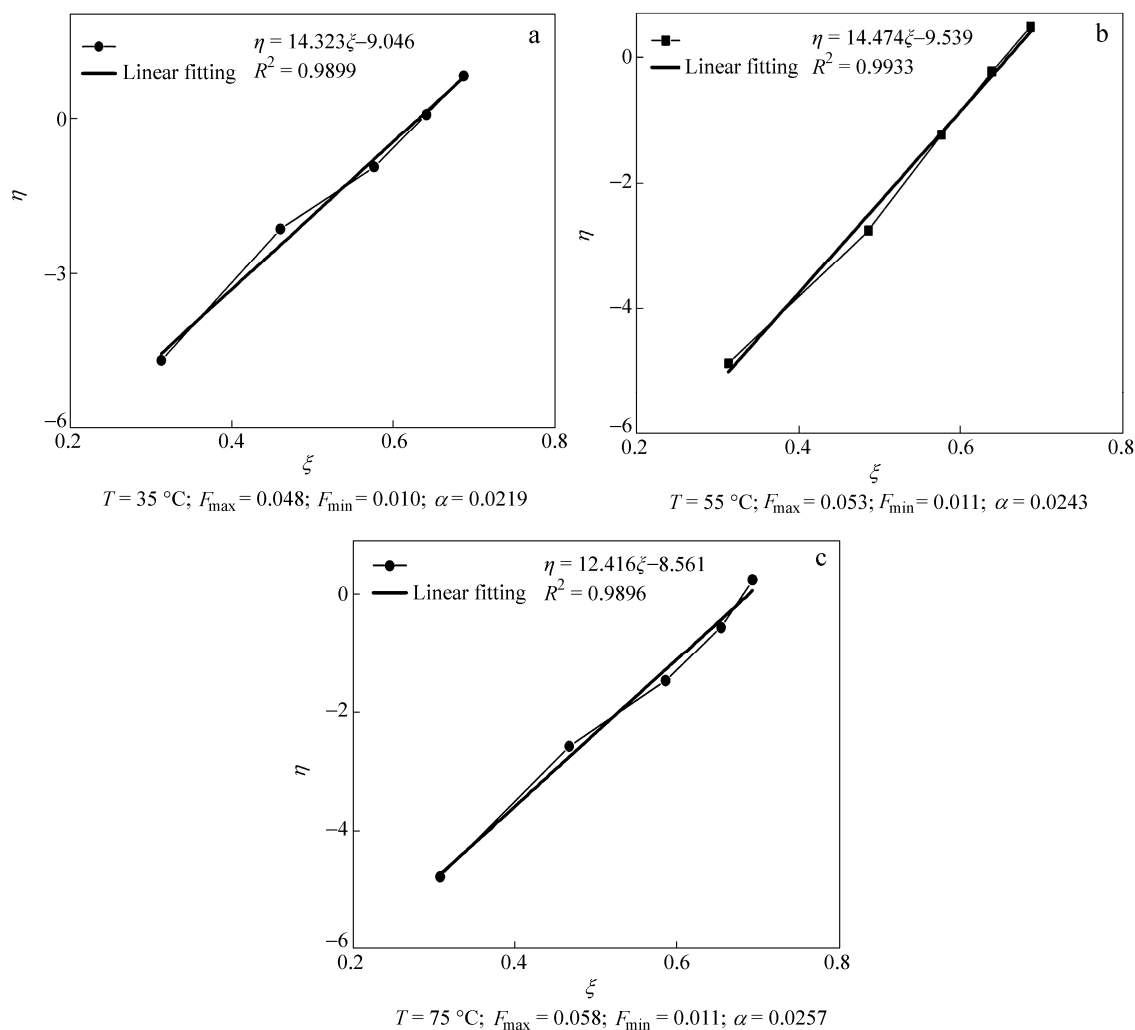


Fig. 3 K-T method to fit the reactivity ratios of the copolymerization of Bd with Ip

Mao-Huglin (M-H) method^[16] is a new liner iterative method of calculation of monomer reactivity ratios, which aimed to provide relatively exact values based on linear least-squares method with the help of computer. Each iteration step is a K-T plot procedure in the M-H method. Full details of the M-H method are presented elsewhere^[16]. The caculated results of reactivity ratios based on two methods are listed in Table 2.

Table 2. The calculated reactivity ratios of monomers with K-T and M-H methods

$T\text{ (}^{\circ}\text{C)}$	Method	r_{Bd}	r_{Ip}	$r_{\text{Bd}} \cdot r_{\text{Ip}}$
35	K-T	5.28	0.20	1.06
55	K-T	4.94	0.23	1.14
75	K-T	3.86	0.22	0.85
35	M-H	5.72	0.19	1.09
55	M-H	5.31	0.22	1.17
75	M-H	3.96	0.21	0.83

As shown in Table 2, with the increase of temperature, r_{Bd} decreased while r_{Ip} stayed relatively stable regardless of the use of K-T method or M-H method. The reactivity ratios of Bd calculated by M-H method was relative larger than those of K-T method. But to both methods, the reactivity ratios $r_{\text{Bd}} \gg r_{\text{Ip}}$, which indicated that

Bd has tendency to homopolymerization, while Ip tends to copolymerization with Bd due to the low reactivity of the growing chain ending with isoprene monomer because of the large steric effect. The calculated results were similar to those obtained by Dilip^[24] and Zambelli^[25]. It was mentioning that $r_{Bd} \cdot r_{Ip}$ values (1.06) at the temperature of 35 °C in two methods were close to 1 as a feature of ideal copolymerization.

Composition Drift in the Comonomer and TBIR Copolymer

Different copolymer compositions for copolymerization of Bd with Ip were obtained by Mayo-Lewis equation expressed as follows.

$$F_{Bd} = \frac{r_{Bd}(f_{Bd}^0)^2 + f_{Bd}^0 f_{Ip}^0}{r_{Bd}(f_{Bd}^0)^2 + 2f_{Bd}^0 f_{Ip}^0 + r_{Ip}(f_{Ip}^0)^2} \quad (1)$$

F_{Bd} is the instantaneous mole fraction of the comonomer Bd in the copolymer. f_{Bd} , f_{Ip} are the corresponding instantaneous mole fraction of comonomers Bd and Ip in the reaction mixture, respectively.

Integration the equation (1) led to the Meyer-Lowry equation which is described as below:

$$\theta = 1 - \left(\frac{f_{Bd}}{f_{Bd}^0}\right)^\alpha \left(\frac{1-f_{Bd}}{1-f_{Bd}^0}\right)^\beta \left(\frac{f_{Bd}^0 - \delta}{f_{Bd} - \delta}\right)^\gamma \quad (2)$$

where $\alpha = \frac{r_{Ip}}{1-r_{Ip}}$; $\beta = \frac{r_{Bd}}{1-r_{Bd}}$; $\gamma = \frac{1-r_{Bd}r_{Ip}}{(1-r_{Bd})(1-r_{Ip})}$; $\delta = \frac{1-r_{Ip}}{2-r_{Bd}-r_{Ip}}$;

f_{Bd}^0 is the initial mole fraction of comonomer Bd in the initial feed, while f_{Bd} is the corresponding instantaneous mole fraction after a period of time. r_{Bd} , r_{Ip} are the reactivity ratios of the Bd and Ip, respectively. The overall molar conversion (θ) is closely related to the monomer reactivity ratios and the comonomer composition in the copolymerization system on the basis of the Meyer-Lowry equation.

$$\overline{F_{Bd}} = \frac{f_{Bd}^0 - f_{Bd}(1-\theta)}{\theta} \quad (3)$$

In the Eq. (3), $\overline{F_{Bd}}$ is the cumulative average mole fraction of the comonomer Bd in the copolymer. Theoretical f_{Bd} and $\overline{F_{Bd}}$ were acquired for overall monomer conversion at different initial feed compositions, as shown in Fig. 4. It revealed that the consumption rate of Bd increased with the increase of f_{Bd}^0 . While the conversion reached 50%–80%, all the monomer Bd was introduced into the copolymer chains. As shown in Table 3, with the increase in the original feed ratio of Bd/Ip, f_{Bd} increased when the copolymerizations reached the same conversion. As for the same original feed ratio of Bd/Ip, with the increase of reaction temperature (from 35 °C, 55 °C, to 75 °C), f_{Bd} also increased, which was perhaps due to the preferred gas state existence of Bd at higher temperatures.

Table 3. All f_{Bd} values of copolymerizations with different Bd/Ip molar ratios at certain conversions

Table S7. f_{Bd} values of copolymerizations with different Bd/Ip molar ratios at certain conversions							
Conv. (%)	T (°C)	Initial Bd/Ip (mol/mol)					
		0.05	0.10	0.15	0.20	0.25	
f_{Bd} (%)	10	35	3.4	6.7	10.1	13.3	16.3
		55	3.6	7.0	10.3	13.6	16.6
		75	3.6	7.1	10.5	13.8	16.9
	20	35	2.2	4.7	7.3	9.9	12.6
		55	2.5	5.1	7.8	10.5	13.2
		75	2.5	5.2	8.0	10.8	13.6
	30	35	1.4	3.0	4.8	6.8	8.9
		55	1.7	3.5	5.5	7.6	9.8
		75	1.6	3.6	5.7	8.0	10.3

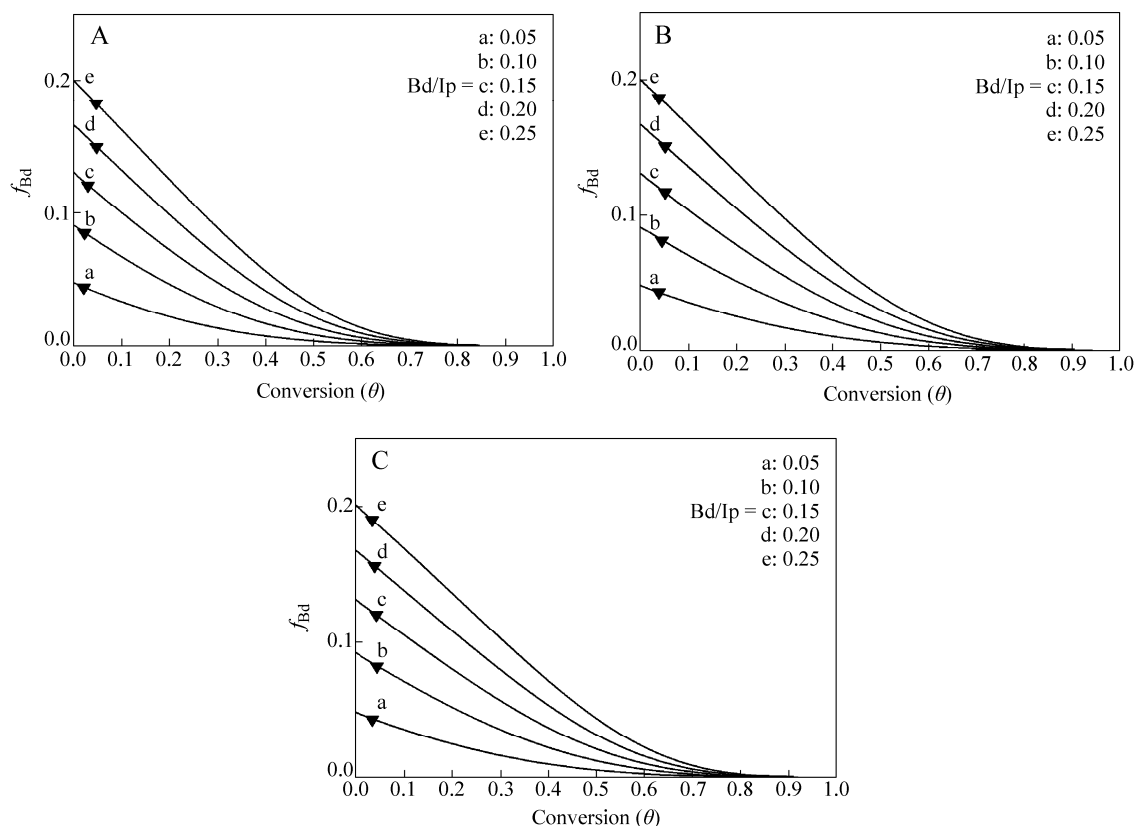


Fig. 4 Instantaneous comonomer composition versus the overall monomer conversion for the different initial Bd/IP feed ratio using reactivity ratios from the K-T method at (A) 35 °C, (B) 55 °C and (C) 75 °C

The changes in the cumulative copolymer average composition were pronounced when the comonomer composition in the original feed ratio changed considerably, as shown in Fig. 5. However, the changes in the comonomer molar content were not as significant as those the f_{Bd} showed. As shown in Table 4, with the increase in the original feed ratio Bd/Ip, $\overline{F_{Bd}}$ increased obviously at the same conversion. To the same original feed ratio Bd/Ip, with the increase of reaction temperature (from 35 °C, 55 °C, to 75 °C), $\overline{F_{Bd}}$ decreased, which was consistent with that accompanied with the increase of f_{Bd} when the reaction temperature increased. All the temperature effects indicated that at higher temperatures more gaseous Bd existed and supplied a retard to contact with catalysts dispersed in liquid monomers, which brought the decrease of r_{Bd} and an effective regulation on copolymer composition distribution.

Table 4. All $\overline{F_{Bd}}$ values of copolymerizations with different initial Bd/Ip molar ratios at certain conversions

Conv. (%)		T (°C)	Bd/Ip (mol/mol)				
			0.05	0.10	0.15	0.20	0.25
$\overline{F_{Bd}}$ (%)	10	35	17.6	30.5	40.1	47.5	53.3
		55	16.0	28.0	37.5	44.9	50.8
		75	16.1	27.6	36.3	43.2	48.7
	20	35	14.9	26.9	36.3	43.8	49.9
		55	13.8	25.0	34.1	41.5	47.6
		75	14.0	24.8	33.4	40.2	45.9
	30	35	12.8	23.5	32.3	39.7	45.9
		55	12.1	22.1	30.7	37.9	44.0
		75	12.0	22.1	30.3	37.1	42.8

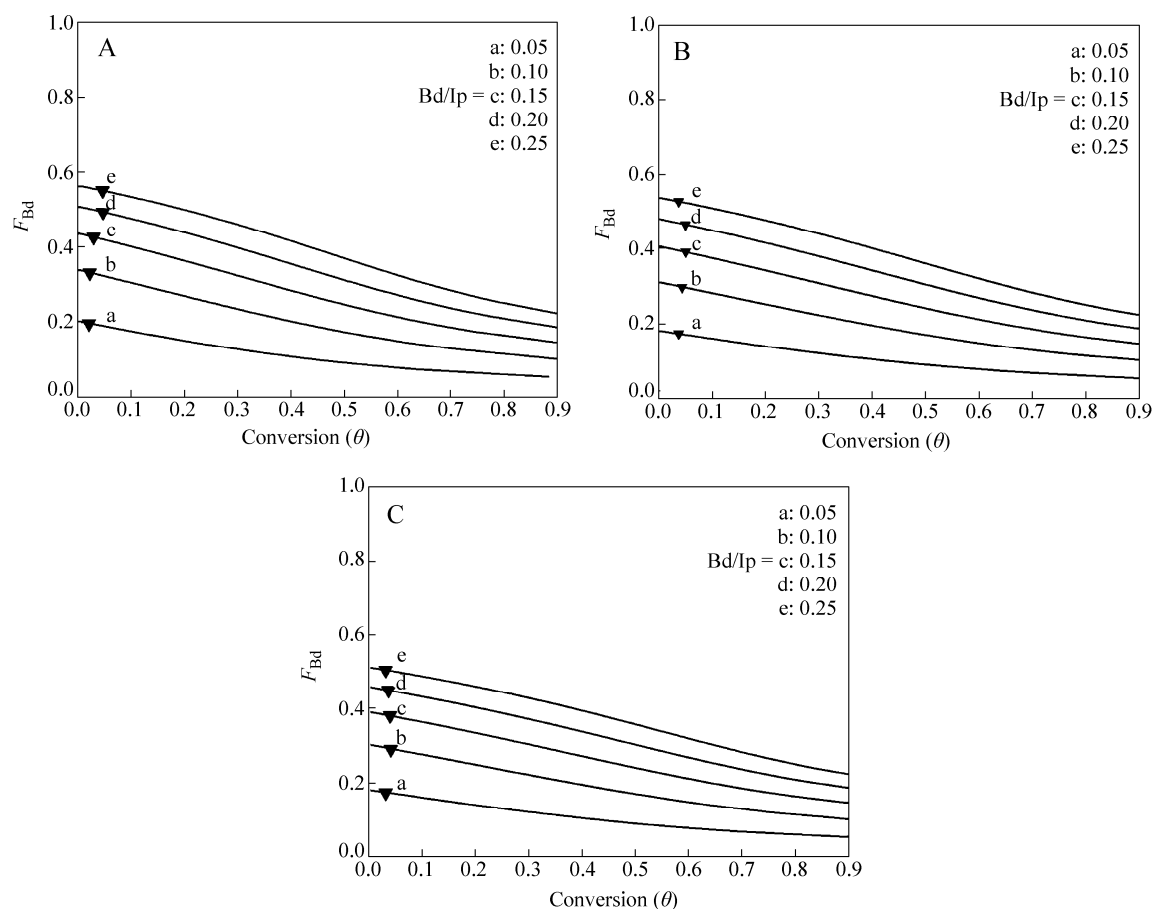


Fig. 5 The average composition versus the overall monomer conversion for the different initial Bd/IP feed ratios using reactivity ratios from the K-T method at (A) 35 °C, (B) 55 °C and (C) 75 °C

CONCLUSIONS

A series of TBIR copolymers were synthesized by the catalyst system $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(i\text{-Bu})_3$. All the copolymers showed high *trans*-1,4-selective structures to Bd and Ip units (*trans*-1,4: > 96%). The reactivity ratios of Bd and Ip were calculated based on K-T and M-H methods at the temperatures of 35 °C, 55 °C and 75 °C, respectively. Further composition drift in the comonomer and TBIR copolymer was also obtained based on K-T and M-H methods. It was worth mentioning that at the same feed ratio and conversion, the $\overline{F}_{Bd}$ decreased with the increase of temperature, which was beneficial for obtaining the copolymers with more uniform comonomer sequence distribution. Of course, the obtained monomer reactivity ratios and copolymerization temperature will play an extremely important role in the control of TBIR synthesis.

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