

Synthesis of a High-Trans 1,4-Butadiene/Isoprene Copolymers with Supported Titanium Catalysts

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ABSTRACT: The copolymerization of butadiene (Bd) and isoprene (Ip) with a supported titanium-triisobutyl aluminum catalyst system was studied. An analysis using differential scanning calorimetry, X-ray diffraction, and ¹³C-NMR spectra indicated that products with 25–60 mol % Bd units were random copolymers and that the melting temperatures and glass-transition temperatures (T_g) were 30–40 and –74°C (or thereabout), respectively, which were very similar to those of natural rubber. The chemical structure of these copolymers was characterized by a high-trans 1,4-configu-

ration: the trans 1,4-content of Ip units was greater than 98%, and the trans 1,4-content of Bd units was greater than 90%. The reactivity ratio of Bd was greater than that of Ip ($r_{Bd} = 5.7$ and $r_{Ip} = 0.17$). The sequence distribution of the monomer units of the copolymers followed a first-order Markov statistical model. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1800–1807, 2003

Key words: catalysts; copolymerization; conjugated polymers

INTRODUCTION

It is generally accepted that high-trans 1,4-configuration diene polymers possess excellent dynamic properties, including excellent antifatigue, low rolling resistance, low heat buildup, good green strength, and low abrasion loss, which are necessary for high-performance tire stock.^{1–5} The trans 1,4-configuration polymer chains have excellent flexibility, which contributes to the low-temperature and dynamic properties of the polymers. The stiffness factor of *trans*-1,4-polyisoprene (1.30) is lower than that of *cis*-1,4-polyisoprene (1.67). The lower the stiffness factor is, the greater the flexibility is of the polymer chains.⁶ However, high-trans diene homopolymers (trans 1,4-content > 95%), such as *trans*-1,4-polyisoprene (TPI) or natural gutta-percha and *trans*-1,4-polybutadiene (TPB), have great crystalline tendencies.^{7–10} With the advent of technology, three stages of sulfur vulcanization of TPI have been developed.⁷ To reduce the crystallinity of TPI and obtain elastomers, high-share sulfur should be used (4–5 phr sulfur).¹¹ Huang and coworkers^{3,5} pointed out that TPI rubber possesses good green strength, excellent antifatigue, and low rolling resistance. However, the relatively high melt-

ing temperature ($T_m = 54^\circ\text{C}$) has some negative effects on processing properties. As for TPB, intrinsic drawbacks, such as high melt-processing temperatures (ca. 170–190°C), consequent processing instability, fast crystallization, and consequent heterogeneous vulcanization, hinder greatly its applications as an elastomer.^{9,10} As a solution to these problems with TPB, an abundant and low-cost butadiene (Bd) resource can be used, and a new kind of trans synthetic rubber can be exploited for high-performance tire stock; the copolymerization of Bd and isoprene (Ip) has received considerable attention. It has been demonstrated that this copolymerization is an effective way not only of reducing the crystallinity of the polymers greatly but also of obtaining copolymers with high-trans configurations based on vanadium,¹² anion,^{2,13} and alfin¹⁴ catalyst systems. However, the commercialization of Bd–Ip copolymerization with these catalyst systems has not been carried out for some reason.

Huang and coworkers^{8,9} reported the synthesis of TPI and TPB with a trans 1,4-content greater than 98% in the presence of supported titanium catalyst systems. The activities of the supported titanium catalyst systems could reach as high as 50,000 g TPI/g Ti and 60,000 g TPB/g Ti. Little is known about the copolymerization of Bd and Ip with supported titanium catalyst systems and the structures of the copolymers. In this article, the syntheses and structures of high-trans Bd–Ip copolymers with supported titanium catalysts are reported in detail. Our recent research has shown that vulcanized trans Bd–IP copolymer rubber (TBIR)

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possesses excellent dynamic properties. The antifatigue properties of TBIR are much better than those of general sidewall stock [natural rubber (NR)/butadiene rubber (BR) = 50/50]. Therefore, it appears that TBIR is a promising candidate as sidewall stock for high-performance tires.

EXPERIMENTAL

Materials

Titanium tetrachloride (TiCl_4 ; >98% purity; Qilu Petrochemical Co., Shandong, China), triisobutyl aluminum [$\text{Al}(\text{i-Bu})_3$; >98% purity; Yanshan Petrochemical Co., Beijing, China], and anhydrous magnesium dichloride (MgCl_2 ; >98% purity; Beijing Institute of Chemical Technology, Beijing, China) were used without further purification. Hydrogenation gasoline (polymerization-grade; Qilu Petrochemical) was refluxed over Na for 24 h and then was distilled and stored over molecular sieves under dry nitrogen.

Bd (polymerization-grade; Qilu Petrochemical) was evaporated from a container, dried by passage through a column packed with molecular sieves, and absorbed into a reactor with the proper solvent at about 0°C.

Ip (polymerization-grade; Shanghai Jinshan Petrochemical Co., Shanghai, China) was refluxed for about 1 h over CaH_2 and then was distilled and stored over molecular sieves under dry nitrogen.

Nitrogen (extra-pure-grade, 99.999% purity) was dried through a P_2O_5 column.

Preparation of the catalyst and copolymerization

A milling kettle with a certain number of stainless balls was degassed thoroughly by evacuation and purged with nitrogen several times under heat before

use. Prescribed amounts of anhydrous MgCl_2 were added into the milling kettle and were milled for about 24 h, and then a prescribed amount of TiCl_4 was added; the mixture was milled for about 2 days. A supported titanium catalyst ($\text{TiCl}_4/\text{MgCl}_2$) was obtained. The titanium content of the catalyst used in this work was 1.8 wt % (unless noted otherwise).

The copolymerization of Bd and Ip was carried out in glass reactors with magnetic stirrers that were dried thoroughly by evacuation and purging with nitrogen several times under heat before use. Prescribed amounts of the solvent (hydrogenation gasoline), monomers (Bd and Ip) in a consent ratio, $\text{Al}(\text{i-Bu})_3$, and titanium catalyst were added to the reactors at certain temperature for copolymerization; the reaction was terminated with ethyl alcohol, and the products were coagulated, repeatedly washed with ethyl alcohol, and then dried in an evacuated oven at 30°C.

Measurements

T_m and the glass-transition temperature (T_g) was measured with a Shimadzu DSC-50 (Japan) at a heating rate of 10°C/min with nitrogen protection. The intrinsic viscosity of the copolymers was determined with an Ubbelohde viscometer in toluene at $30 \pm 0.05^\circ\text{C}$. X-ray diffraction (XRD) studies of the samples were carried out with a Rigaku D/MAX 2500 X-ray diffractometer (Japan) (45 kV, 300 mA) at a scanning speed of 4°/min with a 2θ value of 10°. The Fourier transform infrared (FTIR) spectra of the copolymers were taken on a Nicolet FTIR spectrophotometer (Japan) with films on KBr discs. $^1\text{H-NMR}$ examinations were performed with a Bruker FT-AC-80 instrument (Germany). The spectra were obtained with CCl_4 as a solvent at room temperature. $^{13}\text{C-NMR}$ spectra of the copolymers were obtained with a Bruker FT-AC-80

TABLE I
Thermal Analysis of Bd-*Ip* Copolymer

Sample	f_1^0 (mol %)	C (wt %)	CE (Kg of P/ mol of Ti)	$[\eta]$ (dg L ⁻¹)	T_g (°C)	Copolymer T_m (ΔH)	TPI and TPB [$^\circ\text{C}$ (Jg ⁻¹)]	
							T_i (ΔH)	T_m (ΔH)
1 ^a	0	3.8	52.4	3.1	-70.1			52.4 (25.6)
2 ^a	5.5	3.8	51.7	3.4	-75.2	36.0 (1.5)		
3 ^a	11.5	4.2	55.8	4.4	-74.4	32.2 (1.0)		
4 ^a	14.8	5.1	63.1	4.9	-78.8	36.6 (0.3)		
5 ^a	20	4.6	58.6	5.3	-77.7	39.1 (0.1)		
6 ^a	27	6.3	81.2	7.9	-79.9	31.3 (1.4)	69.3 (6.3)	135.0 (1.7)
7 ^a	35.4	6.5	81.4	8.4	-85.9	33.8 (6.0)	73.9 (9.9)	138.3 (2.2)
8 ^a	100	21.8	238.7	—	—		73.9 (80.9)	150.3 (55.6)
9 ^b	10	25	83.2	1.4	-73.4	32.5 (16.7)		
10 ^b	20	38	125.1	1.8	-73.8	31.2 (10.2)		

C = conversion; CE = catalytic efficiency.

^a Copolymerization conditions: Ti:M molar ratio = 1×10^{-5} :1, Al:Ti molar ratio = 100:1, [M] = 3.0 mol/L, 50°C, and 90 min.

^b Copolymerization conditions: Ti:M molar ratio = 2×10^{-4} :1, Al:Ti molar ratio = 100:1, [M] = 2.0 mol/L, 40°C, 11 h, and hydrogen pressure = 0.02 MPa.

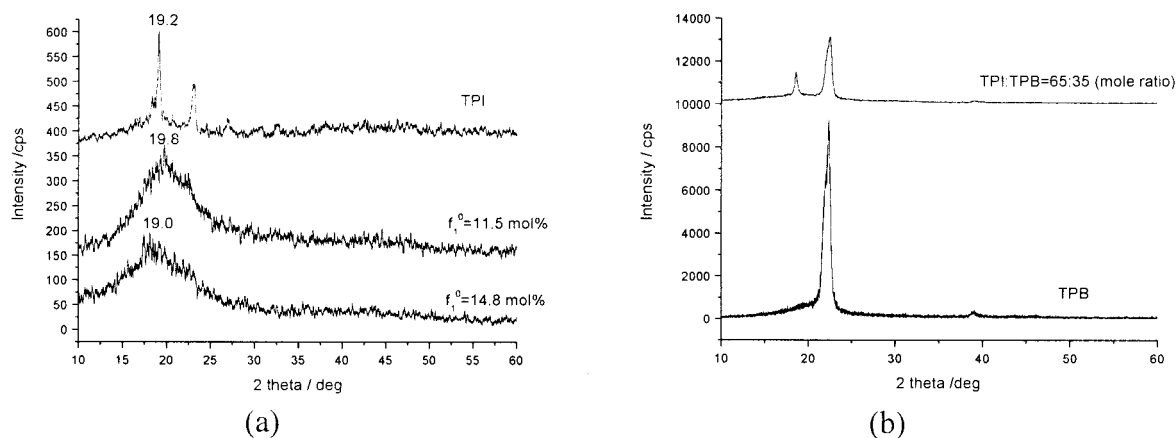


Figure 1 XRD patterns of polymers with supported titanium catalyst systems. (a) TPI and copolymers (b) TPB and blends of TPI and TPB.

with 10,000 scans at a pulse repetition time of 5 s for 45° pulses. The solution for NMR measurements was prepared by the dissolution of the copolymer in CCl_4 to make a 10 wt % solution.

The microstructures and composites of the copolymers were determined as indicated in the literature.^{15–17}

RESULTS AND DISCUSSION

Synthesis of the Bd–Ip copolymer

The catalytic efficiency of the supported titanium catalyst system increased with an increase in the Bd molar content in the feed (f_1^0), as can be seen in Table I. This might be related to the high reactivity of the Bd monomer. Compared with the vanadium catalyst system, the supported titanium catalyst system showed a relatively high activity in the stereospecific copolymerization of Ip and Bd at a normal temperature.¹² In general, the molecular weight of the copolymers was rather high. The fact that the molecular weight of the copolymers increased with an increase in f_1^0 was related to the aforementioned copolymerization rate. The decreases in the molecular weights of samples 9 and 10 indicated that hydrogen was an effective molecular weight controller in the copolymerization reaction systems. The intrinsic viscosity of the copolymers decreased greatly with the addition of hydrogen. However, the catalytic activity of the supported titanium catalyst decreased with the addition of hydrogen.

The T_g and T_m values of the polymers are listed in Table I. First, the results showed that T_g and T_m of TPI were -70.2 and 52.4°C , respectively, whereas the melting-transition temperature (T_t) and T_m of TPB were 73.9 and 150.3°C , respectively. Both TPI and TPB had a high melting enthalpy. Second, when f_1^0 was less than 20%, the products obtained were copolymers

with one T_g and one T_m . The crystalline melting enthalpy (ΔH) and T_m of the copolymers were much lower than those of TPI and TPB, and the ΔH values of the copolymers decreased greatly with an increase in f_1^0 . Third, when f_1^0 was greater than 20%, very faint peaks of T_t and T_m at 69 – 74 and 130 – 140°C , respectively, were observed, which indicated that there were TPB crystals in the obtained products. The Bd molar content in the polymer (F_1) of toluene extraction fractions of sample 6 was measured. The F_1 values of the toluene-soluble fraction and toluene-insoluble fraction were 65 and 83%, respectively. The results showed that the products obtained with high f_1^0 values were copolymers, not mixtures of TPB and copolymers. However, the copolymers had more compositional heterogeneity than what was obtained with low f_1^0 values. As reported in the literature,¹⁰ the trans 1,4-configuration Bd chains very easily formed crystals in which one folding chain only included 3–4 Bd units. Therefore, it was easy to form crystals even for relatively short Bd blocks in the copolymers. Although such crystals might act as physical crosslinkage particles, which contributed to the mechanical properties of the copolymers, when the content of TPB crystals increased to one certain value, the presence of such crystals did have a bad effect on the processing properties and mechanical properties of the copolymers.

TABLE II
Comparison of the Intensity of the XRD Peak ($2\theta = 19.2^\circ$) of the Polymers

Samples	Reflection peak	$2\theta = 19.2^\circ$	
		High	Area
8	TPB	0	0
1	TPI	192	8498
3	$f_1^0 = 11.5\%$	82	4769
4	$f_1^0 = 14.8\%$	63	4399

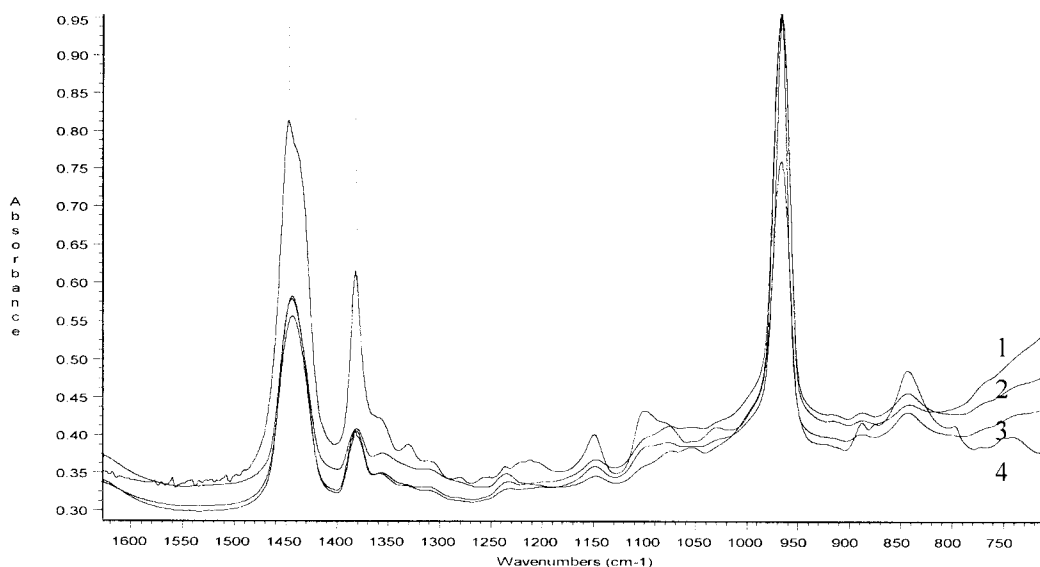


Figure 2 IR spectra of Bd-Ip copolymers: (1) $f_1^0 = 20\%$, (2) $f_1^0 = 11.5\%$, (3) $f_1^0 = 14.8\%$, and (4) $f_1^0 = 5.5\%$. The copolymerization conditions conform to those given in Table I.

Fourth, the T_g values of the copolymers ($5 \leq f_1^0 \leq 20\%$) were very similar to that of NR ($T_g = -72^\circ\text{C}$), and this indicated that the copolymers potentially possessed good comprehensive properties as rubber materials.

Because of these results, we focused our attention on the copolymers obtained with optimum f_1^0 values (5–20%).

XRD measurements

XRD patterns of the polymers are shown in Figure 1. The characteristic reflection peak of TPB ($2\theta = 22.4^\circ$) had a greater intensity than that of TPI ($2\theta = 19.2^\circ$), and this meant that TPB had a much higher degree of crystallinity than TPI. Compared with the blends of TPI and TPB (65:35 TPI/TPB molar ratio), the products synthesized were copolymers, but not blends. The crystalline forms of the copolymers conformed to that of TPI. However, the reflection peaks of the copolymers dispersed, and the intensity of these peaks decreased greatly with an increase in f_1^0 , as can be seen in Table II. The results indicated that the Bd units destroyed the structural regularity of TPI chains. There-

fore, the degree of crystallinity of the copolymers decreased.

FTIR analysis^{15,16}

IR spectra of samples 2–5 are listed in Figure 2. In the region between 400 and 1600 cm^{-1} , a number of vibrations of the two monomers could be observed. The bands at 1384 and 967 cm^{-1} , which represented the trans 1,4-structure of Ip units and the trans 1,4-structure of Bd units, respectively, were rather intense. The bands at 889, 738, and 911 cm^{-1} , which represented the 3,4-structure of Ip, the cis 1,4-structure of Bd, and the 1,2-structure of Bd, respectively, were very faint and sometimes even disappeared from the IR spectra. It could be concluded that the products obtained with supported titanium catalysts were mainly of the trans 1,4-configuration. The absence of the 775- cm^{-1} band indicated that there was no TPB crystalline phase in these products, and this agreed with the differential scanning calorimetry analysis.

The compositions and microstructures of the copolymers are summarized in Table III according to the IR

TABLE III
Compositions and Microstructures of the Copolymers

f_1^0 (mol %)	F_1 ($^1\text{H-NMR}$; mol %)	F_1 (IR; mol %)	Microstructure				
			Ip units (%)		Bd units (%)		
			Trans 1,4	3,4	Trans 1,4	Cis 1,4	1,2
5.5	26.3	26.0	99.1	0.9	90.2	9.6	0.2
11.5	40.9	40.6	99.0	1.0	95.7	4.0	0.3
14.8	49.4	51.5	98.8	1.2	97.4	2.2	0.4
20.0	57.5	60.0	98.9	1.1	99.4	0.2	0.4

Copolymerization conditions conform to those given in Table I.

TABLE IV
Effect of the Polymerization Conditions on the Microstructures of the Copolymers

Al/Ti molar ratio	Temperature (°C)	[M] (mol L ⁻¹)	Time (min)	F ₁ (mol %)	Microstructure of the copolymers (%)				
					Bd units			Ip units	
					Trans 1,4	Cis 1,4	1,2	Trans 1,4	3,4
50	30	2.0	120	61.8	96.9	2.8	0.3	99.8	0.2
50	50	2.0	120	55.0	96.2	3.2	0.6	99.5	0.5
50	70	2.0	120	58.7	97.0	2.4	0.6	99.4	0.6
20	40	2.0	180	30.0	93.2	6.2	0.3	99.3	0.7
50	40	2.0	180	45.5	95.1	4.7	0.1	99.5	0.5
80	40	2.0	180	46.0	95.2	4.3	0.1	99.6	0.4
100	50	1.9	90	58.6	95.3	4.3	0.4	99.6	0.4
100	50	5.0	90	60.6	99.5	0	0.5	99.5	0.5
100	50	10	90	45.9	96.8	2.3	0.9	99.4	0.6

$f_1^0 = 20$ mol %. Samples 1–6 and 10–11, the Ti:M molar ratio = 1×10^{-4} :1. For samples 7–9, the Ti:M molar ratio = 1×10^{-4} :1.

spectra. In Table III, it can be seen that the copolymers with supported titanium catalysts were mainly of the trans 1,4-configuration. The Bd units had trans 1,4-contents greater than 90%, whereas the Ip units had trans 1,4-contents greater than 98%; this was a distinguishing feature of coordination polymerization with supported titanium–Al(i-Bu)₃ catalyst systems. The feed ratio had little effect on the microstructure of the Ip units; however, the trans 1,4-content of the Bd units decreased slightly with a decrease in f_1^0 . At the same time, we could also see from Table III that the values of F_1 were much higher than those of f_1^0 , and this meant that Bd was more reactive than Ip and more easily formed long blocks. Therefore, f_1^0 should be controlled under a certain value for the synthesis of random copolymers.

Table IV summarizes the effects of the copolymerization temperature, Al/Ti molar ratio, and monomer concentration on the microstructures of the resulting copolymers. The results showed that the copolymerization conditions did not exert much of an influence on the microstructures of the copolymers. Both Bd and Ip repeat units had trans 1,4-contents greater than 90%. With an increase in the temperature and monomer concentration and a decrease in the Al/Ti molar ratio, the F_1 values decreased. This might be related to the change in the monomer reactivity and Bd solubility under different conditions.

As can be seen in Table V, the trans 1,4-content of the Bd units decreased with an increase in the titanium content of the supported titanium catalyst. This might be ascribed to the increase in the dissociating titanium content with the increase in the supported titanium content. Therefore, for the synthesis of high-trans-configuration copolymers, the supported titanium content should not be too high. As is well known, high-cis 1,4-polyisoprene and cis-trans mixture structure polybutadiene could be synthesized with the TiCl₄–Al(i-Bu)₃ catalyst system,¹⁸ whereas

high-trans 1,4-polyisoprene and high-trans 1,4-polybutadiene could be obtained with TiCl₄/MgCl₂–Al(i-Bu)₃ catalyst systems.^{8,9} The supported catalyst systems possessed not only high catalytic efficiency but also high-trans-configuration characteristics because of the change in the coordination environment of titanium active centers for the Mg–Cl–Ti bridge bonds formed during the comilling of MgCl₂ and TiCl₄.

¹H-NMR analysis¹⁷

¹H-NMR spectra of Bd–Ip copolymers are shown in Figure 3. The compositions of the copolymers obtained from ¹H-NMR spectra were very consistent with those obtained by IR spectra, as shown in Table III.

Reactivity ratio of copolymerization

The reactivity ratio is an important parameter of a copolymerization reaction. The reactivity ratios of Bd and Ip were determined according to the Tudos improved linear graph method.¹⁹ The copolymerization conversions were controlled below 5% to meet the evaluation requirements. Figure 4 shows the linear

TABLE V
Effect of the Supported Titanium Content on the Microstructure of the Copolymer

Ti (wt %)	Bd units, %			Ip units, %	
	Trans 1,4	Cis 1,4	1,2	Trans 1,4	3,4
1.8	96.9	2.8	0.3	99.8	0.2
2.4	93.0	6.9	0.1	99.5	0.5
3	90.3	9.2	0.5	99.4	0.6
4	87.7	11.3	1.0	99.3	0.7

Conditions: Ti:M molar ratio = 1×10^{-4} :1, Al:Ti molar ratio = 50:1, $f_1^0 = 20$ mol %. [M] = 3.0 mol L⁻¹, 50°C, and 120 min.

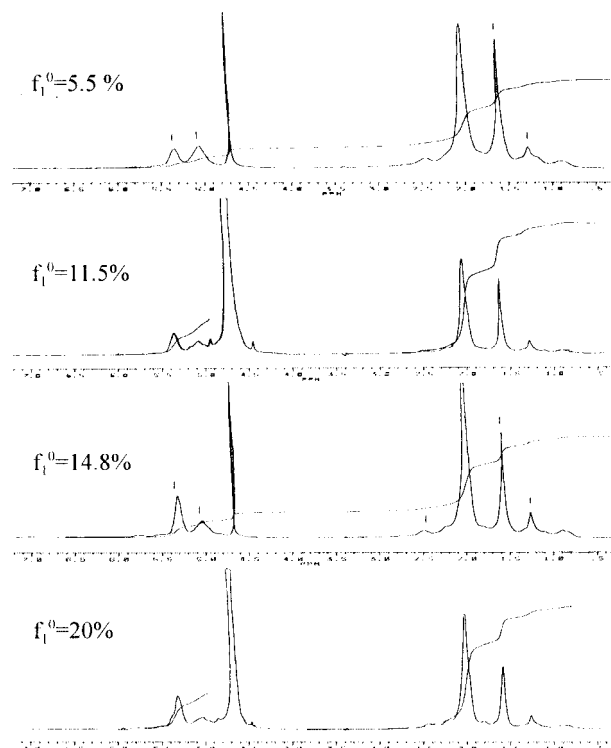


Figure 3 ^1H -NMR spectra of Bd-Ip polymers. The copolymerization conditions conform to those given in Table I.

relationship between η and ξ . The linear slope was $r_{\text{Bd}} + r_{\text{Ip}}/\alpha$, and the intercept was $-r_{\text{Ip}}/\alpha$; therefore, the reactivity ratios could be obtained. The reactivity ratio of Bd was $r_{\text{Bd}} = 5.7$, whereas the reactivity ratio of Ip was $r_{\text{Ip}} = 0.17$. $r_{\text{Bd}}r_{\text{Ip}}$ was 0.97. The data showed that the reaction activities of the two monomers were quite different, and Bd was more reactive than Ip with the supported titanium catalyst systems.

^{13}C -NMR analysis and sequence distribution

The ^{13}C -NMR spectra of the copolymers are shown in Figure 5, and the assignments of the peaks and the

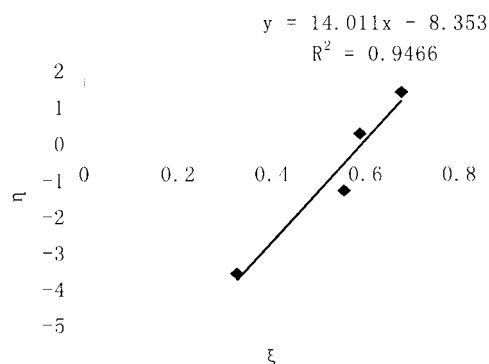


Figure 4 η versus ξ . The copolymerization conditions conform to those given in Table I.

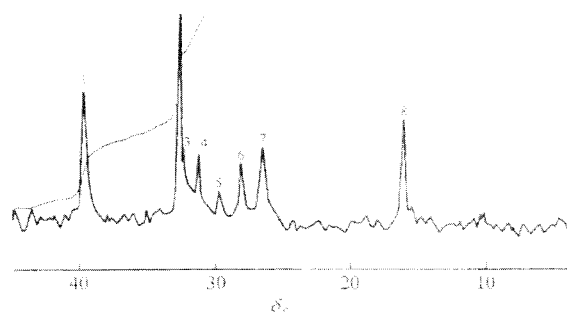


Figure 5 Aliphatic region of the ^{13}C -NMR spectrum of a Bd-Ip copolymer ($f_1^0 = 14.8\%$).

dyad concentrations calculated from the ^{13}C -NMR spectra are listed in Tables VI and VII, respectively.^{20,21}

In Figure 5, we can see that the results of the ^{13}C -NMR spectra conformed well with the previous analysis. A chemical shift (δ_c) of 16.5 indicated that there was no cis configuration of Ip units in the copolymers. Copolymers with supported titanium catalysts were mainly of the trans 1,4-configuration. The presence of the dyad structures BI and IB further confirmed that the products were copolymers. The presence of peak 1 and peak 8 indicated that Ip units in the copolymers were in head-end linkages.

The number-average sequence length (n) of the monomer repeat units could be calculated according to the following equations:

$$n_B = (2[\text{BB}] + [\text{BI}] + [\text{IB}]) / ([\text{IB}] + [\text{BI}]) \quad (1)$$

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

The Bernoullian statistical probability model and the first-order Markov statistical probability model were used to verify the copolymer sequence distribution and number-average sequence length.^{22,23}

The basic hypothesis of the Bernoullian statistical probability model is that the propagation reactions are only related to the monomer structures. P_B and P_I represent the reaction probabilities of Bd and Ip. The following equations conform to the Bernoullian model:

$$[\text{BB}] = P_B^2 \quad (3)$$

$$[\text{II}] = P_I^2 \quad (4)$$

$$[\text{BI}] + [\text{IB}] = 2P_B P_I \quad (5)$$

$$P_B + P_I = 1 \quad (6)$$

$$n_B = 1 / (1 - P_B) \quad (7)$$

$$n_I = 1 / P_B \quad (8)$$

TABLE VI
¹³C-NMR Chemical Shifts and Assignments of the Copolymers^{20,21}

No.	Chemical shift	Assignment
1	39.57	
2	32.54	
3	32.02	
4	31.07	
5	29.47	
6	27.96	
7	27.22	
8	16.51	

If *I* or *i* represents the Ip unit and *B* or *b* represents the Bd unit, the right carbon atom lies in *I* or *B*, *i* or *b* is next to *I* or *B*, and 4 or 1 represents the series number of the carbon atom in the monomer unit.

The basic hypothesis of the first-order Markov model is that the propagation reactions are related to both the monomer structures and the ending structures of active centers. P_{BI} represents the reaction probability of the Bd active centers and Ip monomer. The following equations conform to the first-order Markov model:

$$[BB] = P_{IB}(1 - P_{BI}) / (P_{BI} + P_{IB}) \quad (9)$$

$$[II] = P_{BI}(1 - P_{IB}) / (P_{BI} + P_{IB}) \quad (10)$$

$$[BI] + [IB] = 2P_{BI}P_{IB} / (P_{BI} + P_{IB}) \quad (11)$$

$$n_B = 1/P_{BI} \quad (12)$$

$$n_I = 1/P_{IB} \quad (13)$$

The results are listed in Table VII.

It can be seen in Table VII that the measured values agreed well with the calculated values of the first Markov model. Therefore, the sequence distributions of the copolymer with supported titanium catalysts conformed to the first Markov model. In addition, data calculated by the first-order Markov model revealed that the Bd molar content in the feed played an

TABLE VII
 Dyad Distribution and the Number-Average Sequence Length of the Copolymer

f_1^0 (mol %)	Calculated value															
	Measured value				Bernoullian model					First-order Markov model						
	[BB]	[II]	n_B	n_I	[BB]	[II]	P_B	n_B	n_I	[BB]	[II]	P_{BI}	P_{IB}	n_B	n_I	
5.5	0.18	0.51	2.19	4.32	0.11	0.44	0.34	1.51	2.98	0.19	0.50	0.45	0.24	2.23	4.26	
11.5	0.21	0.39	2.03	2.96	0.16	0.35	0.41	1.68	2.46	0.20	0.40	0.50	0.34	2.01	2.98	
14.8	0.33	0.28	2.63	2.38	0.28	0.23	0.53	2.11	1.90	0.30	0.30	0.40	0.40	2.51	2.51	

important role in the formation of random copolymers; the optimum value of f_1^0 was about $15 \pm 5\%$, and the optimum value of F_1 in the copolymer was about $50 \pm 10\%$. When f_1^0 was much higher, n_B increased, and this indicated that the synthesized copolymers possessed more Bd blocks. When f_1^0 was much lower, n_I increased, and this indicated that the synthesized copolymers possessed more Ip blocks.

High-trans Bd-Ip copolymers were synthesized. TBIR possessed excellent dynamic properties, such as high green strength, low heat-up, and excellent anti-fatigue properties. The anti-fatigue properties of TBIR were 100 times greater than those of NR, 10 times greater than those of BR, and much better than those of general sidewall stock (NR/BR = 50/50). The physical and mechanical properties of TBIR will be reported soon.

CONCLUSIONS

The high trans 1,4-configuration was a distinguishing feature of coordination diene polymerization with supported titanium catalyst systems. Trans Bd-Ip copolymers were obtained with a $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(\text{i-Bu})_3$ catalyst system. The Bd molar content in the feed played an important role in the formation of random copolymers. The optimum f_1^0 value was 0.15 ± 0.05 . The values of T_m and T_g of the copolymers obtained under the optimum feed were 30–40 and -74°C (or thereabout), respectively. The Ip units of the copolymers had trans 1,4-contents above 98%, and the Bd units had trans 1,4-contents above 90%. The copolymerization conditions had little effect on the microstructures of the copolymers. The reaction activity of Bd was greater than that of Ip, and the following reactivity ratios were obtained: $r_{\text{Bd}} = 5.7$ and $r_{\text{Ip}} = 0.17$. The sequence distributions of the monomer

units in the copolymers followed the first-order Markov model according to our calculations.

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