

Gas Phase Polymerization of 1,3-Butadiene with Supported Neodymium-Based Catalyst: Investigation of Molecular Weight

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ABSTRACT: The gas phase polymerization of 1,3-butadiene (Bd), with supported catalyst $\text{Nd}(\text{naph})_3/\text{Al}_2\text{Et}_3\text{Cl}_3/\text{Al}(\text{i-Bu})_3$ or/and $\text{Al}(\text{i-Bu})_2\text{H}$, was investigated. The polymerization of Bd with neodymium-based catalysts yielded *cis*-1,4 (97.2–98.9%) polybutadiene with controllable molecular weight (MW varying from 40 to $80 \times 10^4 \text{ g mol}^{-1}$). The effects of reaction temperature, reaction time, $\text{Nd}(\text{naph})_3/\text{Al}(\text{i-Bu})_3$ molar ratio, and cocatalyst component on the catalytic activity and molecular weight of polymers were ex-

amined. It was found that there are two kinds of active sites in the catalyst system, which mainly influenced the MW and molecular weight distribution of polybutadiene. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1945–1949, 2004

Key words: molecular weight distribution; gas phase polymerization; 1,3-butadiene; supported catalysts; conjugated dienes

INTRODUCTION

It has been established that rare earth metal-based compounds are effective catalysts for the polymerization of conjugated dienes such as 1,3-butadiene or isoprene.^{1–4} Neodymium-based catalysts are particularly favored, being the most active, and give polymers with high *cis*-1,4 content (>98%). Polybutadiene (PBd) rubber is commercially manufactured by solution polymerization. Recently, gas phase polymerization of Bd, with SiO_2 -supported rare earth catalysts, at the laboratory scale has been the focus of a number of studies.^{5–11} These studies generally focus on the kinetics of polymerization,^{9,11} molding, and simulation.^{7,8} The gas phase polymerization of 1,3-butadiene, with supported half-sandwich-titanium complexes, was also reported by Kaminsky and coworkers.¹²

For use as a synthetic rubber, control of both *cis*-1,4 microstructure and molecular weight (MW) of PBd are very important properties. In the solution polymerization of Bd, few studies have focused on the control of MW and MWD of the resulting polymer,^{13–15} and until now the problem of how to control these characteris-

tics of PBd in gas phase polymerization has not been examined. This article reports on an investigation of molecular weight of PBd in gas phase polymerization of 1,3-butadiene with SiO_2 -supported neodymium-based catalyst $\text{Nd}(\text{naph})_3/\text{Al}_2\text{Et}_3\text{Cl}_3/\text{Al}(\text{i-Bu})_3$ (TIBA) or/and $\text{Al}(\text{i-Bu})_2\text{H}$ (DIBAH). The molecular weight of PBd in the range of $40\text{--}80 \times 10^4$ could be controlled by the ratio of $\text{Al}(\text{i-Bu})_3/\text{Al}(\text{i-Bu})_2\text{H}$ of the cocatalyst.

EXPERIMENTAL

Materials

1,3-Butadiene (provided by Shanghai Gaoqiao Petrochemicals Co., China) was purified by passing through two successive columns containing potassium hydroxide and active alumina, respectively. Silica gel (provided by QiLu Petrochemicals Co., China) was activated and pretreated before use. $\text{Al}(\text{i-Bu})_3$ and $\text{Al}(\text{i-Bu})_2\text{H}$ (AKZO Nobel, Deer Park, TX), with 99% purity, were used without further purification. $\text{Al}_2\text{Et}_3\text{Cl}_3$ (EASC; provided by Zhenhai Petrochemicals Co., China) was distilled before use. $\text{Nd}(\text{naph})_3$ was prepared according to the processes described in the literature.²

Preparation of supported catalyst

The supported catalyst was prepared in a 50-mL ampoule by mixing $\text{Nd}(\text{naph})_3$, $\text{Al}_2\text{Et}_3\text{Cl}_3$, $\text{Al}(\text{i-Bu})_3$, and/or $\text{Al}(\text{i-Bu})_2\text{H}$ under argon atmosphere. After ageing the mixture at 50–60°C for a given time, silica gel was added and stirred. By removing the solvent in vacuum, the supported catalyst powder was obtained.

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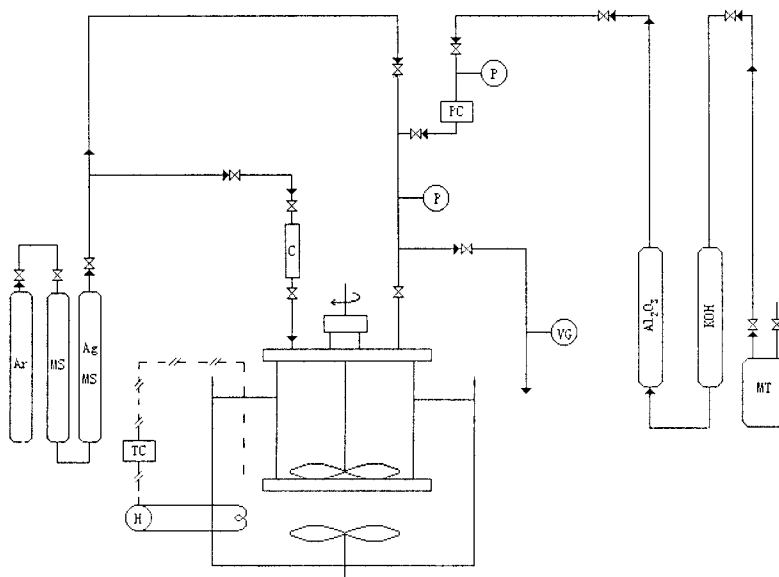


Figure 1 Gas phase stirred bed reactor for butadiene polymerization: R, reactor; TC, temperature controller; PC, pressure controller; MT, monomer tank; VG, vacuum gauge; C, catalyst injection column; MS, molecular sieves column.

All manipulations were carried out under argon atmosphere using standard Schlenk line techniques. The amount of Al and Nd was calculated by the amount of aluminum alkyl and Nd(naph)₃ used.

Polymerization

Gas phase polymerization was carried out in a 0.25-L stirred bed reactor in a semibatch manner with the experimental system shown in Figure 1. Before polymerization, the reactor was charged with inert particulate material and heated in vacuum for 1 h at 95°C and purged with argon three times. After cooling to reaction temperature, the catalyst powder was introduced into the reactor under argon atmosphere. The reactor was evacuated for about 5 min before the monomer feed was started. The polymerization was started by addition of Bd and terminated by addition of ethanol.

The product was immersed in ethanol containing 5% hydrochloric acid and 2,6-di-*tert*-butyl-4-methyl

phenol for 24 h, then washed with ethanol and dried in vacuum at 40°C. The activity of gas phase polymerization was measured by weighing the polymer obtained.

Characterization of polymers

The microstructure of the polymers was measured by infrared (IR) spectroscopy according to the method of Silas et al.¹⁶ IR analysis was performed using a Bruker Vector 22 FTIR spectrophotometer (Bruker Instruments, Billerica, MA). Films were cast from chloroform solution onto KBr plates. The absorbencies occurred at 740 cm⁻¹ (*cis*-1,4), 970 cm⁻¹ (*trans*-1,4), and 910 cm⁻¹ (*vinyl*-1,2). The number- and weight-average molecular weights (M_n and M_w , respectively) and molecular weight distribution (MWD, M_w/M_n) were determined by gel permeation chromatography (GPC) using a Waters 208 instrument (Waters Chromatography Division/Millipore, Milford, MA) with an RI detector (R410) at 30°C and calibrated with polystyrene

TABLE I
Gas Phase Polymerization of Bd with Nd(naph)₃/Al₂Et₃Cl₃/Al(*i*-Bu)₃ Catalyst^a

Temperature (°C)	Activity (kg/PBd/mol ⁻¹ /Nd/h ⁻¹)	M_w (10 ⁴)	MWD	Microstructure of PBd (%)		
				<i>cis</i> -1,4	<i>trans</i> -1,4	<i>vinyl</i> -1,2
30	1015	58	5.52	98.4	0.38	1.22
40	1275	61	5.05	98.7	0.32	0.98
50	1431	57	5.33	98.7	0.17	1.13
60	934	53	6.51	97.2	0.54	2.26
70	746	50	6.87	97.3	0.57	2.13

^a Polymerization conditions: [Nd] = 2.6 × 10⁻⁵ mol/L, Al/Nd = 100, Cl/Nd = 4, 30 min at 0.2 MPa.

TABLE II
Effect of Al/Nd on Gas Phase Polymerization of Bd^a

Al/Nd (molar ratio)	Activity (kg/PBd/mol ⁻¹ /Nd/h ⁻¹)	M_w (10 ⁴)	MWD	Microstructure of PBd (%)		
				<i>cis</i> -1,4	<i>trans</i> -1,4	<i>vinyl</i> -1,2
60	456	85	2.75	98.5	0.43	1.07
80	1083	84	2.80	98.9	0.51	0.59
100	1275	61	5.05	98.7	0.32	0.98
120	1281	80, 3.6	2.45, 1.63	98.8	0.37	0.83

^a Catalyst system: Nd(naph)₃/Al₂Et₃Cl₃/Al(i-Bu)₃. Polymerization conditions: $T = 40^\circ\text{C}$, $[\text{Nd}] = 2.6 \times 10^{-5}$ mol/L, Cl/Nd = 4, 30 min at 0.2 MPa.

standards. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL min⁻¹.

RESULTS AND DISCUSSION

Gas phase polymerization of Bd with Nd(naph)₃/Al₂Et₃Cl₃/Al(i-Bu)₃ catalyst

The gas phase polymerization of Bd with Nd(naph)₃/Al₂Et₃Cl₃/Al(i-Bu)₃ catalysts was conducted at different temperatures, and the results are shown in Table I. At the experimental scale, the supported neodymium-based catalyst system showed high activity, reaching its highest value at 50°C. Increasing temperature resulted in a slightly lower MW and broader MWD. To obtain relatively high catalyst activity and polymers with MW of about 60×10^4 g mol⁻¹ and MWD of about 5, the optimum temperature was 40–50°C. The polymers were characterized by high *cis*-1,4 content, about 98%, which varied only slightly in the polymerization temperature range of 20–70°C. Generally speaking, gas phase polymerization with highly active catalysts favors formation of a gel fraction during the polymerization of Bd, although little gel was found under our conditions.

Effect of aluminum alkyl cocatalyst

It is known that the aluminum alkyl cocatalyst has an important influence on the polymerization of Bd cat-

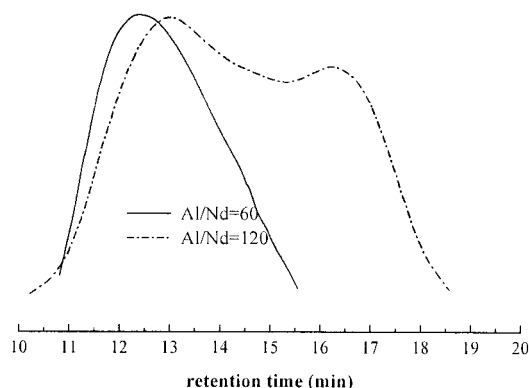


Figure 2 GPC curves of polybutadiene at different Al/Nd molar ratios. Polymerization conditions are the same as in Table II.

alyzed by rare earth-based catalyst. To verify this point, the effect of Al/Nd molar ratio on the gas phase polymerization of Bd was examined, and the results are depicted in Table II and Figure 2.

The catalytic activity increased with increasing Al/Nd molar ratio. A larger amount of Al(i-Bu)₃ system gives lower molecular weight PBds with broader MWD. This may be attributable to the chain-transfer reaction by excess Al(i-Bu)₃, which is similar to the solution polymerization of Bd.^{14,17,18} The resulting polymers, at different Al/Nd molar ratios, have high *cis*-1,4 content, above 98.5%.

As shown in Figure 2, at low Al/Nd molar ratio (Al/Nd = 60), the MWD of PBd is narrow ($M_w/M_n = 2.75$) and monomodal. A high Al/Nd molar ratio (Al/Nd = 120) shows a bimodal distribution. Therefore, it can be supposed that there are two kinds of active sites formed at the high TIBA level.

The composite cocatalyst, composed of TIBA and DIBAH, was used and the results are shown in Table III and Figure 3. Under the polymerization conditions, catalytic activities are considerably high, at about 1000 kg PBd mol⁻¹ Nd h⁻¹, and the *cis*-1,4 content of PBd is also high, over 98%. The M_w of PBd decreased rapidly with increasing amount of Al(i-Bu)₂H, from 84×10^4 to 43×10^4 g mol⁻¹, and the MWD becomes much

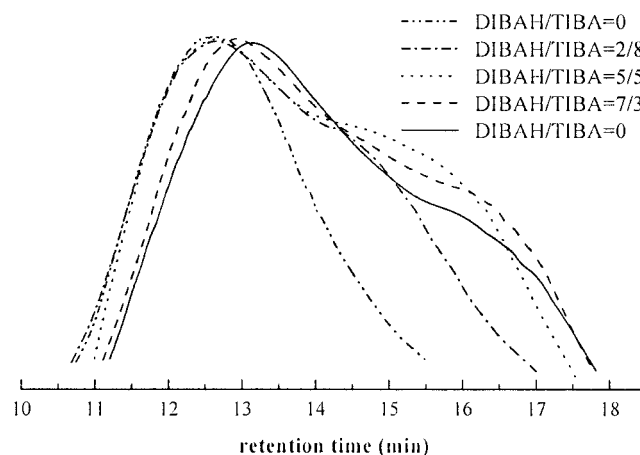


Figure 3 GPC curves of polybutadiene using composite aluminum alkyl cocatalyst. Polymerization conditions are the same as in Table III.

TABLE III
Effect of Composite Cocatalyst on the Gas Phase Polymerization of Bd^a

DIBAH/TIBA (molar ratio)	Activity (kg/PBd/mol ⁻¹ /Nd/h ⁻¹)	M_w (10 ⁴)	MWD	Microstructure of PBd (%)		
				<i>cis</i> -1,4	<i>trans</i> -1,4	<i>vinyl</i> -1,2
0	1027	84	2.80	98.9	0.45	0.65
2/8	1138	80	6.19	98.5	0.32	1.18
5/5	1062	53	7.80	98.4	0.44	1.16
7/3	938	45	8.11	98.7	0.20	1.10
10/0	551	43	7.56	98.3	0.52	1.18

^a Polymerization conditions: [Nd] = 2.6×10^{-5} mol/L, Al/Nd = 80, Cl/Nd = 4, $T = 40^\circ\text{C}$, 45 min at 0.2 MPa.

broader, from 2.80 corresponding to a DIBAH/TIBA molar ratio of 0, to 8.1 with a DIBAH/TIBA ratio of 7/3. The results indicate that, using a composite aluminum alkyl cocatalyst and varying its molar ratio of the two components, can effectively control the MW and MWD of PBd. With the increase of DIBAH in the cocatalyst, the shoulder on the low molecular weight side of the GPC curves becomes more obvious, which coincides with the trends of MWD. Thus the polybutadiene rubber with high MW and narrow MWD, or a practical MW and broad MWD, can be procured individually by changing the components and the amount of aluminum alkyl cocatalyst.

Effect of polymerization time

The effect of polymerization time on the MW and MWD of PBd was investigated and is listed in Table IV. It has been observed that, with increasing polymerization time, the PBd prepared maintains a high *cis*-1,4 content, although the catalyst activities decrease gradually. The polymerization rate at each instant of time was determined by the gaseous Bd feed rate required to maintain constant pressure in the reactor. The polymerization rate of the gas phase polymerization of Bd is shown in Figure 4. Evidently the polymerization rate has a peak between 10 to 15 min, which is in agreement with the trends of the catalytic activity. The observed decline in polymerization rate was attributed to the deactivation of active sites and the interparticle monomer diffusion resistances.

Figures 5 and 6 depict the GPC elution curves of PBd obtained with different cocatalysts at different polymerization times. Within the starting period of the polymerization, the GPC elution curves of PBds, obtained with Nd-based catalysts, showed a bimodal distribution, suggesting that the gas phase polymerization of Bd proceeds with two active centers. It has been proposed^{19–21} that two different sites are generated in Nd-catalyzed polymerization: one is a fast but short-lived center (C_1^*) and the other is a slow growing but stable center (C_2^*); the second (slow) type of chain growth has been described as proceeding in a *quasi*-living manner. Obviously, the effect of polymerization time on the MWs and MWDs of PBd can be well explained by the mechanism of the two active sites. Because the active center C_1^* is fast growing, is readily deactivated, and transfers the C_1^* , it leads to PBd with MW independent of the reaction time. Thus the position of the higher MW peak scarcely changes as the polymerization time is prolonged. The active center C_2^* is stable and slow growing, which forms polymers with MW increasing with increasing of polymerization time. Therefore a longer polymerization time gives a slightly higher MW PBd with relatively narrower MWD.

Comparing Figure 5 with Figure 6, it can be seen that the cocatalyst has a substantial effect on the formation and distribution of the two active centers. Clearly, in the beginning of polymerization, the formation of C_1^* is promoted when using Al(*i*-Bu)₃ as cocatalyst. Using the composite cocatalyst Al(*i*-Bu)₃/

TABLE IV
Effect of Polymerization Time on MW and MWD of PBd

Aluminum alkyl	Time (min)	Catalytic efficiency (kg/PBd/mol ⁻¹ /Nd/h ⁻¹)	M_w (10 ⁴)	MWD	<i>cis</i> -1,4 Content (%)
TIBA ^a	15	2240	82, 1.7	3.64, 1.48	98.4
	30	1281	80, 3.6	2.45, 1.63	98.8
	45	1335	59	7.20	98.5
	60	1513	68	6.61	97.8
DIBAH/TIBA ^b	10	2259	88, 8.1	3.41, 1.11	98.1
	20	1860	82, 10	2.89, 1.13	98.4
	30	1348	61, 11	2.08, 1.23	98.0

^a [Nd] = 2.6×10^{-5} mol/L, Al/Nd = 120, Cl/Nd = 4, 40°C at 0.2 MPa.

^b [Nd] = 2.6×10^{-5} mol/L, DIBAH/TIBA = 3/7 (molar ratio), Al/Nd = 100, Cl/Nd = 4, 40°C at 0.2 MPa.

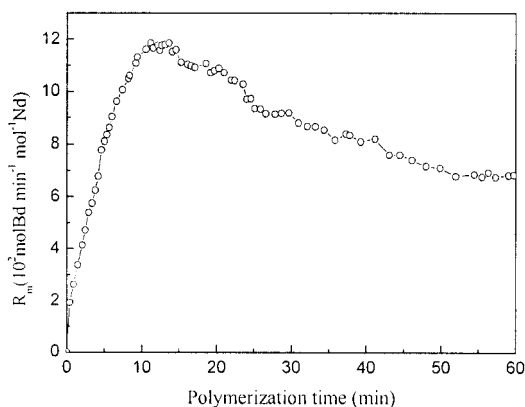


Figure 4 Polymerization rate of gas phase polymerization of Bd. Conditions: $[N] = 2.6 \times 10^{-5}$ mol/L; DIBAH/TIBA = 2/8; Al/Nd = 80; Cl/Nd = 4; 40°C at 0.2 MPa.

Al(i-Bu)₂H seems to promote the formation of C₂^{*}. With further polymerization, the relative amount of C₁^{*} increased, which may be related to new active centers caused by chain-transfer reactions of C₁^{*}.

CONCLUSIONS

High activity with high *cis*-1,4 content and controllable molecular weight gas phase polymerization of Bd were achieved with the SiO₂-supported Nd(naph)₃/Al₂Et₃Cl₃/Al(i-Bu)₃ or/and Al(i-Bu)₂H catalysts. The catalytic activity and MW of polymers depended on the reaction temperature, the reaction time, the Nd(naph)₃/Al(i-Bu)₃ ratio, and cocatalyst component. The high *cis*-1,4 content of the polymer was not significantly influenced by the polymerization conditions examined. The catalytic system has two kinds of active species that initiate the polymerization to produce polymer with high and low MW, respectively. Both the amount and the component of aluminum alkyl cocatalyst affected the MW and MWD of polymers because of the number and nature of the catalyst sites

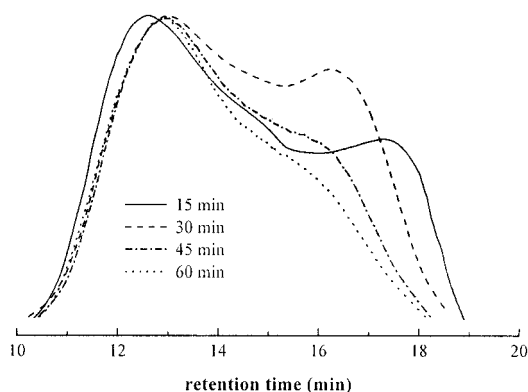


Figure 5 GPC curves of PBd at different reaction times. Conditions: $[N] = 2.6 \times 10^{-5}$ mol/L; TIBA as cocatalyst; Al/Nd = 120; Cl/Nd = 4; 40°C at 0.2 MPa.

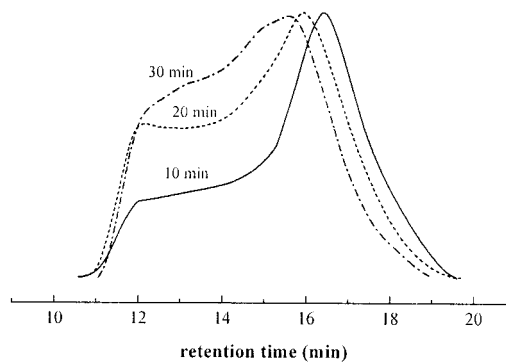


Figure 6 GPC curves of PBd at different reaction times. Conditions: $[N] = 2.6 \times 10^{-5}$ mol/L; DIBAH/TIBA = 3/7; Al/Nd = 100; Cl/Nd = 4; 40°C at 0.2 MPa.

created. Chain transfer to the cocatalyst is an important factor governing MWD.

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