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Characterization of Polymer-Supported Rare-Earth Metal Complexes and Their Catalytic Behavior in Polymerization of Conjugated Dienes

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CHARACTERIZATION OF POLYMER-SUPPORTED RARE-EARTH METAL COMPLEXES AND THEIR CATALYTIC BEHAVIOR IN POLYMERIZATION OF CONJUGATED DIENES

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ABSTRACT

The polymerization and catalytic behavior of catalyst systems composed of polymer-supported rare-earth metals were investigated. The catalyst systems show high catalytic activity and stereospecificity for butadiene polymerization. The catalytic efficiency for SMC (styrene-2-(methylsulfanyl)ethyl methacrylate copolymer).NdCl₃-Al(*i*-C₄H₉)₃ system is twice or three times that of the NdCl₃.4DMSO system. The activity of the ternary system SAAC (styrene-acrylic acid copolymer).Nd-Ph₃CCl-Al(*i*-C₄H₉)₃ was up to 170 kg polybutadiene/(g Nd·h). The *cis*-1,4 content of polybutadiene was more than 98%. This system was also used for isoprene polymerization. The *cis*-1,4 content of the polyisoprene obtained was about 96%.

INTRODUCTION

Certain transition metals pendant on the polymer chain have high catalytic activity in comparison with typical Ziegler-Natta catalysts [1-4]. In recent years, for this purpose, only those with *d*-electrons, such as Fe, Co, Ni, Ti, and V, have been reported [5-7]. Recently, we [8, 9] described a new catalyst system composed of polymer-supported neodymium complex for the polymer-

ization of conjugated dienes. In this paper we introduce our recent results on polymer-supported rare-earth metal complexes.

EXPERIMENTAL

Materials

Commercial pure grade *n*-hexane, toluene, and alkyl chlorides were purified by the usual procedures. Acrylic acid and methylacrylic acid, as well as styrene, were repeatedly vacuum distilled before use. 2-(Methylsulfinyl)ethyl methacrylate [10-13], rare earth chlorides (LnCl_3 , where $\text{Ln} = \text{La, Pr, Nd, Eu, Ho, Er, Tm, Yb}$) [14], and neodymium chloride-dimethylsulfoxide complex ($\text{NdCl}_3 \cdot 4\text{DMSO}$) [15] were prepared according to the literature. The polypropylene powder was obtained from Xiang Yang Chemical Plant, Beijing. Butadiene and isoprene were dried over active alumina before use.

Preparation of Polymer Supports and Their Rare Earth Metal Complexes

Styrene-acrylic acid copolymer (SAAC), styrene-methylacrylic acid copolymer (SMAC) [16], and polypropylene-graft-polyacrylic acid (PP-g-PAA) [17] were prepared according to the literature. The content of the functional group $-\text{COOH}$ in the polymer was determined by acid-base titration. Styrene (S) and 2-(methylsulfinyl)ethyl methacrylate (M) were copolymerized at 70°C for 48-50 h in toluene in vacuum-sealed tubules with azobisisobutyronitrile as initiator. The copolymer (SMC) obtained was dissolved in tetrahydrofuran, reprecipitated in hydrogenated petroleum, and dried under vacuum at 40°C for 48 h. The content of S in the polymer was determined by elementary analysis.

For the preparation of polymer-supported rare-earth (Ln) metal complexes, two methods were developed. In the first method, rare-earth chloride was directly mixed with polymer in methyl ethyl ketone, and the reaction product was precipitated out immediately or by addition of a precipitant. In the second method, the polymer suspension was reacted with a solution of rare-earth chloride, and the reaction product was then washed with the solvent to remove the unabsorbed rare-earth chloride. The content of Ln in the polymer-supported rare-earth metal complexes was determined by complexometric titration after ignition.

The IR spectra of the polymer supports and their complexes were taken in KBr pellets employing a Perkin-Elmer infrared spectrophotometer, Model 599B.

Polymerization Procedure and Analysis of Polymer

In addition to the comparative tests of activity which were carried out in a 100-mL stainless-steel reactor equipped with a magnetic stirrer, the other polymerization was carried out in 50-mL ampules under Ar, carefully excluding moisture and air. The polymerization was terminated by adding an ethanol solution that contained phenyl- β -naphthylamine. The resulting polymer was precipitated with an excess of ethanol and dried under vacuum below 40°C to constant weight.

The intrinsic viscosity $[\eta]$ of these polymers was determined with an Ubbelohde viscometer in toluene solution at 30°C. The infrared spectra of polymer films on NaCl plates were recorded on a Perkin-Elmer 599B IR spectrophotometer. The relative amounts of *cis*-1,4, 1,2, and *trans*-1,4-polybutadiene were determined by measuring the corresponding optical density D_ν at $\nu = 738, 911, \text{ and } 967 \text{ cm}^{-1}$, respectively. For polyisoprene the relative amount of 1,4 and 3,4 structure was determined by D_ν at $\nu = 840 \text{ and } 890 \text{ cm}^{-1}$, respectively.

RESULTS AND DISCUSSION

The parameters of polymer-supported rare-earth metal complexes obtained are listed in Table 1. In the IR spectra of SAAC.Nd, bands at 1 450, 1 500, and 1 700 cm^{-1} , characteristic of $-\text{COOH}$ and $\text{C}=\text{O}$ groups in SAAC, appear broadened and shortened (Fig. 1). This is believed to be related to the splitting of vibration absorption band of the carboxyl group on its combination with the rare-earth cation [18]. Thus the $-\text{COOH}$ groups of the polymer have reacted with Nd^{3+} to form $-(\text{COO})_3\text{Nd}$, as shown schematically in Fig. 2. The Nd-O bond in SAAC.Nd is rich in the covalent bond in comparison with low-MW molecules of rare-earth carboxylates. The complex PP-*g*-PAA.Nd gives an analogous IR-spectrum in which the absorption peak of the $\text{C}=\text{O}$ group is shortened and that of the $-\text{COOH}$ group shifts and appears at 1 535 cm^{-1} (Fig. 3). In the IR spectra of SMC.LnCl₃ (Fig. 4), the characteristic absorption band of the S-O group is shifted from 1 044 cm^{-1} in SMC to 998-1 006 cm^{-1} in SMC.LnCl₃, indicating the formation of the complex with the coordinate bond >S-OLnCl_3 .

It is clearly seen from Table 2 that the formation of metal complex increases the thermal stability of the copolymer SMC. The color of SMC.LnCl₃ closely resembles that of the respective parent chloride, changing from lighter to darker shade with an increasing amount of metal in it. The weight percentage of rare-earth metal in the complex gradually increases from La to Yb,

TABLE 1. Parameters of Polymer-Supported Nd Complexes

Polymer support	Functional groups		Quantity of bound metal		Type of Nd(III) binding with polymer support
	wt%	$\mu\text{mol/g}$	mol/g	mol/mol of functional group	
SAAC	14.3	3.2	6.7	0.21	$\left(\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagdown \\ \text{O}^- \end{array} \right)_3 \text{Nd}$
PP-g-PAA	8.6	1.9	1.4	0.07	$\left(\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagdown \\ \text{O}^- \end{array} \right)_3 \text{Nd}$
SMC	14.3	3.0	6.8	0.23	$> \text{S}=\text{O} \rightarrow \text{NdCl}_3$

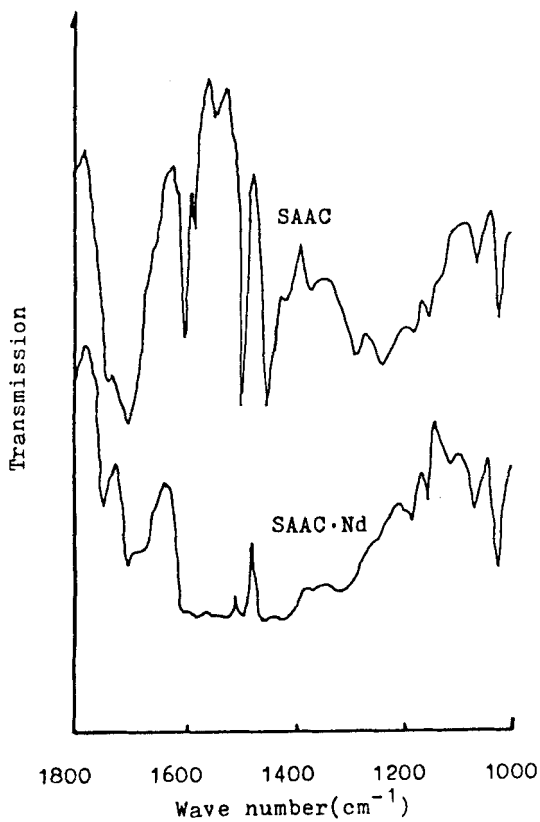


FIG. 1. IR absorption spectra: SAAC and SAAC·Nd complex.

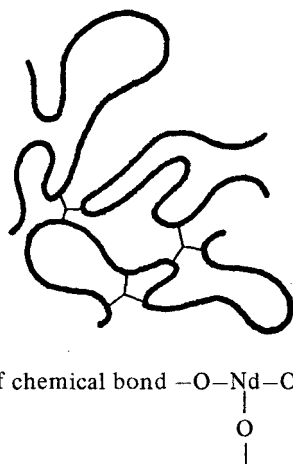


FIG. 2. Schematic of chemical bond -O-Nd-O- in macromolecule.

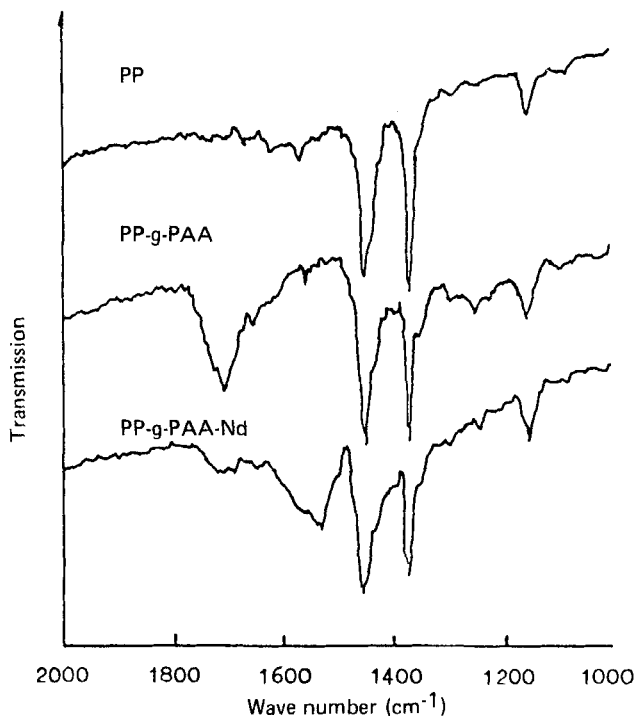


FIG. 3. IR absorption spectra: PP, PP-g-PAA, and PP-g-PAA·Nd.

while the mole number is nearly the same. This may be related to the similar complexing ability of the S—O group with different rare-earth chlorides.

It is seen from Table 3 that the catalytic system formed from the polymer-supported Nd complex shows high catalytic activity and stereospecificity for butadiene polymerization. The catalytic efficiency for the $\text{SMC.NdCl}_3\text{-Al}(i\text{-C}_4\text{H}_9)_3$ system is twice or three times that of the $\text{NdCl}_3\cdot 4\text{DMSO}$ system. The activity of the ternary system, $\text{SAAC.Nd-Ph}_3\text{CCl-Al}(i\text{-C}_4\text{H}_9)_3$, was up to 170 kg polybutadiene/(g Nd·h). The *cis*-1,4 content of polybutadiene was more than 98%.

In the ternary systems formed from SAAC.Nd, the activity is very different for different kinds of aluminum alkyl halides as the third component (Table 4). The following order of activity was found: $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} > \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2 > \text{Al}(\text{C}_2\text{H}_5)_2\text{Br}$. When we used alkyl chloride in place of aluminum alkyl halide, the catalytic activity depended on the kinds of aluminum compounds as well as the solvent of catalyst preparation, as shown in Table 5. Triphenylchloromethane

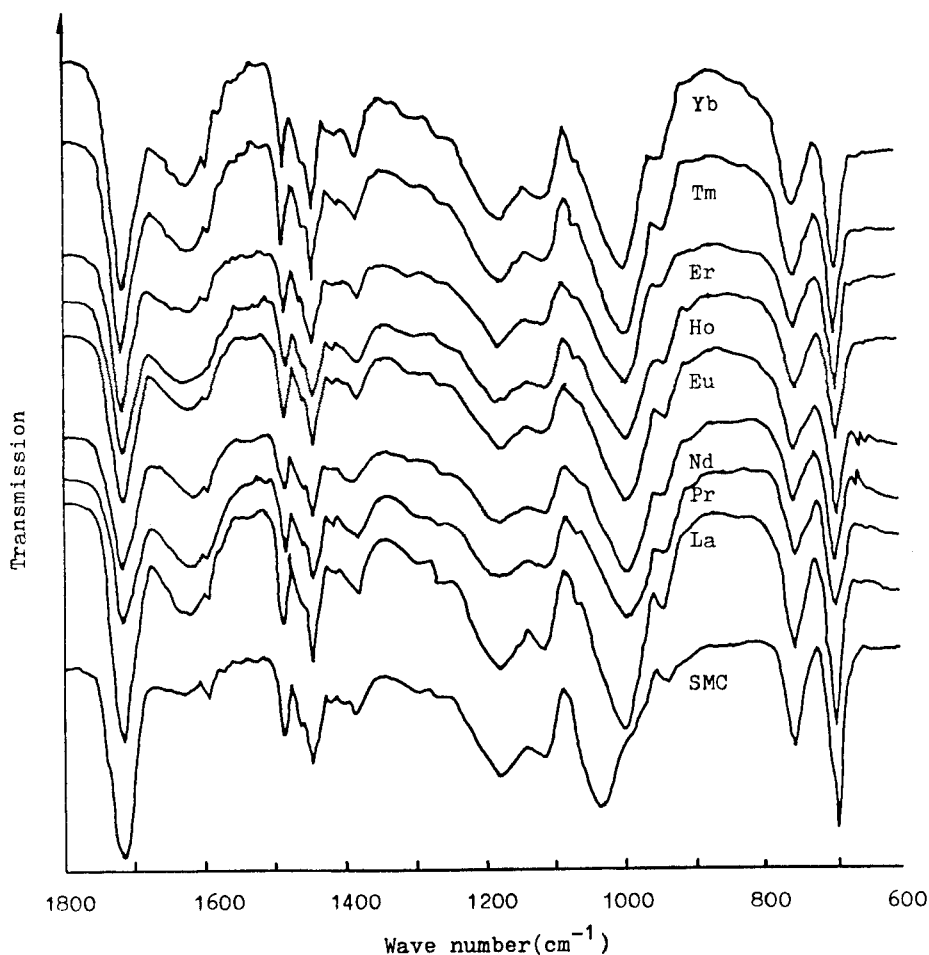


FIG. 4. IR absorption spectra: SMC and SMC·LnCl₃ complexes.

is the best of all the alkyl chlorides. In comparison with hexane, toluene is a good solvent. The activity of this catalyst is also dependent on the amount of the third component used. The highest catalytic activity and the lowest intrinsic viscosity of the polymer were found when Ph₃CCl was added at a Cl/Nd ratio of 3-5. When Al(C₂H₅)₂Cl was used instead, the useful region of the Cl/Nd ratio was narrower and there was a maximum (Fig. 5).

TABLE 2. Physical Characteristic of SMC and SMC.LnCl₃

Complex	Color	$T_s, ^\circ\text{C}^a$	$T_d, ^\circ\text{C}^a$	Content of Ln, mol%
SMC	White	—	240	—
SMC.LaCl ₃	White	239	252	8.39 (0.0604)
SMC.PrCl ₃	Light green	256	260	9.35 (0.0664)
SMC.NdCl ₃	Reddish violet	252	264	9.85 (0.0683)
SMC.EuCl ₃	White	249	258	9.88 (0.0650)
SMC.HoCl ₃	Light yellow	252	264	10.34 (0.0627)
SMC.ErCl ₃	Light pink	248	250	10.62 (0.0635)
SMC.TmCl ₂	White	248	252	11.30 (0.0669)
SMC.YbCl ₃	White	243	256	11.16 (0.0645)

^aSoftening point and decomposition temperature measured with a Japan Rigaku thermal analyzer.

Table 6 presents the effect of various aluminum alkyls in polymer-supported Nd complex system on the polymerization of butadiene. The order of their activity is $\text{Al}(i\text{-C}_4\text{H}_9)_3 > \text{Al}(i\text{-C}_4\text{H}_9)_2\text{H} > \text{Al}(\text{C}_2\text{H}_5)_3$. The activity of the system increases with increasing Al/Nd ratio, and the $[\eta]$ of the polybutadiene obtained decreases sharply (Fig. 6), as occurs with conventional Ziegler-Natta catalysts.

For the binary system composed of SMC.LnCl₃ (Ln = Pr, Nd), the catalytic activity of the Pr system is not as high as that of Nd, but the *cis*-1,4 content of the polybutadiene remains the same (Table 7).

The ternary system of SAAC.Nd was also used for isoprene polymerization. The *cis*-1,4 content of the polyisoprene obtained was about 96% (Table 8).

From data listed in Table 9, we can see that a much lower or higher content of Nd in SAAC.Nd led to a decrease of the catalyst activity. The reason may be that when the Nd content is at a low level, that is, the amount of Nd per unit support volume is small, the active center formed will also be insufficient, and when the Nd content is at a high level, a portion of Nd is embedded, and only the Nd metal on the surface of the formed catalyst will be activated, as usually occurs in Ziegler-Natta heterogeneous catalyst systems. The activity

TABLE 3. Activity of Various Catalyst Systems^a

Catalyst system	Nd/Bd, $\mu\text{mol/g}$	Al/Nd atomic ratio	Time, min	Activity, kg PB/(g Nd·h)	$[\eta]$, dL/g	Microstructure, %	
						<i>cis</i> -1,4	<i>trans</i> -1,4
SAAC.Nd-Ph ₃ CCl-Al(<i>i</i> -C ₄ H ₉) ₃	0.1	2 000	20	137	3.5	98.8	0.7
	0.2	1 500	10	169	2.2	98.4	1.2
	0.2	1 000	10	143	2.8	98.5	0.9
	0.2	500	15	83	3.3	98.0	1.3
	0.3	500	15	93	3.4	98.8	0.7
	0.3	1 000	15	56	2.7	98.1	1.1
SMC.NdCl ₃ -Al(<i>i</i> -C ₄ H ₉) ₃	0.3	1 000	30	33	2.8	98.0	1.2
	0.3	300	30	17	6.5	98.4	1.0
	0.2	200	30	19	8.5 ^b	98.6	0.7
	0.3	1 000	30	16	2.7	98.7	0.8
NdCl ₃ .4DMSO-Al(<i>i</i> -C ₄ H ₉) ₃	0.3	300	30	8	5.9	99.0	0.6
	0.3	300	30	8	5.9	99.0	0.6

^aMonomer butadiene; M = 16–17 g; M/hexane 1.6 g/mL; ternary system, Cl/Nd (atomic ratio) = 4.^bBlock polymerization, M = 21 g.

TABLE 4. Polymerization of Butadiene^a with SAAC.Nd- $\text{AlR}_n\text{X}_{3-n}$ - $\text{Al}(i\text{-C}_4\text{H}_9)_3$ Catalyst Systems

$\text{AlR}_n\text{X}_{3-n}$	Conversion, %	$[\eta]$, dL/g
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	92	7.3
$\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$	72	7.3
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}$	46	8.0

^aPolymerization conditions: $[\text{M}] = 10 \text{ g}/100 \text{ mL}$ hexane, $\text{Nd}/\text{M} = 1 \text{ } \mu\text{mol}/\text{g}$, Cl/Nd atomic ratio = 3, Al/Nd atomic ratio = 80, 50°C , 8 h.

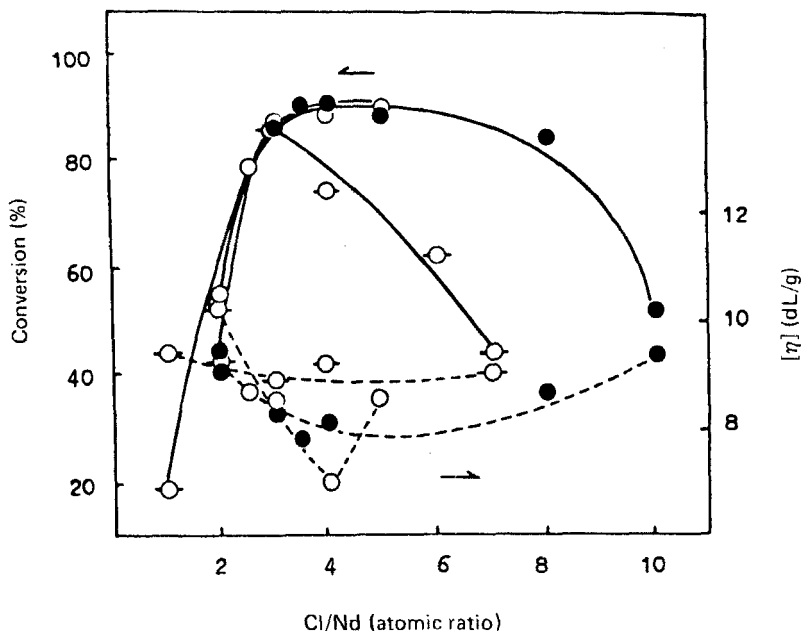


FIG. 5. Effect of Cl/Nd ratio on polymerization. Polymerization conditions: (○) SAAC.Nd- $\text{Ph}_3\text{CCl}-\text{Al}(i\text{-C}_4\text{H}_9)_3$ system; $\text{Nd}/\text{Bd} = 0.2 \text{ } \mu\text{mol}/\text{g}$; $\text{Al}/\text{Nd} = 300$; 50°C ; 6 h. (●) SAAC.Nd- $\text{Ph}_3\text{CCl}-\text{Al}(i\text{-C}_4\text{H}_9)_3$ system; $\text{Nd}/\text{Bd} = 0.3 \text{ } \mu\text{mol}/\text{g}$; $\text{Al}/\text{Nd} = 200$; 50°C ; 4 h. (○) SAAC.Nd- $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{Al}(i\text{-C}_4\text{H}_9)_3$ system; $\text{Nd}/\text{Bd} = 0.3 \text{ } \mu\text{mol}/\text{g}$; $\text{Al}/\text{Nd} = 200$; 50°C ; 8 h.

TABLE 5. Effect of Various Alkyl Chlorides on Polymerization of Butadiene^a

RCl	Nd/Bd, μmol/g	RCl, mmol/mL		Conversion, %	[η], dL/g	Microstructure, %		
		Toluene	Hexane			<i>cis</i> -1,4	<i>trans</i> -1,4	
Ph ₃ CCl	0.2	0.1		92	9.0	98.4	1.0	0.6
	0.2	0.5		92	8.5	99.0	0.4	0.6
	0.2		0.1	72	8.8	98.7	0.9	0.4
PhCH ₂ Cl	0.2	0.5		80	10.8	98.4	1.0	0.6
	0.2		0.5	22	13.5	98.8	0.8	0.4
CH ₂ =CHCH ₂ Cl	0.2	0.5		76	9.8	99.0	0.7	0.3
	0.2		0.5	14	10.2	98.6	0.9	0.5
CCl ₄	0.2	0.5		66	11.9	98.9	0.8	0.3
	0.2		0.5	42	12.4	98.4	1.0	0.6
C ₂ H ₅ CH ₂ CH ₂ Cl	0.3	0.5		Trace	—	—	—	—
(CH ₃) ₂ CHCH ₂ Cl	0.3	0.5		Trace	—	—	—	—
(CH ₃) ₂ CHCH ₂ CH ₂ Cl	0.3	0.5		Trace	—	—	—	—

^aLong-chain saturated alkyl chlorides: Cl/Nd atomic ratio = 3, Al/Nd atomic ratio = 200, 50 °C, 8 h. Other chlorides: Cl/Nd atomic ratio = 3.5, Al/Nd atomic ratio = 200, 50 °C, 6 h.

TABLE 6. Polymerization of Butadiene with SAAC.Nd-Al(C₂H₅)₂Cl-AlR₃ Catalyst Systems^a

AlR ₃	Conversion, %	[η], dL/g
Al(<i>i</i> -C ₄ H ₉) ₃	92	7.3
Al(<i>i</i> -C ₄ H ₉) ₂ H	34	4.0
Al(C ₂ H ₅) ₃	24	—

^aPolymerization conditions: Nd/M = 1 mmol/g, Cl/Nd atomic ratio = 3, Al/Nd atomic ratio = 80, 50°C, 8 h.

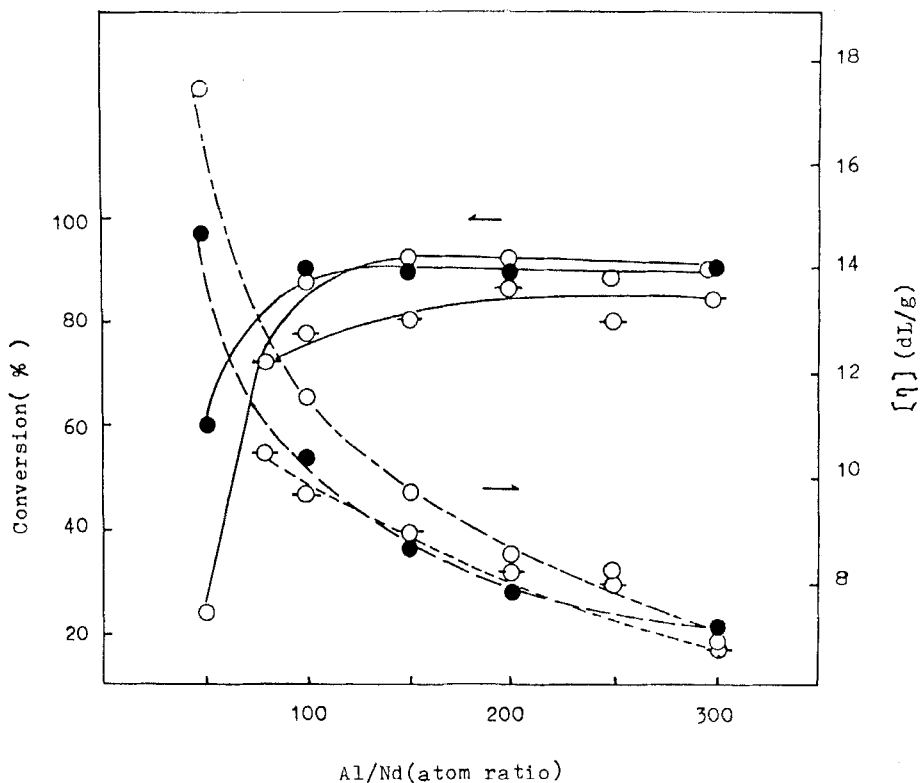


FIG. 6. Effect of Al/Nd ratio on polymerization. Polymerization conditions: (○) SAAC.Nd-Ph₃CCl-Al(*i*-C₄H₉)₃ system; Nd/Bd = 0.2 μmol/g; Cl/Nd = 3.5; 50°C; 6 h. (●) SAAC.Nd-Ph₃CCl-Al(*i*-C₄H₉)₃ system; Nd/Bd = 0.3 μmol/g; Cl/Nd = 3.5; 50°C; 4 h. (—○—) SAAC.Nd-Al(C₂H₅)₂Cl-Al(*i*-C₄H₉)₃ system; Nd/Bd = 0.3 μmol/g; Cl/Nd = 3; 50°C; 8 h.

TABLE 7. Polymerization of Butadiene with SMC.LnCl₃-Al(*i*-C₄H₉)₃ Catalyst Systems^a

Complex	Nd/Bd, μmol/g	Al/Nd atomic ratio	Conversion, % (50°C, 5 h)	[η], dL/g	Microstructure, %		
					<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
SMC.NdCl ₃	5	100	88	4.6	98.1	1.3	0.6
	2.5	100	70	7.2	98.0	1.4	0.6
SMC.PrCl ₃	5	100	52	3.7	97.9	1.4	0.7
	2.5	100	28	5.0	97.9	1.4	0.7

^a[Ln] = 25 μmol/mL toluene.

TABLE 8. Polymerization of Isoprene with SAAC.Nd-Ph₃CCl-Al(*i*-C₄H₉)₃ Catalyst System

Nd/isoprene, μmol/g	Cl/Nd atomic ratio	Al/Nd atomic ratio	Conversion, % (50°C, 8 h)	[η], dL/g	Microstructure, %	
					<i>cis</i> -1,4	3,4
0.5	3.5	50	78	10.8	94.2	5.8
0.4	3.5	100	90	8.8	96.5	3.5
0.5	3.5	100	98	7.0	93.9	6.1
0.4	3.5	150	94	7.4	95.0	5.0
0.5	3.5	150	98	5.8	94.9	5.1

TABLE 9. Effect of Various Polymer-Supported Nd Complexes and Content of Nd in the Complexes on Polymerization of Butadiene^a

Complex	Grain size, mesh	Nd, mmol/g	Conversion, %	[η], dL/g	Microstructure, %		
					<i>cis</i> -1,4	<i>trans</i> -1,4	1,2
SMAC.Nd	160	0.72	76	9.4	98.4	1.1	0.5
SAAC.Nd	160	0.53	62	9.6	98.7	0.9	0.4
	160	0.66	90	9.0	98.6	1.1	0.3
	Unground	0.66	90	7.4	98.6	1.0	0.4
	160	0.73	88	9.3	98.8	1.0	0.2
	160	0.87	84	12.4	98.8	0.8	0.4

^aPolymerization conditions: Nd/M = 0.2 μ mol/g; third component, Ph₃CCl; Cl/Nd atomic ratio = 3.5; cocatalyst, Al(*i*-C₄H₉)₃; Al/Nd atomic ratio = 200; 50°C; 6 h.

of the system prepared from SMAC.Nd is not as high as that of SAAC.Nd. This may be due to the steric effect of methyl groups on the polymer chains. The various polymer-supported Nd complexes make little difference to the microstructures of the polybutadiene obtained.

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