

Soluble neodymium chloride 2-ethylhexanol complex as a highly active catalyst for controlled isoprene polymerization

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Dedicated to memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

Soluble $\text{NdCl}_3 \cdot 3\text{EHOH}$ (2-ethyl hexanol) in hexane combined with AlEt_3 is highly active for isoprene polymerization in hexane. The $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ has higher activity than the typical binary catalyst $\text{NdCl}_3 \cdot 3\text{PrOH}$ (isopropanol)/ AlEt_3 and ternary catalyst NdV_3 (neodymium versatate)/ $\text{AlEt}_2\text{Cl}/\text{Al}(i\text{-Bu})_2\text{H}$. The molecular weight of polyisoprenes can be controlled by variation of $[\text{Nd}]$, $[\text{Al}]/[\text{Nd}]$ ratio and polymerization temperature and time. The $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst polymerized isoprene to afford products featuring high *cis*-1,4 stereospecificity (ca. 96%), high molecular weight (ca. 10^5) and relatively narrow molecular weight distributions ($M_w/M_n = 2.0\text{--}2.8$) simultaneously. More importantly, some living polymerization characteristics were demonstrated: (a) absence of chain termination; (b) linear correlation between M_n and polymer yield; (c) increment of molecular weight in the ‘seeding’ polymerization. Though some deviation from the typical living polymerization such as molecular weight distribution is not narrow enough and the line of M_n and polymer yield does not extrapolate to zero, controlled polymerization with the current catalyst can still be concluded.

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1. Introduction

Neodymium (Nd)-based catalysts are highly effective in stereospecific polymerization of 1,3-dienes. Typical Nd-based catalyst systems are mostly classified into two types, that is, binary systems derived from $\text{NdCl}_3 \cdot n\text{L}$ (L is an organic electron-donating ligand and n is the coordination number) and AlR_3 , and ternary systems composed of Nd carboxylate (e.g. naphthenate and versatate), AlR_3 (e.g. $\text{Al}(i\text{-Bu})_3$, $\text{Al}(i\text{-Bu})_2\text{H}$ and AlEt_3) and a chloride-containing compound (e.g. AlEt_2Cl , $t\text{-BuCl}$ and Me_2SiCl_2). Both types of catalysts show high activity and high *cis*-1,4 stereospecificity in hydrocarbon

solution, providing polybutadiene, polyisoprene and butadiene–isoprene copolymers with high *cis*-1,4 content (>95%). These polymers exhibit excellent properties widely used as tires and other elastic materials [1–8].

In comparison with the ternary system, binary system has not been employed extensively in commercial application due to relatively lower activity resulting from poor solubility in aliphatic solvents. Promoting catalytic behaviors of binary system can be set about: (a) improving dispersion state of the solid NdCl_3 ; (b) improving the solubility using suitable electron-donating compound. Kwag et al. [9] prepared nano-sized NdCl_3 as a state of colloid in a nonpolar medium and found that its catalytic activity was comparable to that of the ternary Nd-based catalyst. Barbotin et al. [10] reported improved activity of binary system by supporting NdCl_3 on Lewis acid treated silica. $\text{NdCl}_3 \cdot 3\text{TBP}$ (tributyl phosphite)

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was soluble in toluene, but toxicity and negative effect of toluene on activity and molecular weight of the resulting polymer make it unfavorable in practical application [11].

Living polymerization has become a field of rapidly growing interest and importance but there are few reports on lanthanide-mediated 1,3-diene polymerization. According to Refs. [12,13], the molecular weight of polymer increases with monomer conversion, but rather broad molecular weight distribution makes it deviate from living polymerization. $\text{NdCl}_3 \cdot 3\text{PrOH}/\text{AlEt}_3$ could display the behavior of a quasi-living polymerization only at -70°C , but the chain transfer occurred violently as the temperature increased [14]. Dong et al. [15–17] prepared polyisoprene with narrow molecular weight distribution ($M_w/M_n < 2.0$) using MAO-activated $\text{Nd}(\text{O}^i\text{Pr})_3$ catalyst, but did not reported the catalyst for living polymerization. Up to now, living polymerization using Nd-based catalysts activated by AlR_3 at room temperature or above remains blank.

In this article, a novel composition of $\text{NdCl}_3 \cdot 3\text{EHOH}$ was synthesized. This complex featured high solubility in hexane, in contrast to hexane-insoluble $\text{NdCl}_3 \cdot 3\text{PrOH}$ and $\text{NdCl}_3 \cdot n\text{EHOH}$ ($n = 1.5, 2.5$) [18]. The $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst was highly active in isoprene polymerization giving polymers with high *cis*-1,4 stereoregularity (ca. 96%), high molecular weight (ca. 10^5) and a relatively narrow molecular weight distribution ($M_w/M_n = 2.0\text{--}2.8$). More importantly, some living polymerization characteristics were demonstrated: (a) absence of chain termination; (b) linear correlation between M_n and polymer yield; (c) increment of molecular weight in the ‘seedling’ polymerization. Though some deviation from the typical living polymerization such as molecular weight distribution is not narrow enough and line of M_n and polymer yield does not extrapolate to zero, controlled polymerization with the current catalyst can still be concluded.

2. Experimental

2.1. Materials

Isoprene (Fluka) was dried by refluxing over calcium hydride for 2 h and distilled. Butadiene (Jinzhou Petrochemical Company) was purified by passing through two successive columns containing potassium hydroxide and active alumina. Hexane (Beijing Reagents Factory) was dried by heating to reflux over sodium benzophenone ketyl until the solution turned blue and then was distilled before use. EHOH (Beijing Reagents Factory) was dried by refluxing over sodium for 4 h and was distilled. AlEt_3 (Fluka), $\text{Al}(i\text{-Bu})_2\text{H}$ (Akzo Noble) and AlEt_2Cl (Merck) were diluted to 2.0 M solution by hexane. Anhydrous NdCl_3 and $\text{NdCl}_3 \cdot 3\text{PrOH}$ were prepared according to the literature [19,20]. NdV_3 was prepared in our laboratory.

2.2. Synthesis and characteristic of $\text{NdCl}_3 \cdot 3\text{EHOH}$

EHOH (30.0 mL) was added to anhydrous NdCl_3 (3.336 g, 13.0 mmol) in an 100 mL two-neck round-bottom flask. The

NdCl_3 was dissolved in EHOH at 140°C and then reacted for 8 h. The excess EHOH was removed under vacuum at 80°C . The product was purple solid.

The complex was analyzed for the metal Nd, chlorine and EHOH components. The Nd content was determined by EDTA titration using xylenol orange as indicator. The chlorine content was analyzed by the VOLHARD’s method. The EHOH reacted with acetic anhydride, and then the product acetic acid was determined by sodium hydroxide titration using the mixture of cresol red and thymol blue as indicator [21]. The result indicated that the molar ratio of Nd/Cl/EHOH was 1:2.92:3.07. Therefore the NdCl_3 complex was denoted as $\text{NdCl}_3 \cdot 3\text{EHOH}$.

$\text{NdCl}_3 \cdot 3\text{EHOH}$ was synthesized by the direct reaction between NdCl_3 and EHOH and featured high solubility in hexane, while RAO [18] synthesized $\text{NdCl}_3 \cdot 1.5\text{EHOH}$ and $\text{NdCl}_3 \cdot 2.5\text{EHOH}$ from $\text{NdCl}_3 \cdot n\text{PrOH}$ by an alcohol interchange reaction, the resulting complexes were insoluble in hydrocarbon solution. The different synthetic method could result in discrepancy of solubility of the corresponding complex.

2.3. Polymerization procedure

All the manipulations were performed under a dry nitrogen atmosphere. A detailed polymerization procedure (run 2) is described as a typical example. Hexane (1.40 mL), $\text{NdCl}_3 \cdot 3\text{EHOH}$ (0.10 M solution in hexane, 0.20 mL), butadiene (1.0 M solution in hexane, 0.20 mL) and AlEt_3 (2.0 M solution in hexane, 0.20 mL) ($[\text{Al}]/[\text{Nd}] = 20$) were placed in an ampoule with a septum via syringes, and then this catalyst solution ($[\text{Nd}] = 1.0 \times 10^{-5}$ mol/mL) was aged at room temperature for 1 h before use. Regarding the ternary catalyst, its preparation method was as follows (run 8): hexane (1.30 mL), NdV_3 (0.10 M solution in hexane, 0.20 mL), AlEt_2Cl (0.20 M solution in hexane, 0.30 mL) and $\text{Al}(i\text{-Bu})_2\text{H}$ (2.0 M solution in hexane, 0.20 mL) were placed in an ampoule with a septum via syringes, and then this catalyst solution ($[\text{Nd}] = 1.0 \times 10^{-5}$ mol/mL) was aged at room temperature for 1 h before use.

Hexane (17.0 mL) and isoprene (3.0 mL) were injected into a crown-sealed ampoule, and then the above preformed catalyst (0.30 mL) was added to induce the polymerization. Polymerization was carried out at 50°C for 1 h and then quenched by adding 10 mL of ethanol containing 2,6-di-*tert*-butyl-*p*-cresol (1%) as a stabilizer. The polymer was coagulated, repeatedly washed with ethanol, cut into small pieces, and finally dried under vacuum at 40°C to constant weight. The polymer yields were determined by gravimetry.

2.4. Polymer characterization

The molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) of polymers were measured by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, a series of four columns (HMW 7 THF, HMW 6E THF (two), HMW 2 THF) and Waters 2414 refractive index

detector. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min. The molecular weights of polyisoprenes were determined using a polystyrene calibration. Sample solutions (ca. 0.2 mg/mL) were filtered through a 0.45 μm microfilter before injection.

The microstructure of polyisoprenes was determined from IR spectra measured with Vertex-70 FTIR spectrophotometer. Film samples were prepared on a KBr disc by casting carbon disulfide solution (ca. 2–8 mg/mL) of polymer. The proportion of *cis*-1,4 and 3,4-unit was determined from the absorption bands at 836 and 890 cm^{-1} , according to the following formulas reported in literature [22].

$$1,4 - cis(\%) = 100 \times (145 \times A_{836} - 1.95 \times A_{890})/B$$

$$3,4(\%) = 100 \times (19.9 \times A_{890} - 1.79 \times A_{836})/B$$

$$B = (145 \times A_{836} - 1.95 \times A_{890}) + (19.9 \times A_{890} - 1.79 \times A_{836})$$

where A_{836} and A_{890} are the absorbance at 836 and 890 cm^{-1} , respectively.

3. Results and discussion

3.1. Comparison of catalytic activity of three catalytic systems

Three catalytic systems, i.e. $\text{NdCl}_3 \cdot 3\text{EtOH}/\text{AlEt}_3$, $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{AlEt}_3$ and $\text{NdV}_3/\text{AlEt}_2\text{Cl}/\text{Al}(i\text{-Bu})_2\text{H}$, were examined in isoprene polymerization with the variation of $[\text{Nd}]$ concentration. The results are summarized in Table 1.

All the catalytic systems are active in isoprene polymerization. The catalytic activity increases in the order: $\text{NdV}_3/\text{AlEt}_2\text{Cl}/\text{Al}(i\text{-Bu})_2\text{H} < \text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{AlEt}_3 < \text{NdCl}_3 \cdot 3\text{EtOH}/\text{AlEt}_3$. The $\text{NdCl}_3 \cdot 3\text{EtOH}/\text{AlEt}_3$ catalyst achieves the highest activity among the three catalysts. The binary catalysts readily produce polymer with higher M_n than the ternary catalyst system. The *cis*-1,4 contents of all the polymers are approximately 96%, indicating similar stereospecificity of both binary and ternary system in isoprene polymerization.

The ternary NdV_3 -based catalyst produces polymer with bimodal molecular weight distribution (Fig. 1(b)). This clearly

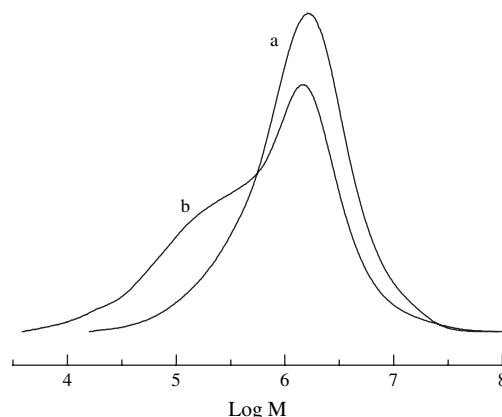


Fig. 1. The molecular weight distribution curves of polyisoprenes with (a) $\text{NdCl}_3 \cdot 3\text{EtOH}/\text{AlEt}_3$ (run 2) and (b) $\text{NdV}_3/\text{AlEt}_2\text{Cl}/\text{Al}(i\text{-Bu})_2\text{H}$ catalyst (run 8).

indicates that two kinds of active sites are presented in the ternary catalytic system, i.e. the fast propagating and insoluble species which leads to high molecular weight, and the slow propagating and soluble species which leads to low molecular weight [23,24]. In the case of binary $\text{NdCl}_3 \cdot 3\text{EtOH}$ catalyst, the molecular weight distribution curves are unimodal and the peak position corresponds to that of high molecular weight part of the bimodal molecular weight distribution curves of ternary catalyst system as seen in Fig. 1(a). This seems that the active species of binary system have structure similar to the insoluble and fast propagating active species of ternary catalyst system. In 1987, Shan demonstrated existence of two kinds of active species in the ternary system $\text{Nd}(\text{O}^i\text{Pr})_3/\text{AlEt}_3/\text{AlEt}_2\text{Cl}$ by analyzing the single crystal of active species of X-ray diffraction pattern (Fig. 2) [25]. Boisson et al. suggested that the A type active species in Fig. 2 were responsible for the high molecular polymers and B type were for the low molecular weight polymers [26]. Therefore the active species of $\text{NdCl}_3 \cdot 3\text{EtOH}$ -based catalyst might be of similar structure to A type active species.

$\text{NdCl}_3 \cdot 3\text{EtOH}$ -based catalyst gives higher polymer yield than $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ -based catalyst, indicating that the flexible ligand is favorable for the catalytic activity. $\text{NdCl}_3 \cdot 3\text{EtOH}$ is well-soluble in hexane and by activation with AlEt_3 , a colloid was formed which is well-dispersed in the solvent and

Table 1

Effect of catalyst concentration on isoprene polymerization (conditions: in hexane at 50 °C for 1 h, $[\text{IP}] = 1.50 \text{ M}$, $[\text{Al}]/[\text{Nd}] = 20$)

Run	Catalyst system	$[\text{Nd}]$ (mM)	Yield (%)	$M_n \times 10^{-3}^a$	M_w/M_n^a	<i>cis</i> -1,4 ^b (%)	3,4 ^b (%)
1	$\text{NdCl}_3 \cdot 3\text{EtOH}/\text{AlEt}_3$	0.05	21.8	1133	2.02	95.8	4.2
2		0.15	80.5	583	2.86	95.9	4.1
3		0.25	94.2	380	3.15	95.6	4.4
4	$\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{AlEt}_3$	0.05	11.2	1095	2.02	95.6	4.4
5		0.15	70.8	578	2.83	95.8	4.2
6		0.25	90.3	408	3.37	95.6	4.4
7	$\text{NdV}_3/\text{AlEt}_2\text{Cl}/\text{Al}(i\text{-Bu})_2\text{H}$	0.05	2.3	526	3.27	95.7	4.3
8		0.15	29.4	111	9.23	95.4	4.6
9		0.25	47.4	73	12.0	95.3	4.7

^a Determined by GPC (THF, PSt calibration).

^b The microstructure was determined by FTIR.

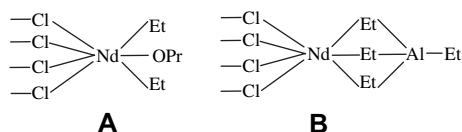


Fig. 2. Two possible kinds of active centers for the $\text{Nd}(\text{O}^i\text{Pr})_3/\text{AlEt}_3/\text{AlEt}_2\text{Cl}$ (1/10/1.5) ternary system (reprinted from Ref. [24]).

relatively stable. Whereas, $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ is insoluble in hexane and precipitate formed immediately when contacting with AlEt_3 . The low activities of $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ are due to its large particle size and only neodymium atoms located at the surface that can participate in reaction to form active species [27]. It is obvious that soluble $\text{NdCl}_3 \cdot 3\text{EHOH}$ is more facile to be alkylated by AlEt_3 , generates more active sites and exhibits higher activity as consequence.

3.2. Effect of [Nd]

The effect of [Nd] of $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst was examined at a fixed $[\text{Al}]/[\text{Nd}]$ ratio of 20, the results are listed in Table 1. The polymer yield increases with increasing [Nd] while M_n decreases as expected. Variation of [Nd] has little effect on the *cis*-1,4 stereospecificity, but affects the molecular weight distribution significantly. Thus, the M_w/M_n increases from 2.02 to 3.37 when [Nd] is raised from 0.05 to 0.25 mM.

3.3. Effect of $[\text{Al}]/[\text{Nd}]$ ratio

The effect of $[\text{Al}]/[\text{Nd}]$ ratio was examined with $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst at a fixed [Nd] of 0.10 mM (Table 2). The polymer yield increases with increasing $[\text{Al}]/[\text{Nd}]$ ratio from 15 to 40, M_n decreases and M_w/M_n tends to increase, which is ascribable to an increase in concentration of alkylated species and hence an increase in concentration of active centers. High *cis*-1,4 contents of around 96% are attained, which are independent on the $[\text{Al}]/[\text{Nd}]$ ratio. Therefore, the polymerization of isoprene with $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst at low $[\text{Al}]/[\text{Nd}]$ ratio (<20) could obtain polymer with high *cis*-1,4 content (ca. 96%) and narrow molecular weight distribution (ca. 2.0) simultaneously.

Table 2

Effect of $[\text{Al}]/[\text{Nd}]$ ratio and polymerization temperature on isoprene polymerization with $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst (conditions: in hexane for 1 h, $[\text{IP}] = 1.50 \text{ M}$, $[\text{Nd}] = 0.10 \text{ mM}$)

Run	$[\text{Al}]/[\text{Nd}]$	Temp. (°C)	Yield (%)	$M_n \times 10^{-3}^a$	M_w/M_n^a	<i>cis</i> -1,4 ^b (%)	3.4^b (%)
10	15	50	53.1	1133	1.99	96.2	3.8
11	20	50	66.5	706	2.48	95.8	4.2
12	30	50	69.3	393	3.67	95.5	3.5
13	40	50	74.5	342	4.09	95.4	3.6
14	20	0	9.5	947	2.00	96.8	3.2
15	20	30	17.9	1080	2.10	96.0	4.0
16	20	70	79.9	531	2.83	95.2	4.8

^a Determined by GPC (THF, PSt calibration).

^b The microstructure was determined by FTIR.

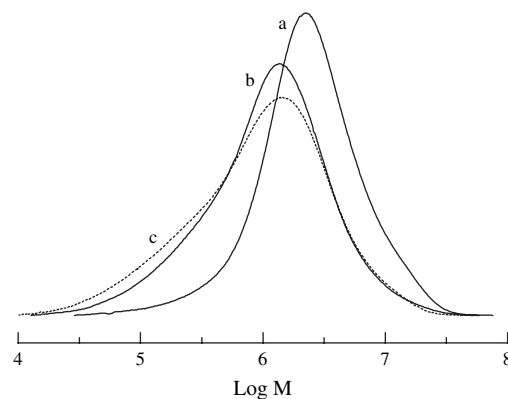


Fig. 3. Effect of [Nd] and [Al] ratio on the molecular weight distribution curves of polyisoprene by using $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst in hexane at 50 °C for 1 h with $[\text{IP}] = 1.50 \text{ M}$. (a) $[\text{Nd}] = 0.10 \text{ mM}$, $[\text{Al}] = 2.0 \text{ mM}$, (b) $[\text{Nd}] = 0.20 \text{ mM}$, $[\text{Al}] = 4.0 \text{ mM}$, (c) $[\text{Nd}] = 0.10 \text{ mM}$, $[\text{Al}] = 4.0 \text{ mM}$.

Comparison of molecular weight distribution curves elucidates that variation of either [Nd] or [Al] is predominant on affecting molecular weight distribution of polyisoprene as shown in Fig. 3. When [Nd] was fixed the molecular weight distribution curve of polymers shifts to low molecular weight region and becomes broader with increasing of [Al] from 2.0 mM to 4.0 mM; whereas, the molecular weight distribution curve doesn't move and only the profile changes slightly with variation of [Nd]. This indicates that [Al] has more significant effect on the molecular weight and the molecular weight distribution as compared to [Nd] and [Al] is an efficient molecular weight regulator in isoprene polymerization with this binary catalyst system.

3.4. Effect of polymerization temperature

The effect of polymerization temperature on isoprene polymerization with $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst at a relatively low $[\text{Al}]/[\text{Nd}]$ ratio of 20 and [Nd] of 0.10 mM is summarized in Table 2. The polymerization is remarkably accelerated by raising polymerization temperature from 0 to 70 °C, while the M_n of polymer has tendency to decrease, M_w/M_n varies from 2.0 to 2.8 and *cis*-1,4 content of polymers is almost unchanged.

3.5. Controlled polymerization

Polymerizations of isoprene using $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst were carried out at 50 °C in hexane under conditions of relatively low [Nd] of 0.10 mM and $[\text{Al}]/[\text{Nd}]$ ratio of 20. The polymer yield continuously increases with polymerization time prolonging (Fig. 4). The value of $\ln[M]_0/[M]_t$ is proportional to the polymerization time, which indicates that the concentration of the living polymer chain remains constant during polymerization and termination reaction seems to be negligible. As shown in Fig. 5, it is clear that the M_n increases proportionally along with increasing polymer yield though it does not extrapolate to zero. The M_w/M_n of the polymers keeps at low value and does not change significantly during the

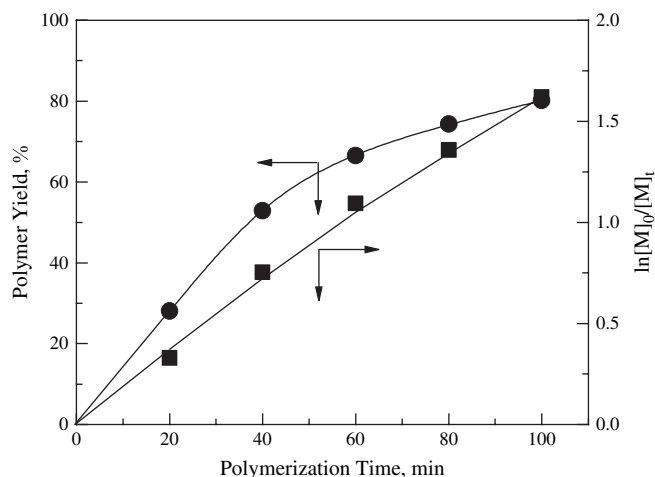


Fig. 4. Plots of the polymer yield and $\ln[M]_0/[M]_t$ against polymerization time for isoprene polymerization by using $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst in hexane at 50°C , $[\text{IP}] = 1.50\text{ M}$, $[\text{Nd}] = 0.10\text{ mM}$, $[\text{Al}]/[\text{Nd}] = 20$.

polymerization, though M_w/M_n is not as low as that in typical living polymerization. Moreover, the molecular weight distribution profiles of polyisoprene obtained keep unimodal and symmetrical through the entire polymerization process. From the results above, it seems that the $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst has some characteristics of living polymerization at a relatively high temperature of 50°C .

'Seeding' polymerization is essential characteristic of the living polymerization system. $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst was examined by feeding the same amount of isoprene monomer twice in the time interval of 12 h at room temperature. It can be seen from Fig. 6 that the molecular weight distribution curve of polyisoprene obtained during first polymerization (100% yield) shifted to a higher molecular weight region along with a narrow molecular weight distribution (M_w/M_n 2.0) and the final polymer with the yield of 196% had M_n nearly twice as much as the first one. The result of seeding polymerization strongly supports the fact that the $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$

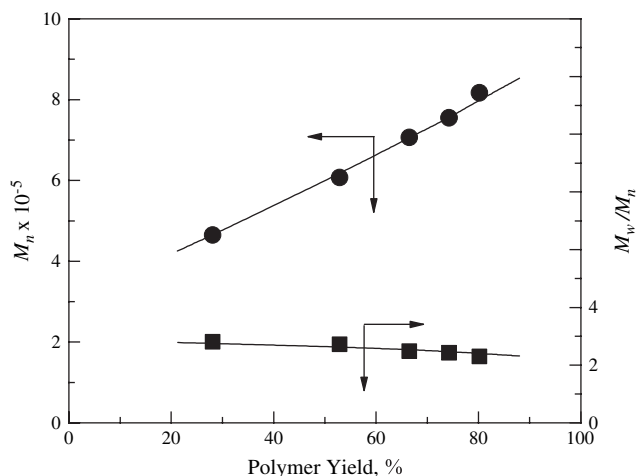


Fig. 5. Plots of the M_n and M_w/M_n of polyisoprene against the polymer yield by using $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst in hexane at 50°C , $[\text{IP}] = 1.50\text{ M}$, $[\text{Nd}] = 0.10\text{ mM}$, $[\text{Al}]/[\text{Nd}] = 20$.

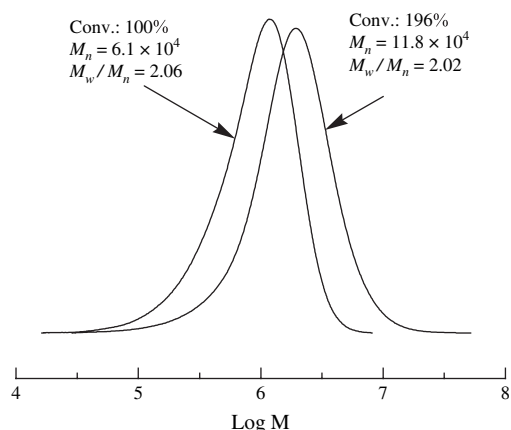


Fig. 6. Seeding techniques for isoprene polymerization with $\text{NdCl}_3 \cdot 3\text{EHOH}/\text{AlEt}_3$ catalyst in hexane at 25°C , $[\text{IP}] = 0.80\text{ M}$, $[\text{Nd}] = 0.08\text{ mM}$, $[\text{Al}]/[\text{Nd}] = 20$.

catalyst has some living polymerization characteristics and ability to obtain polyisoprene with controllable molecular weight.

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