Polymerization of 1,3-Butadiene Using Neodymium Chloride Tripentanolate–Triethyl Aluminum Catalyst Systems

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ABSTRACT: Neodymium chloride tripentanolate catalysts of the general formula NdCl₃ $\times nL$ with n = 3, L = 1-pentanol (II), 2-pentanol (III), and 3-pentanol (IV) were prepared by an alcohol interchange reaction between neodymium chloride n isopropanolate (I) with pentanols. These NdCl₃ tripentanolates (II-IV) were characterized by gravimetric and elemental analysis. They were evaluated for homopolymerization of 1,3-butadiene using triethyl aluminum as cocatalyst in cyclohexane solvent. The role of positional isomers of pentanols (1, 2, and 3) in catalytic activity on conversion, intrinsic viscosity, and microstructure was studied. The neodymium chloride tripentanolate-2 (III) has high catalytic activity followed by (II) and (IV). The conversions were increased with increases in catalyst, cocatalyst concentrations, and temperature, and decreases in intrinsic viscosity values. The microstructure was determined by Fourier transform-infrared spectroscopy (FTIR) and found to have a predominantly *cis*-1,4 structure (>99%), which was marginally influenced by variation in cocatalyst concentrations and temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 595-602, 1999

Key words: *cis*-1,4-polybutadiene; neodymium chloride; tripentanolates; binary catalyst; microstructure

INTRODUCTION

High-*cis*-1,4-polybutadiene has been produced by catalysts based on rare earth metals.¹ Marina et al.² have reviewed the literature on rare earth metal-catalyzed polymerization of dienes up to 1984. Two main types of catalyst systems have been widely used for 1,3-butadiene polymerization:

• Ternary catalyst systems consisting of lanthanide salts, alkyl aluminum halides, and trialkyl aluminum. These are soluble/homogeneous catalyst systems based on naphthenoic, 3 versatic, 4,5 and octanoic $^{6-8}$ salts of neodymium.

• Binary catalyst systems consisting of a rare earth chloride and trialkyl aluminum.⁹ These catalysts were not studied further due to low activity. The addition of electron donor organic ligands to the NdCl₃–AlR₃ system enhances the activity without any decrease in stereospecificity.¹⁰ Many binary catalysts based on NdCl₃ and AlR₃ complexed with electron donor organic ligands such as alcohols,^{10,11} tetrahydrofuran,¹² pyridine,¹³ dimethyl sulfoxide,¹⁴ phosphates,^{15,16} and amines¹⁷ were reported.

This article describes the synthesis and characterization of new neodymium chloride tripen-

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tanolate catalysts and their catalytic activity toward 1,3-butadiene polymerization in combination with triethyl aluminum.

EXPERIMENTAL

Materials

1,3-Butadiene (Indian Petrochemicals Corp. Ltd., Vadodara, India) was purified by passing it through three successive columns containing molecular sieves, sodium hydroxide, and trialkyl aluminum. Solutions of butadiene in cyclohexane (12 wt %) were used for the polymerization. Anhydrous neodymium chloride (Aldrich Chemical Co. Inc., USA) was used as received. Triethyl aluminum (Ethyl Corp., Baton Rouge, LA) was diluted to 10–15 wt % with dried cyclohexane. Lower alcohols, such as methanol, ethanol, isopropanol, and cyclohexane (S.d. Fine Chemicals Pvt. Ltd., Boisar, India), were dried by refluxing over sodium wire, distilled, and finally kept over molecular sieves (3A). Higher alcohols like 1-pentanol, 2-pentanol, and 3-pentanol (Aldrich) were dried over activated molecular sieves by dynamic drying. Solvents such as toluene and benzene (Ranbaxy Laboratory Ltd., S.A.S. Nagar, India) were used as received. All manipulations involving airsensitive compounds were performed inside an Atmosbag (Aldrich) continuously purged with ultra-high pure nitrogen.

Preparation of Neodymium Chloride Alcoholates

The anhydrous chlorides of rare earth metals were found to dissolve in methanol, ethanol, and isopropanol to provide alcoholates of general formula $MCl_3 \times n \text{ ROH}^{18}$:

$$MCl_3 + n ROH \rightarrow MCl_3 \times n ROH$$

The direct reaction of anhydrous metal chlorides with higher alcohol of C_4 and above led to the side reactions with replacement of chlorine¹⁹ and the solubility of rare earth halide decreased with increasing chain length of the alcohol. Due to these reasons, the alcoholates were prepared in two steps.

Preparation of Neodymium Chloride Isopropanolate

Isopropanol (50 mmol) was added to an hydrous $\rm NdCl_3$ (1 mmol) in a 250-mL three-neck roundbottom flask with a reflux condenser, thermowell, nitrogen gas inlet connected to a bubbler, and kept in a thermostatically controlled oil bath. The reactants were refluxed for 3 h at 80°C. The excess alcohol was removed under vacuum at 25°C. The dried product was recrystallized from isopropanol by dissolving at 25°C and then cooling to 10°C, yielding a bluish-white solid of neodymium chloride $\times n$ -isopropanolate (**I**):

 $NdCl_3 + niC_3H_7OH \rightarrow NdCl_3 \times niC_3H_7OH (I)$

Preparation of Neodymium Chloride Tripentanolates

The neodymium chloride tripentanolates were prepared by dissolving the neodymium chloride $\times n$ isopropanolate (I) separately in an excess of 1-pentanol, 2-pentanol, and 3-pentanol. They were allowed to react for 3 h at 80°C and for 1 h at 100°C. The resulting mixtures were dried under vacuum at 40°C to remove excess pentanol and isopropanol, yielding light-blue solids of neodymium chloride tripentanolate catalysts of compositional formula NdCl₃ \times tripentanolate-1 (II), NdCl₃ \times tripentanolate-2 (III), and NdCl₃ \times tripentanolate-3 (IV). These tripentanolates were characterized by elemental analysis and gravimetry; the results are given in Table I:

 $(\mathbf{I}) + n \operatorname{C}_{5}\operatorname{H}_{11}\operatorname{OH} \rightarrow \operatorname{NdCl}_{3} \times n\operatorname{C}_{5}\operatorname{H}_{11}\operatorname{OH}$

Preparation of Catalyst

The neodymium chloride tripentanolates (II–IV) were treated with an appropriate amount of AlEt₃ in 10-15 wt % cyclohexane under nitrogen atmosphere. The NdCl₃ tripentanolates were first reacted with AlEt₃ to form a finely dispersed catalytically active complex. The resultant mixture was aged for 30 min at 25°C and used for the stereospecific polymerization of 1,3-butadiene.

Polymerization

The polymerization reactions were performed under nitrogen in a 250-mL three-neck round-bottom flask equipped with a magnetic poly(tetra-fluoroethylene (PTFE) bar, thermowell, gas inlet, and reflux condenser. The flask was kept in a thermostated oil bath. In a typical reaction, 83.5 mL of cyclohexane containing 10 g of 1,3-buta-diene was charged into a flask containing a binary catalyst mixture of 0.6 mhm (millimoles/100 g of monomer) of NdCl₃ × tripentanolate and AlEt₃ (15

Catalyst	Metal (Nd) (%)	Elemental		
		Carbon	Hydrogen	Metal/alcohol (molar ratio)
\mathbf{I}^{a}	40.02 (39.08) ^e	30.02 (29.26)	6.50 (6.26)	1/3.5
\mathbf{II}^{b}	27.75 28.03	$\begin{array}{c} 35.02\\ 34.98\end{array}$	7.02 6.99	1/3.0
III ^c	27.11 (27.62)	36.00 (35.88)	7.23 (7.23)	1/3
\mathbf{IV}^{d}	$\begin{array}{c} 27.02 \\ (27.21) \end{array}$	35.75 (35.39)	7.10 (7.07)	1/3

Table I Characterization of $NdCl_3 \times n$ Alcoholates

^a $\mathrm{NdCl}_3 \times 3,5$ -isopropanolate.

 $^{\rm b}\,{\rm NdCl}_3^{\rm o} \times 3$ pentanolate-1.

 $^{\circ}$ NdCl₃ \times 3 pentanolate-2.

^d NdCl₃ \times 3 pentanolate-3.

^e Calculated values are in parentheses.

mmol). The polymerization was initiated at 25° C and terminated with methanol containing 0.5% di*tert*-butylparacresol. The precipitated rubber was dried under vacuum at room temperature for 8 h.

Characterization

The percent neodymium in tripentanolates was estimated gravimetrically after incinerating with conc nitric acid. The percent of carbon and hydrogen was estimated with a 1106 Carlo Erba elemental analyzer. Intrinsic viscosities (η) of polybutadiene samples were determined in toluene at 30°C using an Ubbelhode viscometer. The microstructure (*cis*-1,4, *trans*-1,4, and *vinyl*-1,2) was determined using a Perkin–Elmer 1600 series Fourier transform-infrared spectrometer (FTIR).

RESULTS AND DISCUSSION

The binary catalysts of neodymium chloride tripentanolates (**II–IV**), hereafter called catalysts,

Tab	le II	Effect o	f Pentanol	Structure
on (Cataly	tic Activ	vity	

		Catalys	ts/conve (%) ^b	rsions
Cocatalyst concn (mhm) ^a	Al/Nd (molar ratio)	III	II	IV
10 15 20	16.6 25.0 33.3	$35 \\ 45 \\ 45$	$12 \\ 35 \\ 40$	4 5 8

^a Millimoles/100 g of monomer.

^b See Table I for explanations of catalyst numbers.

and triethyl aluminum (a cocatalyst) in cyclohexane initiated the homopolymerization of 1,3-butadiene. However, NdCl₃ alone under the above experimental conditions with AlEt₃ could result in a catalyst with poor activity toward 1,3-butadiene polymerization. It was known that the alkylation of transition metal halide by AlEt₃ to form a metal carbon bond was a necessary step in an active center formation. Comparison of a typical Z—N catalyst, TiCl₄–AlR₃, with the binary lanthanide chloride system $LnCl_3$ –AlR₃ shows that the covalent nature of TiCl₄ is stronger than that of $LnCl_3$. Hence the latter is less easily alkylated by AlR₃. This may be one cause of the $LnCl_3$ –AlR₃ system's low activity.¹⁰



Figure 1 Effect of catalyst concentration on conversion (\bigcirc) and intrinsic viscosity (\square) .

~ .	Ν	licrostructure	(%)
(mhm)	<i>cis</i> -1,4	trans-1,4	vinyl-1,2
0.2	99.2	0.7	0.1
0.4	99.1	0.8	0.1
0.6	98.2	1.5	0.3
1.0	98.1	1.6	0.3

In the NdCl₃ × *n* ROH complex (ROH = pentanols), the positive nature of the neodymium ion is somewhat decreased, due to the donor property of oxygen of the pentanols, whereas at the same time the lattice of NdCl₃ is changed.^{20,21} These results favor the opportunity for alkylation,⁶ which ultimately forms a product with high catalytic activity. The active species of the neodymium catalyst system may be a bimetallic complex possibly involving the alkylated neodymium metal ion, as given below. Ballard et al.²² isolated the bimetallic complex of Ln and Al, which was confirmed by Rafikov et al.²³



When $NdCl_3$ tripentanolate, cocatalyst, and 1,3butadiene were added simultaneously, the activity was very low. For this reason, first catalyst and then cocatalyst were added and aged for 30 min at 25°C to get an active binary catalyst for the polymerization of 1,3-butadiene. This shows that the aging of the catalyst⁶ and the order of addition are important to get satisfactory results.¹⁰

Polymerization of 1,3-Butadiene

Effect of Catalyst Concentration

The effect of $NdCl_3 \times tripentanolate-1$ (II) catalyst concentration at a fixed cocatalyst (AlEt₃) concn of 15 mhm was studied on the homopolymerization of 1,3-butadiene at 50°C for 30 min in cyclohexane; the results are summarized in Figure 1 and Table III. A maximum conversion of 44 wt % was obtained at a catalyst concentration of 1

mhm. The intrinsic viscosity values show a decreasing trend with increasing catalyst concentration. The increase in conversion may be due to the availability of more active centers with the increase in catalyst concentration,¹⁰ resulting in decreased molecular weight of the polymer so formed.

Effect of Cocatalyst Concentration

The concentration of cocatalyst (AlEt₃) was varied from 10-20 mhm with a fixed catalyst concentration of 0.6 mhm at 50°C for 30 min. The results, depicted in Figures 2 and 3 and Table IV, show that as the cocatalyst concentration increased, the conversions also increased steadily, whereas the intrinsic viscosity values of the resulting polymers continuously decreased due to the greater chain transfer reactions occurring at a higher alkyl aluminum concentration. The ability of the organoaluminum compounds to act as a chain transfer agents in Z-N polymerization is well documented in the literature.²⁴ Recently there was agreement in the literature that the molar mass drop caused by an increase of AlR₃ in the polymerization medium was due solely to chain transfer.²⁵ Yang et al.¹² also found an increase in conversion and a decrease in intrinsic viscosity values when they varied $NdCl_3 \times n$ THF/AlR₃ at a fixed neodymium concentration.



Figure 2 Effect of cocatalyst concentration on conversion: (\mathbf{V}) NdCl₃ × tripentanolate-1 (II); (\mathbf{O}) NdCl₃ × tripentanolate-2 (III); (\mathbf{I}) NdCl₃ × tripentanolate-3 (IV).



Figure 3 Effect of cocatalyst concentration on intrinsic viscosity: (\bigcirc) NdCl₃ × tripentanolate-1 (**II**); (\bigcirc) NdCl₃ × tripentanolate-2 (**III**); (\square) NdCl₃ × tripentanolate-3 (**IV**).

Effect of Temperature

The effect of temperature on conversion, intrinsic viscosity, and microstructure of the $NdCl_3 \times trip-$ entanolate–AlEt₃ catalyst system was studied with a catalyst concentration of 0.6 mhm and a cocatalyst concentration of 15 mhm for 30 min; the results are given in Figures 4 and 5 and Table

Table IVEffect of Cocatalyst Concentration onMicrostructure

	Cocatalyst	Microstructure (%)		
Catalyst ^a	concn (mhm)	<i>cis</i> -1,4	trans-1,4	vinyl-1,2
	10	99.4	0.6	0.0
II	15	98.3	1.4	0.3
	20	98.0	1.6	0.4
	10	99.0	0.7	0.3
III	15	98.6	1.1	0.3
	20	97.8	1.7	0.5
	10	99.2	0.5	0.3
IV	15	97.3	1.4	0.3
	20	96.2	3.1	0.7

^a See Table I for definitions of catalyst numbers.



Figure 4 Effect of temperature on conversion: (∇) NdCl₃ × tripentanolate-1 (**II**); (\bigcirc) NdCl₃ × tripentanolate-2 (**III**); (\blacksquare) NdCl₃ × tripentanolate-3 (**IV**).

V. The conversions increased and the intrinsic viscosity values decreased with increase in temperature from 25–75°C. At higher temperatures, the rate of chain transfer to both solvent and



Figure 5 Effect of temperature on intrinsic viscosity: (\bigcirc) NdCl₃ × tripentanolate-1 (**II**); (\bigcirc) NdCl₃ × tripentanolate-2 (**III**); (\square) NdCl₃ × tripentanolate-3 (**IV**).

		Microstructure (%)		
$Catalyst^{a}$	Temperature (°C)	cis-1,4	trans-1,4	vinyl-1,2
II	25	98.5	1.1	0.4
	50	98.2	1.4	0.4
	75	96.8	2.6	0.6
III	25	98.9	1.1	0.0
	50	97.9	1.7	0.4
	75	96.4	3.2	0.4
IV	25	99.7	0.3	0.0
	50	98.2	1.5	0.3
	75	96.6	2.9	0.5

Table VEffect of Temperature on Microstructure

^a See Table I for definitions of catalyst numbers.

cocatalyst increased, resulting in decreased intrinsic viscosity.

Effect of Time

The effect of time on conversion, intrinsic viscosity, and microstructure was studied with NdCl₃ × tripentanolate-3 (**IV**) catalyst at 50°C with a cocatalyst concentration of 15 mhm and catalyst concentration of 0.6 mhm; the results are given in Figure 6 and Table VI. This catalyst (**IV**) was chosen because the activity was found to be less, and consequently the sampling was easier for the study under our experimental conditions. It has been observed that both conversion and intrinsic



Figure 6 Effect of time on conversion (\bullet) and intrinsic viscosity (\bigcirc) with the NdCl₃ × tripentanolate-3 (**IV**) catalyst system.

viscosity increase with increasing time. Wilson¹ also observed a linear relationship between molecular weight and conversion.

Effect of Structure of Alcohol

The effect of the structure of alcohol on the catalytic activity, expressed in terms of conversion of 1,3-butadiene to polybutadiene at a fixed NdCl₃/ROH molar ratio with varying Al/Nd molar ratio, was studied; the results are given in Figure 2 and Table II. The results show that all of the three alcohols (1-, 2-, and 3-pentanols) form tripentanolates with $\mathrm{NdCl}_3~(\mathrm{II-IV})$ and can function as active binary catalysts for 1,3butadiene polymerization but to different degrees. The difference in activity of three isomers of pentanols is quite large, and the catalytic activity of neodymium chloride tripentanolates decrease in the following order: $NdCl_3 \times tri$ pentanolate-2 (III) > $NdCl_3 \times tripentanolate-1$ $(II) > NdCl_3 \times tripentanolate-3 (IV)$. This indicates that the conversions are higher with neodymium chloride tripentanolates made from

Table VI Effect of Time on Microstructur	e VI Effect	of Time on	Microstructure
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		Microstructure (%)
Time (min)	<i>cis</i> -1,4	trans-1,4	vinyl-1,2
30	99.2	0.8	0.0
60	98.6	1.2	0.2
90	98.3	1.3	0.4
120	97.9	1.6	0.5
150	97.8	1.7	0.6



Figure 7 Typical IR spectrum of high-*cis*-1,4-poly-butadiene.

 $NdCl_3$ and 2-pentanol, followed by 1-pentanol and then 3-pentanol. The effect of these alcohols on conversion was also checked by varying temperature (Fig. 4), and the same trend was observed. The $NdCl_3 \times$ tripentanolate-3 (**IV**) catalyst was less active under the above experimental conditions. This may be due to the steric hindrance of two ethyl groups present adjacent to alcohol moiety, which prevents the formation of active species. Jinua et al.¹⁰ also found inactivity of *tert*-butyl alcohol toward 1,3-butadiene polymerization compared to 1-butanol and 2-butanol.

Microstructure

Microstructure refers to the total *cis*-1,4, *trans*-1,4, and *vinyl*-1,2 structures present in polybutadiene. The IR spectrum (Fig. 7) of the high-*cis* polybutadiene obtained with neodymium chloride tripentanolate (**II–IV**) catalysts shows absorption at 740, 912, and 965 cm⁻¹ due to *cis*-1,4, *vinyl*-1,2, and *trans*-1,4 peaks. The effect of variation of catalyst, cocatalyst concentrations, temperature, time, and structure of alcohol on microstructure is shown in Tables III–VI.

The polybutadiene obtained with $NdCl_3 \times trip$ entanolate catalysts has very high cis-1,4 structures (>99%). The cis-1,4 content decreased from 99 to 96% with increases in cocatalyst concentration (Table IV) and temperature (Table V), whereas the decrease was marginal with increases in catalyst concentration (Table III) and time (Table VI). Ochme¹³ and Zhiquan et al.²⁶ found a decrease in cis-1,4 content with increases in catalyst and cocatalyst concentrations. This indicates that the cis-1,4 content can be increased by reducing the molar ratio of Al/Nd and temperature. The interesting feature of these three pentanolate catalysts (**II-IV**) is that, although their catalytic activity is not the same, the polybutadienes produced all had very high cis-1,4 structure, varying from 99.4% to 99.0% at a cocatalyst concentration of 10 mhm (Table IV). This shows that the position of the hydroxyl group in alcohol of the neodymium chloride tripentanolate catalyst have the least effect on stereospecificity. All of these experimental results indicate that the mechanism of 1,3-butadiene with rare earth catalysts may involve the bidentate coordination of diene monomer in the cisoid conformation, followed by an anti-syn (cis-trans) isomerisation of growing allylic units prior to monomer insertion, as proposed by Hsieh and Yeh.²⁷

The *trans*-1,4 units in polybutadiene (Tables III–VI) increased from 0.31% to 3.18% with the variation of catalyst, cocatalyst, and temperature. This may be due to the increase in *anti-syn* isomerisation as the temperature and Al/Nd mol ratio was increased.

The *vinyl*-1,2 unit content in polybutadiene was very low (<1%) and varied from 0.0% to 0.85% with the variation of catalyst, cocatalyst, temperature, and time (Tables III–VI). This may be due to the quick formation of more external σ -allyl species than internal σ -allyl species, as observed by Hsieh²⁷ and Faller,²⁸ leading to low 1,2-polymer.

CONCLUSIONS

Binary catalysts of $NdCl_3$ tripentanolates-1, -2, and -3/AlEt₃ initiated the homopolymerization of 1,3-butadiene and produced stereospecific polybutadiene with high *cis*-1,4 and low vinyl-1,2 structures. The catalytic activity was dependent on the variation of Al/Nd mole ratio, temperature, time, and position of hydroxyl group in pentanols. The microstructure was unaffected by the position of the hydroxyl group and was increased by reducing the mol ratio of Al/Nd and temperature.

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