A Highly Reactive and Monomeric Neodymium Catalyst†

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Received December 6, 2001; Revised Manuscript Received April 2, 2002

ABSTRACT: Ultrahigh *cis*-polybutadiene is prepared in 1,3-butadiene polymerization by the Nd catalyst of Nd(neodecanoate)$_3$ (**ND**)/AlEt$_2$Cl/Al(^{i}Bu)$_3$ in the rubber industry. However, the catalytic activity remains low, and the reason is unclear. According to our matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectroscopic study, **ND** is a mixture of various oligomeric and hydrated compounds. The hydrated oligomeric structure would mainly lower the catalytic activity. To design a better Nd catalyst, Nd(neodecanoate)$_3$·(neodecanoic acid) (**NDH**) was designed to satisfy the requisite of anhydrous and monomeric structure. **NDH** was prepared through ligand-exhange method between neodymium acetate and neodecanoic acid in an organic medium. **NDH** was identified and characterized with infrared (IR), MALDI−TOF mass, and synchrotron X-ray absorption spectroscopies (XAS) and with computer simulations. Weakly bound neodecanoic acid with the carbonyl peak at ca. 1670 cm^{-1} and carboxylate anion coordinated to Nd at ca. 1600 cm^{-1} were observed in the IR study. The molecular ion peak (m/z = 838.7) in MALDI mass and the pronounced absorption edge at 6216 eV in the Nd L_{III} XANES (X-ray absorption near edge structure) spectra support its monomeric structure. **NDH** is of monomeric structure, satisfying the 8-coordination number in the optimized structure by molecular mechanics. A significant improvement in the catalytic activity for 1,3-butadiene polymerization is achieved through **NDH**. The Nd catalyst shows a high activity (2.5×10^6 g/(Nd mol h)) and produces polybutadiene with 98% cis content.

Introduction

Lanthanide-based catalyst in 1,3-butadiene polymerization has drawn particular interest since it gives a higher cis microstructure (up to 99%) than the transition-metal catalysts based on Ti, Co, and Ni metals do and exhibits pseudo-living character which is a very rare case in Ziegler−Natta catalyst reactions.[1−8] The high stereoregularity provides excellent dynamic mechanical properties, especially higher tensile strength, lower heat buildup, and better abrasion resistance.[9] The pseudo-living character allows the introduction of many polar functional groups into the polybutadiene for surface modification,[10] for rebuilding polymer architectures,[11] and for extending its application to tires.[12] Since the early discoveries of Shen and co-workers for binary lanthanide-based catalysts (LnX_3/AlR_3 (X = F, Cl, Br, I))[3] and of Throckmorton for ternary (Ce(OCOR)$_3$/AlR_2Cl/AlR_3)[4] in the 1960s, many kinds of binary and ternary lanthanide-based catalysts have been developed.[1−5] Of these lanthanide-based catalysts, the Nd-based catalyst composed of Nd(neodecanoate)$_3$/AlEt$_2$Cl/Al(^{i}Bu)$_3$ has been intensively studied due to its higher solubility and better reactivity than other lanthanide catalysts.[5]

The neodymium compound Nd(neodecanoate)$_3$(**ND**), however, still possesses a few problems in the aspect of activity and of gel formation in 1,3-butadiene polymerization because only about 6% Nd is active.[13] Little is known about the low activity.

The aims of this study are to find the relationship of the polymerization activity and the structure of neodymium compounds with spectroscopic techniques and contrive a novel neodymium compound Nd(neodecanoate)$_3$·(neodecanoic acid)(**NDH**) and use it in 1,3-butadiene polymerization for ultrahigh *cis*-polybutadiene.

Results and Discussion

Synthesis of Neodymium Compounds. Conventionally **ND** is prepared by reacting an aqueous solution of neodymium chloride or neodymium nitrate with an aqueous sodium neodecanoate solution, followed by extraction with an organic solvent (see eq 1).[10b,14] Its appearance is sticky solid.

$$NdCl_3{\cdot}6H_2O + RCOONa \xrightarrow[25\ °C,\ 2\ h]{H_2O} Nd(OOCR)_3 \quad (1)$$

NDH was obtained by ligand exchange between an excess of neodecanoic acid in chlorobenzene. The exchanged acetic acid was trapped with a Dean−Stark apparatus in the reflux condition of chlorobenzene. The product, **NDH**, was purified by gel permeation chromatograpy. In the nonaqueous condition, the polar ligands such as chloride, nitrate, hydroxide, water, and carboxylate salt, which work as coordinating bridges, are avoided (see eq 2). Its appearance is liquid.

$$Nd(OAc)_3{\cdot}6H_2O + RCOOH \xrightarrow[reflux,\ 5\ h]{chlorobenzene} Nd(OOCR)_3{\cdot}(HOOCR) \quad (2)$$

Characterization of Neodymium Compounds. Because of the aqueous synthetic environment and the 8- to 12-coordination ability of neodymium,[15] **ND** no longer exists as monomeric structure. During the synthetic process, it is converted to an oligomeric structure by abundant surrounding ligands such as water, chloride, sodium neodecanoate, and hydroxide, which saturate the coordination sphere of neodymium.

† Presented at a meeting of the Rubber Division, American Chemical Society, Cleveland, Ohio, October 16-19, 2001.

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10.1021/ma012123p CCC: $22.00
Published on Web 05/24/2002

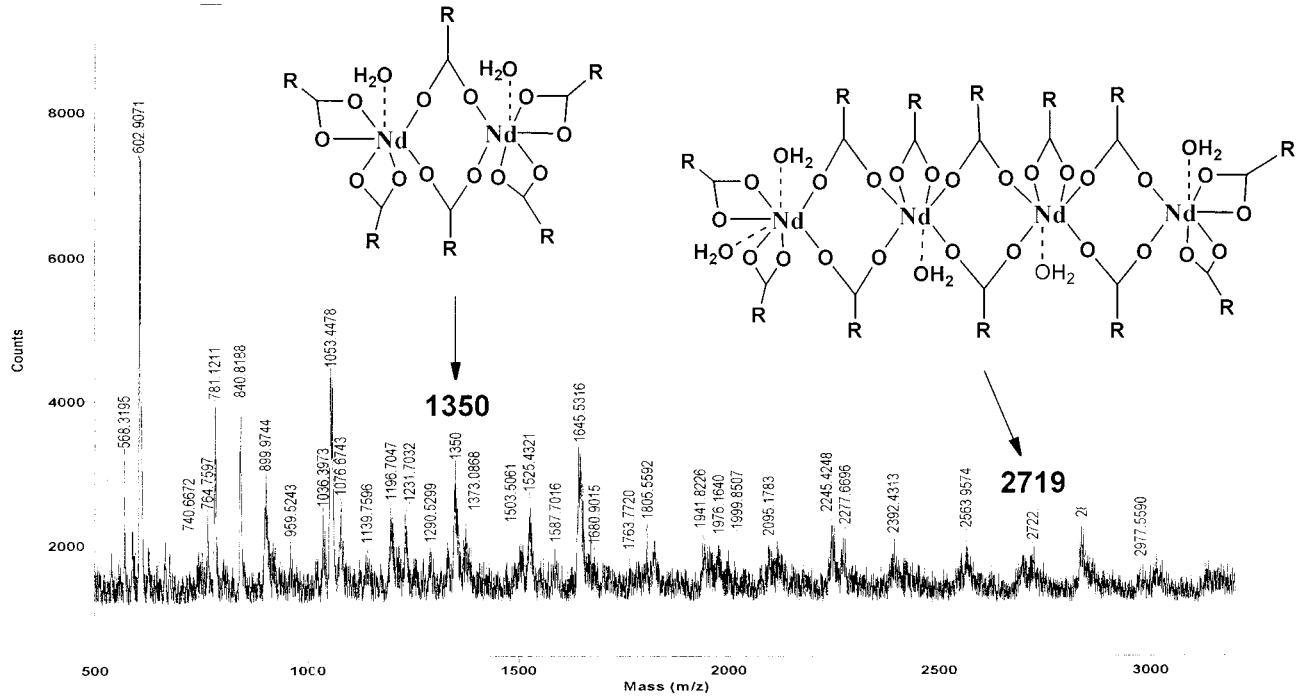

Figure 1. A MALDI mass spectrum of **ND** and two representative structures (dimer, $[M]^+ = 1350$; tetramer, $[M]^+ = 2719$) among the various compounds in **ND**.

These ligands can bridge neodymium ions, resulting in agglomeration of neodymium. MALDI TOF MS has been essential for obtaining structural information, such as molecular weight, molecular weight distribution, functionality type distribution, and chemical composition distribution, since it produces molecular ions with little or no fragmentation.[16] In MALDI, an analyte is dissolved in a solution of a light-absorbing chemical, the so-called matrix, which transfers light energy to analyte, resulting in desorption and ionization. Despite the low stability of **ND** on an acid matrix, structural and molecular weight information can be provided by the MALDI−TOF mass spectrum in the matrix of 2,5-dihydroxybenzoic acid, presently regarded as one of high-quality matrixes.[16c] The MALDI mass spectrum of **ND** (Figure 1) shows a mixture of hydrated oligomeric structures. The two representative structures of water-coordinated dimeric and tetrameric neodymium neodecanoates among the various compounds are shown in the figure. The gas-phase structure of Nd(neodecanoate)$_3$ itself was obtained by molecular mechanics with the Universal Force Field in Cerius^2. The total coordination number is 6. The lack of coordination leads the compound to saturate its coordination sphere with polar surrounding ligands, especially in liquid or in solid phases.

The optimized structure of **NDH** by molecular mechanics was obtained with the Universal Force Field in Cerius^2. **NDH** is of monomeric structure, satisfying the 8-coordination number. A vacant coordination space for the gas-phase **ND** is available, whereas no space is found for **NDH**. Because of the saturated coordination sphere, **NDH** is stable as liquid. The infrared spectra of neodecanoic acid, **ND**, and **NDH** are shown in Figure 2. In the spectrum of neodecanoic acid, the broad hydroxy stretching peak of carboxylic group is shown around 2500−3300 cm^{-1}, and the band at 1700 cm^{-1} corresponds to the stretching of carbonyl.[17] In the spectrum of **ND**, a weak and broad peak of H_2O is shown around 3300 cm^{-1}, the small peak observed at

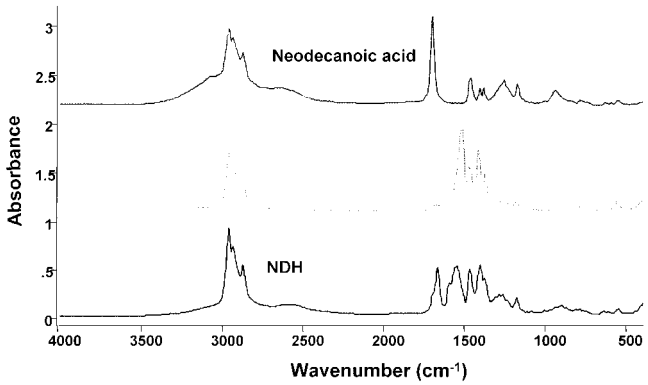

Figure 2. Infrared spectra of neodecanoic acid, **ND**, and **NDH**.

1670 cm^{-1} indicates weakly bound neodecanoic acid, and the carbonyl peak of carboxylate anion coordinated to Nd is shown at 1550 cm^{-1}.[17a] In the spectrum of **NDH**, the carbonyl peak around 1670 cm^{-1} indicates a weakly bound neodecanoic acid, and carboxylate anion coordinated to Nd is shown at 1600 cm^{-1}. Through the comparison of these IR spectra, it is evident that **NDH** contains weakly coordinated carboxylic acid.

The molecular ion peak ($m/z = 838.7$) is observed in the MALDI mass spectrum of **NDH** except for a few peaks with low intensity ($m/z = 907$, 1046, 1355, 1647) although a mass discrimination phenomenon occurs in the particular high molecular organometallic compound (calcd for $C_{40}H_{85}O_8Nd$ $(M)^+$, 830.35; MS-LRFAB mass $m/z = 830.3$) in Figure 3.[16a,d] The mass spectrum suggests **NDH** exists itself as monomeric structure.

An X-ray absorption near edge structure (XANES) spectrum is obtained by synchrotron X-ray absorption spectroscopy (XAS), which provides structural information such as the coordination sphere and the oxidation state of neodymium. The evolvement of normalized XANES spectra of **ND** and **NDH** are shown in Figure 4. The absorption edges arise from the electronic transi-

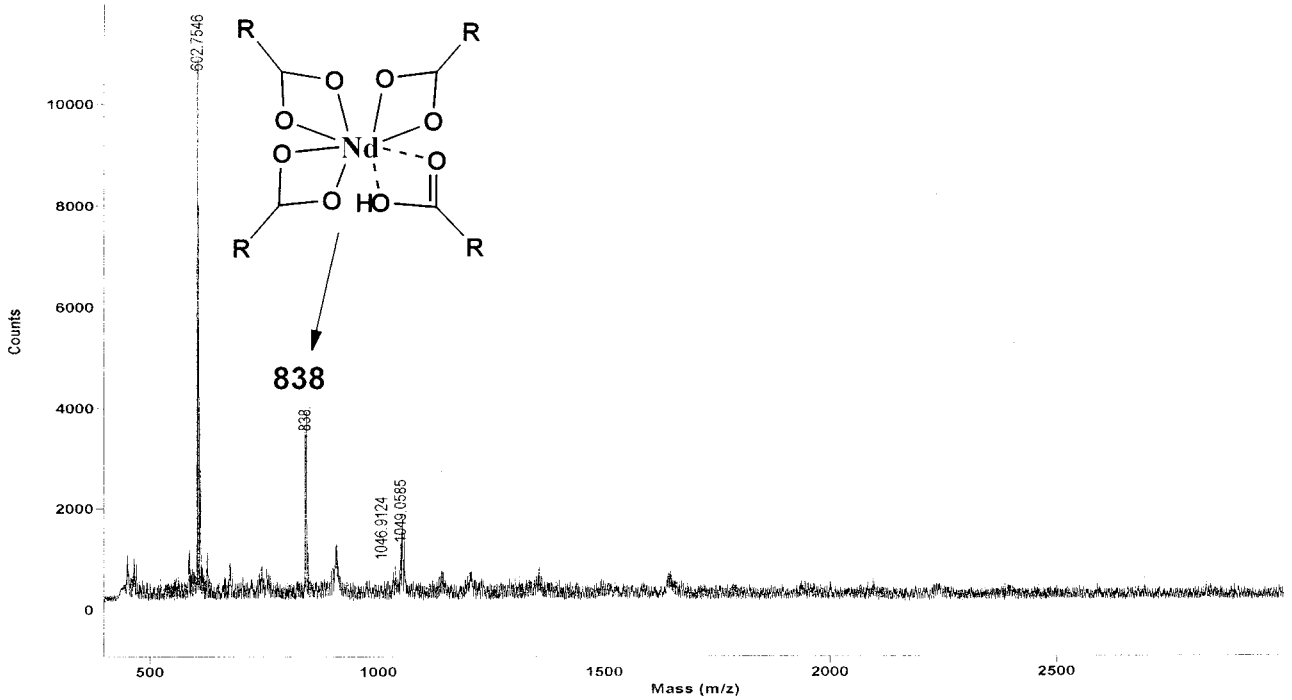

Figure 3. MALDI mass spectrum of **NDH** and its plausible structure.

Table 1. 1,3-Butadiene Polymerization Using ND and NDH

					microstructure				
no.	Nd compd[a]	Nd concn[b]	mole ratio[c]	conv[d] (%)	cis (%)	trans (%)	vinyl (%)	M_w	MWD
1	**ND**	1.1	1/3/15/40	29	97.5	2.0	0.5	5.11	4.57
2	**ND**	1.4	1/3/15/40	65	97.7	1.9	0.4	9.33	4.31
3	**ND**	2.8	1/3/5/50	88	97.1	2.5	0.4	25.34	7.39
4	**NDH**	1.1	1/3/10/40	95	98.5	1.2	0.3	4.13	2.90
5	**NDH**	0.9	1/3/10/30	85	98.3	1.5	0.2	3.38	2.92
6	**NDH**	0.7	1/3/7/30	72	98.1	1.4	0.5	5.08	2.52
7	**NDH**	0.3	1/3/20/60	75	98.4	1.1	0.4	4.42	2.72

[a] ND = Nd(neodecanoate)$_3$; NDH = Nd(neodecanoate)$_3$·(neodecanoic acid). [b] 10^{-4} mol/100 g BD. [c] Nd/Cl/DIBAL/TIBA. [d] 1 h.

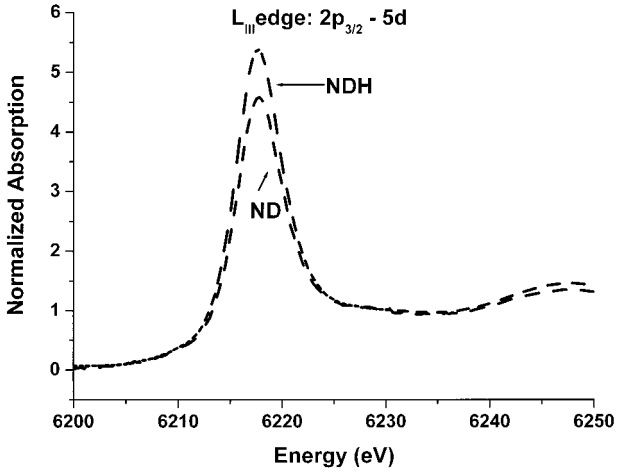

Figure 4. Nd L_{III}-edge XAS spectra of **ND** and **NDH**.

tion from the core $2p_{3/2}$ level to the vacant 5d states of neodymium atom, Nd L_{III} absorption, and are called a "white line (WL)".[18] The WL positions of **ND** and **NDH** are observed at 6216.0 and 6215.7 eV, respectively, and are in the same position as that of $Nd_2(III)O_3$ powder at 6216.1 eV. The WL positions and the high intensity of **ND** and **NDH** indicate that both neodymiums are in a trivalent state with strong ionic character.[18] The higher intensity of **NDH** implies that the structure is more symmetrical than that of **ND**. The XANES results in good agreement with MALDI results suggest that **NDH** is more homogeneous than **ND**.

Polymerization. 1,3-Butadiene polymerization was carried out at 60 °C for 2 h with the addition of cyclohexane, butadiene, **ND**, or **NDH**, $AlEt_2Cl$ as halogen compound, and both $Al(^iBu)_3$ and $Al(^iBu)_2H$ as alkylation compound in a high-pressure reactor. The concentration of neodymium, the mole ratio of catalysts, and the polymerization results are summarized in Table 1. In runs 1−3, **ND** was used as the neodymium catalyst. The contents of cis, trans, and vinyl microstructures are ca. 97.5, 2.0, and 0.5%, respectively, and these values are slightly varied with the amount of catalyst used. GPC studies indicate the weight-average molecular weight is over 500 000 up to 2 000 000, and the polydispersity (M_w/M_n) is over 4.0. The catalytic activity is in the range of $1.7-3.4 \times 10^5$ g/(Nd mol h).

In the runs 4−7, **NDH** was used as the neodymium catalyst. These polymerizations yielded a high catalytic activity ($(0.9-2.5) \times 10^6$ g/(Nd mol h)). The polybutadiene produced has a weight-average molecular weight of around 500 000 and a low value of polydispersity, $M_w/M_n < 3.0$. It is noted that the activity of 2.5×10^6 g/(Nd mol h) in run 7 is one of highest values ever reported.[6−8,19] The contents of cis, trans, and vinyl microstructures are ca. 98.5, 1.0, and 0.5%, respectively. The higher cis content of the polybutadiene of **NDH** was

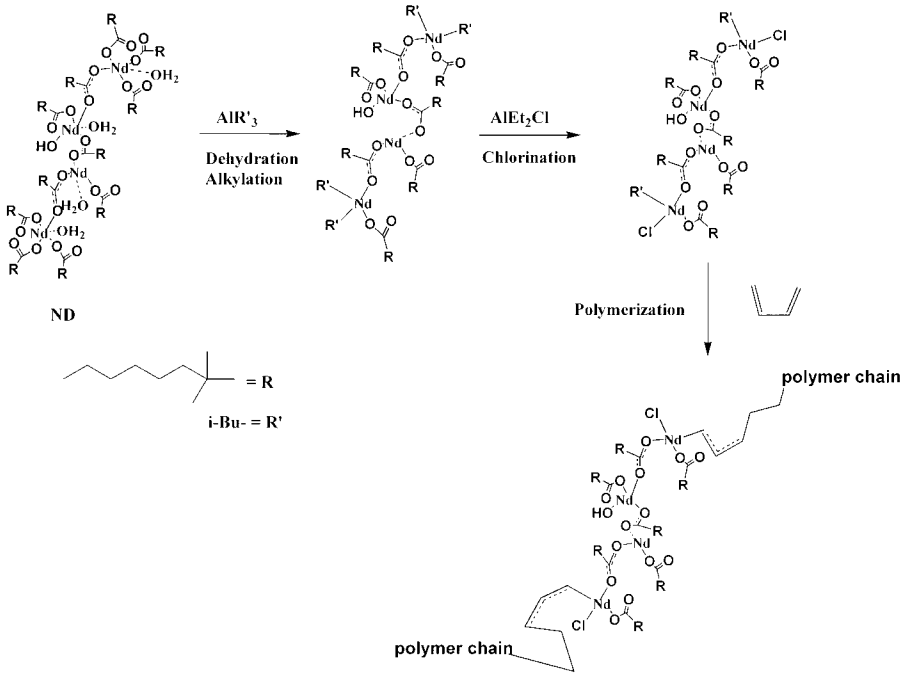

Figure 5. Catalyst activation and propagation mechanism of **ND**.

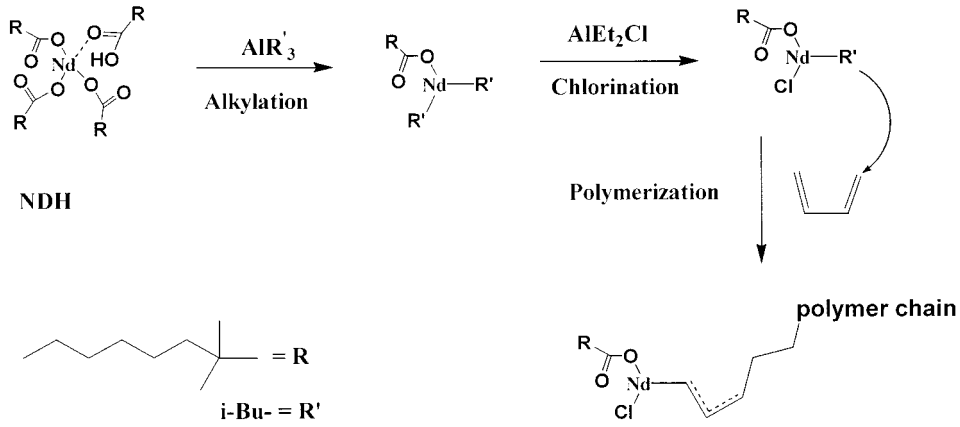

Figure 6. Catalyst activation and propagation mechanism of **NDH**.

obtained because of the low catalyst amount used. The more catalyst amount would facilitate chain-transfer reactions.

The activity difference can also be explained by the structure of neodymium compounds. The low activity of **ND** is attributed to the very structure of it consisting of oligomeric or polymeric structures with polar ligands such as water, hydroxide and carboxylate. The various active centers will form through the reaction with alkylaluminum (Figure 5). Some of the neodymium atoms located in the middle of oligomeric or polymeric structures will remain less reactive, and the others located at the outside of the structure will work as the active center. The coordinated polar ligands will also consume alkylaluminum and decrease the number of active centers. These factors certainly yield a very high molecular weight polymer with a high polydispersity in the 1,3-butadiene polymerization. However, the neodymium atom of **NDH** will readily work as an active center because it possesses the dissociated monomeric structure (Figure 6). Furthermore, the monomeric neodymium catalyst composed of alkylaluminum easily generates active sites and hence shows a higher activity and yields a lower value of polydispersity. The activities of the different Nd catalysts are compared in Table 2, which evidence that the more aggregated one shows the less activity (activity: binary < ternary, $NdCl_3$·THF < **ND** < **NDH**).[19]

Table 2. Catalytic Activity Data of 1,3-Butadiene Polymerization with Various Nd Catalysts

catalyst	activity (g/(Nd mol h))	ref
$NdCl_3$·2THF	0.2×10^5	19d
$ND/AlR_2Cl/AlR_3$	4.3×10^5	19e
$NDH/AlR_2Cl/AlR_3$	25.0×10^5	

Conclusions

The catalytic activity of Nd catalyst was understood in the structural aspect of neodymium compound. According to the spectroscopic evidences, the low activity of **ND** is attributed to its structure, which consists of a mixture of hydrated oligomers. **NDH**, prepared through a ligand-exchange method, is of monomeric structure, satisfying 8-coordination nature and does not contain water, bases, and salts. In the polymerization of 1,3-butadiene, **NDH** shows the high activity of 2.5×10^6 g/(Nd mol h) and produces polybutadiene with over 98% cis content and without gel.

Experimental Section

Preparation of Nd(neodecanoate)$_3$. Nd(neodecanoate)$_3$ was prepared in an aqueous method with $NdCl_3 \cdot 6H_2O$ and sodium neodecanoate according to the literature.[10b,14]

Preparation of Nd(neodecanoate)$_3$·(neodecanoic acid). A mixture of chlorobenzene (80 mL), neodymium acetate (3.2 g), and neodecanoic acid (A, NEO ACIDS C10/Exxon Chemicals, 6.9 g, ave MW 173.7) was refluxed for 3 h in a 100 mL round-bottom flask and filtered. The filtrate was evaporated to dryness with a rotary evaporator (60 °C, 1 Torr) and then purified by gel permeation chromatography (Bio-Beads S-X12, 2.0 × 20 cm; toluene). MALDI mass, *m*/*z*: 838.7. UV−vis (λ_{max} (nm)), ϵ (M^{-1} cm^{-1}) (cyclohexane): 584, 9.2.

1,3-Butadiene Polymerization. Cyclohexane (450 g), 1,3-butadiene (90 g), **NDH** (1.0% cyclohexane) or **ND** (1.0% cyclohexane), diethylaluminum chloride (1.0 M *n*-heptane), diisobutylaluminum hydride (1.0 M *n*-heptane), and triisobutylaluminum (1.0 M *n*-heptane) were added to a 1 L pressure glass reactor under a nitrogen atmosphere and reacted at 60 °C for 2 h. The resulting polybutadiene was terminated by methanol.

Characterization. The microstructures of polybutadiene were measured in CS_2 solution by IR spectroscopy (Bio-Rad, FTS 60-A) according to the literature.[20] Gel permeation chromatography data were obtained using a Waters 2690 system employing connected Waters ultrastyregel columns, HMW7 and HMW6E, with a refractive index detector. Tetrahydrofuran was used as solvent at the flow rate of 1.0 mL/min. MALDI (solvent: CH_2Cl_2, matrix: 2,5-dihydroxybenzoic acid, MW 154) and LRFAB mass spectra were obtained from Korea Basic Science Center.

XAS Measurement and Data Analysis. The neodymium samples were placed in an airtight X-ray absorption spectroscopy (XAS) cell made of Teflon with two Mylar windows (1/2000 in.; window size, 20 mm × 8 mm; optical path length, 2 mm). Nd L_{III}-edge XAS measurement was carried out using Beam Line 3-C (2.0 GeV; 80−150 mA; Si(111) double flat crystal monochromator) at the Pohang Accelerator Laboratory (PAL) at POSTECH, Korea. XAS data were collected at room temperature in the transmission mode using $N_2(I_0)$ and Ar(I) filled ionization detectors. The monochromator was detuned by 20% in incident X-ray beam. All data were internally calibrated using Mn foil (K-edge, 6539 eV). The near-edge region was scanned at equal energy step of 0.30 eV/point to resolve fine structures.

Structure Determination. Model-building and molecular dynamics simulation were performed on a SGI Indigo workstation in the context of Cerius^2 molecular modeling package (Molecular Simulation Inc.).

Acknowledgment. The author gratefully acknowledges the fruitful discussion and suggestion of Dr. Lee, Hosull, R & D director of KKPC. Prof. Kim, Sunghyun, for supporting the acquisition of XAS data and Mr. Lee, SeungHwa, and Mr. Kim, Hyukjeon, for providing IR data are acknowledged. Experiments at Pohang Accelerator Laboratory were supported in part by MOST and POSCO.

Supporting Information Available: Optimized structures of **ND** and **NDH** in gas phase by Universal Force Field in Cerius^2. This material is available free of charge via the Internet at http://pubs.acs.org.

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