

Polymer Chemistry

Volume 17
Number 11
17 March 2026
Pages 1063-1134

rsc.li/polymers



ISSN 1759-9962

PAPER

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Cite this: *Polym. Chem.*, 2026, **17**, 1069

A one-shot activating reagent of neodymium carboxylate for highly *cis*-1,4 specific butadiene polymerization

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A streamlined catalytic system to produce high-*cis* polybutadiene (*cis*-PBD), consisting of neodymium carboxylate and a halogenated MAO-derived activator, was developed. Halogenated MAO was synthesized via the replacement of methyl groups of commercial MAO with chlorides using BCl₃. The polymerization of butadiene under optimal conditions (Al/Nd = 50 and Cl/Nd = 2.1) at 25 °C resulted in nearly complete conversion, producing *cis*-PBD with a high molecular weight ($M_n > 10^5$), a narrow molecular weight distribution ($\mathcal{D} \sim 2$), and a high *cis*-content (>98%). Cl incorporation into both the MAO framework and the active species was confirmed by X-ray total scattering analysis, which showed that halogenated MAO functions as both an alkylating and halogenating agent for the neodymium salt. Halogenated MAO may replace traditional ternary cocatalyst systems, giving a simpler catalyst composition and higher stereoregularity.

Received 5th January 2026,
Accepted 4th February 2026

DOI: 10.1039/d6py00007j

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Introduction

cis-1,4-Polybutadiene (*cis*-PBD) is one of the most widely used elastomers, with many applications such as automotive tires or a modifier of plastics. The high chain flexibility of *cis*-PBD allows operation at lower temperatures and results in low hysteresis energy loss, and its highly ordered structure undergoes strain-induced crystallization, which contributes to its excellent mechanical properties. In particular, for the tire industry, highly *cis*-regular PBD (95% or more) is desired because it exhibits low rolling resistance. The fundamental physical properties dictating the advantages of *cis*-PBD, such as resistance to abrasion or tearing, tensile strength, permanent deformation, and crystallization rate, are dramatically improved with each increasing 1% with respect to *cis*-1,4 content.^{1–4}

The industrial production of *cis*-PBD is performed mainly using Ziegler–Natta catalysts containing nickel, cobalt, titanium, and lanthanide metals, typically achieving a *cis*-1,4 ratio of more than 90%.⁵ In particular, Nd-based Ziegler–Natta catalysts, discovered in the 1960s, swiftly emerged as the predominant focus in both research and industry owing to their exceptional activity and stereoselectivity in diene polymerization.^{6,7} Ternary systems such as Nd-*vers*ate (Nd(*vers*)₃)/alkylalumi-

num (Et₃Al, ^tBu₃Al, methylaluminoxane (MAO), or ^tBu₂AlH)/halogen sources (Et₃Al₂Cl₃, Et₂AlCl, SiCl₄, or ^tBuCl) are the most representative systems, typically yielding *cis*-1,4 isomers with approximately 95–98%.^{8–16}

The activation mechanism of the ternary system consists of three fundamental reactions: removal of coordinating water and excess carboxylic acids from the neodymium center by alkylaluminum, alkylation of neodymium carboxylate by alkylaluminum, and chlorination of the remaining carboxylate or alkyl. The obtained active species has a mixed R/Cl first coordination shell with vacant coordination sites for the monomer and sufficient Lewis acidity (Scheme 1). These mechanisms are supported by the various reactions observed on neodymium



Scheme 1 Proposed activation and propagation mechanism of Nd carboxylate-catalyzed butadiene polymerization.

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the capillary was sealed with UV-curable glue. The sample capillary was placed in high throughput measuring equipment at the beamline and exposed to 112.8 keV X-rays for 600 seconds. Scattered X-rays were captured with a two-dimensional CdTe semiconductor detector. The scattering intensity of an empty capillary was measured under the same conditions and then subtracted as background. The sample's scattering intensity was analyzed using normal procedures to produce the atomic pair distribution function (PDF, $G(r)$) curve.

General procedure for butadiene polymerization

In a 20 mL Schlenk flask, halogenated MAO (4.0 mmol) was diluted with toluene (2.0 mL) under nitrogen. Neodymium 2-ethylhexanoate (80 μ mol) in toluene (3.4 mL) was then added to the halogenated MAO solution. The pale purple solution was obtained after stirring for 20 minutes. The butadiene solution in toluene (2.4 M, 4.2 mL, 10 mmol) was injected and stirred to start the polymerization, which gave a light blue solution, and the system's viscosity progressively increased as the reaction proceeded. After stirring at room temperature for 2 hours, the reaction mixture was poured into acidic methanol containing 2% hydrochloric acid and the precipitated solid was recovered. The polymer was dried under vacuum overnight until it reached a constant weight.

Results and discussion

Halogenated MAO was prepared according to the previous literature²⁹ by adding various amounts of BCl_3 (0.33–2.0 mol% relative to Al) to a commercial MAO solution in toluene at room temperature. The vacuum-dried halogenated MAO was redissolved in toluene, reacted with neodymium 2-ethylhexanoate, and utilized in butadiene polymerization (Table 1). Here, catalyst aging time did not affect the polymerization behavior, and the following polymerizations were started by monomer addition 20 minutes after mixing the Nd precursor and halogenated MAO.

Table 1 Effect of the degree of halogenation of MAO in butadiene polymerization using a neodymium 2-ethylhexanoate–MAO system^a

Run	Cl/Nd	Yield (%)	M_n^b (10^3)	D^b	cis^c (%)	T_g^d ($^\circ\text{C}$)	T_m^d ($^\circ\text{C}$)	ΔH_m^d (J g^{-1})
1	0	75	45	2.0	70	–103	n.d. ^e	n.d. ^e
2	0.5	87	55	1.8	72	–104	n.d. ^e	n.d. ^e
3	1.0	91	43	1.9	79	–105	n.d. ^e	n.d. ^e
4	1.5	90	68	2.4	87	–110	–9	12
5	2.1	99	156	1.7	98	–111	–7	33
6	2.5	99	108	1.8	98	–110	–7	28
7	3.0	97	152	1.8	98	–110	–7	26

^a Polymerization conditions: solvent = toluene, temp. = 25 $^\circ\text{C}$, time = 2 h, Nd = 80 μ mol, Al/Nd = 50, Bd = 10 mmol. ^b Determined by GPC calibrated with polystyrene standards. ^c *cis*-1,4 microstructure ratio determined by ^{13}C NMR. ^d Determined by DSC. ^e Not detected.

Compared with the halogen-free MAO (run 1), halogenated MAO enhanced the *cis*-1,4 specificity and molecular weight of the polymer along with an increase of halogenation degree (runs 2–7). The microstructure of the polymer other than the *cis*-1,4 sequence was mostly the *trans*-1,4 sequence, and the 1,2-sequence was not detected by ^{13}C NMR spectra (see SI Fig. S19–S33). As is already known, the glass transition temperature (T_g) of the obtained polybutadiene was below -100 $^\circ\text{C}$ and it further decreased with an increase of *cis*-1,4 regularity. In addition, a melting temperature of around -10 $^\circ\text{C}$ was observed for a highly *cis*-1,4 specific fraction, which is slightly lower than the reported value of perfectly *cis*-1,4 regular polybutadiene.³⁰ Under these polymerization conditions, monomer conversion was not quantitative when unmodified MAO was used, whereas halogenated MAO gave the polymer almost quantitatively. These tendencies were similar to what has been observed in previously reported ternary systems. The obtained polymers were not completely soluble in THF or chloroform at ambient temperature, giving visible residues. Therefore, the evaluation of molecular weight by GPC and microstructure analysis by NMR were performed at high temperatures. All the GPC traces of the obtained polybutadiene showed a unimodal shape (Fig. S1–S15), and the molecular weight distribution (D) was around 2.0, which was relatively narrow for Nd-based systems. This relatively narrow dispersity suggests the formation of more uniform active species and/or improved control over chain-transfer processes compared to traditional ternary systems. The use of MAO generally contributes to narrowing the molecular weight distribution. However, both the stereospecificity and molecular weight under optimal conditions (runs 5–7) were higher than those obtained for the $\text{Nd}(\text{O}^i\text{Pr})_3/\text{MAO}/t\text{-BuCl}$ system.³¹ We further investigated the effect of polymerization conditions at a Cl/Nd ratio of 2.1 (run 5), which provided a balance between high conversion, high *cis*-1,4 content and high molecular weight.

The halogenated MAO system revealed a distinct low limit in the Al/Nd ratio (Table 2). A low Al/Nd ratio (Al/Nd = 30) led to insufficient activation/halogenation, producing a very small amount of polymer (run 8). Although the polymer yield was not high enough for microstructure quantification by ^{13}C

Table 2 Effect of the Al/Nd ratio on butadiene polymerization using a neodymium 2-ethylhexanoate–halogenated MAO system^a

Run	Al/Nd	Yield (%)	M_n^b (10^3)	D^b	cis^c (%)	T_g^d ($^\circ\text{C}$)	T_m^d ($^\circ\text{C}$)	ΔH_m^d (J g^{-1})
5	50	99	156	1.7	98	–111	–7	33
8	30	4	10	1.5	—	–112	–6	26
9	70	97	30	2.5	97	–111	–6	12
10	20 + 30 ^f	99	151	1.7	98	–110	–7	28

^a Polymerization conditions: solvent = toluene, temp. = 25 $^\circ\text{C}$, time = 2 h, Nd = 80 μ mol, Cl/Nd = 2.1, Bd = 10 mmol. ^b Determined by GPC calibrated with polystyrene standards. ^c *cis*-1,4 microstructure ratio determined by ^{13}C NMR. ^d Determined by DSC. ^e Not determined. ^f Both halogenated MAO (20 equiv. to Nd) and halogen-free MAO (30 equiv. to Nd) were used to maintain the Cl/Nd ratio.



and even longer than the Nd–Al distances in the Nd (vers)₃ⁱBu₃Al/ⁱBu₂AlCl (1 : 10 : 3) system previously observed by EXAFS measurements.

The alkyl-bridged neodymium–aluminum binuclear complexes typically show a Nd–Al distance within the range of 3.1–3.3 Å,^{19,34,35} whereas chloro-bridged neodymium–aluminum multinuclear complexes often show larger distances of Nd and Al (3.6–3.8 Å)^{36–38} (Fig. S35). Therefore, the observed Nd–Al correlation at 3.4 Å in the BCl₃-modified MAO system represents an intermediate state that reflects a higher extent of chlorination and a greater contribution of chloro-bridged environments compared to the unmodified or traditional ternary systems. Such structural characteristics may contribute to the observed high activity and relatively narrow molecular weight distribution.

Conclusions

We presented a strategy for simplifying the formulation of a cocatalyst for Nd-catalyzed butadiene polymerization by using partially halogenated aluminosilane. Moreover, the halogenated MAO gave highly *cis*-1,4 regular, high molecular weight polybutadiene with a narrow molecular weight distribution. Therefore, we successfully demonstrated the advantage of this catalyst system from a practical point of view. Furthermore, X-ray total scattering measurements suggested efficient chlorination at the neodymium center in this system, which may lead to high activity at ambient temperature.

Author contributions

J. Y.: investigation, data curation, and writing the original draft; T. W.: methodology and investigation for PDF analyses; Y. N. and T. S.: review and editing; and R. T.: conceptualization, supervision, and validation. All authors have read and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: NMR spectra of polymers, DSC thermograms and GPC traces of the obtained polymers, and raw profiles or X-ray total scattering data, examples of Nd/Al multinuclear complexes. See DOI: <https://doi.org/10.1039/d6py00007j>.

Acknowledgements

The authors gratefully acknowledge the generous donation of methylaluminumoxane from Tosoh Finechem Co. Ltd. The authors are also grateful to the Natural Science Center for Basic Research and Development (N-BARD) at Hiroshima University for high-temperature NMR measurements. The synchrotron radiation experiments were performed at the BL04B2 beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (T. W.).

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