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Polymerization of Styrene by Rare Earth Coordination Catalysts[†]

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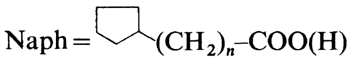
ABSTRACT: Polymerization of styrene has been investigated using homogeneous rare earth coordination catalysts based on a neodymium compound, triisobutylaluminium and/or a third component. Satisfactory results have been obtained by aging catalyst components for 1 h at 60°C, and polymerizing styrene in hexane at 60°C. The addition of CCl_4 as a third component to $Nd(naph)_3$–$Al(iso\text{-}Bu)_3$ system greatly increases catalytic activity. The order of catalytic activity of Nd compounds with different ligands for styrene polymerization is as follows: $Nd(P_{507})_3 \sim Nd(P_{204})_3 > Nd(naph)_3 > Nd(acac)_3 \cdot 3H_2O$. Both $Nd(P_{507})_3$–$Al(iso\text{-}Bu)_3$ and $Nd(P_{204})_3$–$Al(iso\text{-}Bu)_3$ systems prepared in the presence of monomer show high catalytic activity. A syndiotactic-rich polystyrene was obtained with Nd $(naph)_3$–Al $(iso\text{-}Bu)_3$- and/or a third component systems in hexane at 60°C.

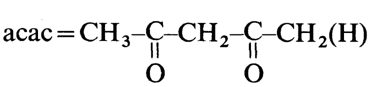
KEY WORDS Rare Earth Coordination Catalyst / Styrene / Polymerization /

In general, rare earth coordination catalysts are composed of two or three components: rare earth compound, Group I—III organometallic compound with/without a third component. Since the 1960's, the discovery of rare earth coordination catalysts in stereospecific polymerization, the polymerization of conjugated dienes, acetylene and its derivatives, and alkylene oxide by rare earth catalysts have been studied.[1–4] Recently we extended the study of using rare earth coordination catalysts toward polymerization of styrene.[5] This paper reports further information on the styrene polymerization using homogeneous neodymium coordination catalysts.

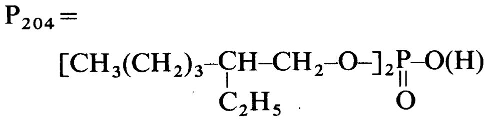
EXPERIMENTAL

Styrene (St) was freed of inhibitor by distillation under nitrogen at reduced pressure. Triisobutylaluminium Al $(iso\text{-}Bu)_3$ was used as purchased. All the reagents (toluene, hexane, chloroform, and tetrachloromethane) were analytical reagents and dried with activated alumina. Neodymium naphthenate $Nd(naph)_3$, and phosphonate $[Nd(P_{507})_3$, $Nd(P_{204})_3]$, and acetylacetonate $Nd(acac)_3 \cdot 3H_2O$ were prepared according to the methods in ref 6. The structures of various ligands in neodymium catalysts used are as follows:

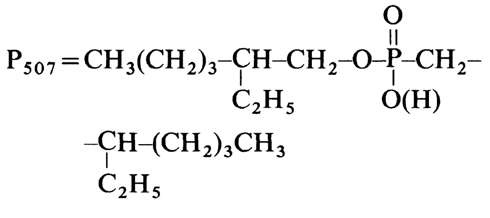




$$acac = CH_3\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_2\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_2(H)$$



$$P_{204} = [CH_3(CH_2)_3\text{–}\underset{\underset{C_2H_5}{|}}{CH}\text{–}CH_2\text{–}O\text{–}]_2\underset{\underset{O}{\|}}{P}\text{–}O(H)$$



$$P_{507} = CH_3(CH_2)_3\text{–}\underset{\underset{C_2H_5}{|}}{CH}\text{–}CH_2\text{–}O\text{–}\overset{\overset{O}{\|}}{\underset{\underset{O(H)}{|}}{P}}\text{–}CH_2\text{–}\underset{\underset{C_2H_5}{|}}{CH}\text{–}(CH_2)_3CH_3$$

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Polymerizations were carried out in a 50 ml ampoule which was heated, evacuated and filled with nitrogen for several cycles before use. Neodymium compound, solvent and Al(iso-Bu)$_3$ were added to the ampoule, aged for an hour at 60°C to obtain a homogeneous catalyst solution, and then a third component was introduced and continuously aged for half an hour at 60°C. Finally styrene was introduced and polymerized at 60°C for a definite reaction time. The polymerization was terminated by adding methanol with 10% HCl. The resulting polymer was precipitated by pouring the reaction mixture into 50 ml methanol, filtered, washed with water and ethanol, and dried at 50°C under vacuum.

Gel permeation chromatography (GPC) measurements of polystyrene (PS) were performed at 30°C on a Waters GPC Model 208, referenced as a standard polystyrene. The ^{13}C NMR spectra were taken on a JEOL FX-90 Q NMR at 30°C. The polymers were dissolved in deuterated chloroform (CDCl$_3$). Tetramethylsilane (TMS) was used as the internal reference. Intrinsic viscosity was determined in benzene at 25°C. The molecular weight of PS ($\bar{M}_v$) was calculated by the formula:

$$[\eta]=9.52\times10^{-3}\bar{M}_v{}^{0.744}(\mathrm{ml\,g^{-1}}).^7$$

RESULTS AND DISCUSSION

In a previous paper, we described that it is easy to polymerize styrene by Nd(naph)$_3$–Al-(iso-Bu)$_3$ catalyst in CHCl$_3$ solvent at 50°C to obtain atactic PS, but is difficult in toluene and hexane.[5] In this study, however, varying catalyst age temperature, it was also easy to polymerize styrene by Nd (naph)$_3$–Al (iso-Bu)$_3$ in toluene and hexane at 60°C, and syndiotactic-rich PS is obtained. Catalyst age temperature is particularly important for obtaining high activity. As seen in Table 1, the catalytic activity increased markedly when catalyst components were aged in a solvent for 1 h at 60°C. Furthermore, it is seen from Table I that molecular weight of PS obtained in toluene is by one order of magnitude higher than that obtained in hexane, but the conversion for the polymerization in toluene is lower than that in hexane.

It was observed that the conversion and molecular weight of the polymer formed with the different third components added to the Nd (naph)$_3$–Al(iso-Bu)$_3$ system are all different (Table II). Halohydrocarbons (CCl$_4$, CHCl$_3$) greatly increase catalytic activity while decreasing PS molecular weight. Water increases both catalytic activity and PS molecular weight. This may be because different active sites were

Table I. Effect of some variables in catalyst preparation.

Solvent (S)	Catalyst preparation	Conversion	$\bar{M}_n\times10^{-4}$	$\bar{M}_w\times10^{-4}$	MWD
		%	GPC		
Toluene	$\mathrm{Nd+S+Al}\xrightarrow[25^\circ\mathrm{C},\,20\,\mathrm{min}]{\text{aging}}\mathrm{+St}$	0	—	—	—
	$\mathrm{Nd+S+Al}\xrightarrow[60^\circ\mathrm{C},\,1\,\mathrm{h}]{\text{aging}}\mathrm{+St}$	15.1	21.1	36.8	1.74
Hexane	$\mathrm{Nd+S+Al}\xrightarrow[25^\circ\mathrm{C},\,20\,\mathrm{min}]{\text{aging}}\mathrm{+St}$	3.9	1.4	3.0	2.18
	$\mathrm{Nd+S+Al}\xrightarrow[60^\circ\mathrm{C},\,1\,\mathrm{h}]{\text{aging}}\mathrm{+St}$	28.6	2.6	6.8	2.63

[a] Nd(naph)$_3$–Al(iso-Bu)$_3$ catalyst system; Polymn. conditions: [Nd] $=5.0\times10^{-2}\,\mathrm{mol\,l^{-1}}$; [M] $=5.0\,\mathrm{mol\,l^{-1}}$; Al/Nd = 8 (mol ratio); 60°C, 24 h.

Table II. Effects of third components (A) on polymerization of styrene

A	A/Nd (mol ratio)	Conversion %	$\bar{M}_v \times 10^{-4}$
No	0	28.6	6.0
H_2O	0.5	33.4	18.5
$CHCl_3$	1.0	95.4	1.1
CCl_4	1.0	100.0	0.8

[a] The catalyst preparation:

$$\mathrm{Nd+S+Al} \xrightarrow[60°\mathrm{C},\,1\,\mathrm{h}]{\text{aging}} +\mathrm{A} \xrightarrow[60°\mathrm{C},\,0.5\,\mathrm{h}]{\text{aging}} +\mathrm{St};$$

hexane solvent, 12 h, other conditions are the same as Table I.

Table III. Effects of catalyst concentration[a]

$[\mathrm{Nd}] \times 10^3$ mol l^{-1}	3.7	7.5	15.0	30.0
Catalytic activity (g PS/g Nd)	195.2	389.4	240.4	120.0

[a] $\mathrm{Nd(naph)_3}$–$\mathrm{Al(iso\text{-}Bu)_3}$–$CCl_4$ system; $CCl_4/\mathrm{Al} = 1.0$ (mol ratio), other conditions are the same as Table II.

Table IV. Effects of Al/Nd mol ratio on conversion for the polymerization of styrene[a]

Al/Nd (mol ratio)	4	6	8	10	12
Coversion (%)	7.5	14.7	58.5	93.7	98.1

[a] Conditions: $[\mathrm{Nd}] = 7.5 \times 10^{-3}$ mol l^{-1}, $[\mathrm{M}] = 7.6$ mol l^{-1}, others are the same as Table III.

Table V. Effects of CCl_4/Al mol ratio on polymerization of styrene[a]

CCl_4/Al (mol ratio)	Conversion %	$\bar{M}_v \times 10^{-4}$
0.3	32.0	10.7
0.5	51.0	6.6
1.0	89.5	2.7
1.5	98.9	1.7
2.0	100.0	0.9

[a] Conditions: $[\mathrm{Nd}] = 1.25 \times 10^{-2}$ mol l^{-1}, others are the same as Table III.

Table VI. Comparison of activities for Nd catalysts with different ligands (Nd L_3)[a]

Nd L_3	$\mathrm{Nd(P_{507})_3}$	$\mathrm{Nd(P_{204})_3}$	$\mathrm{Nd(naph)_3}$	$\mathrm{Nd(acac)_3 \cdot 3H_2O}$
Conversion /%	54.9	52.0	28.6	< 10

[a] The catalyst preparation:

$$\mathrm{Nd+S+Al} \xrightarrow[60°\mathrm{C},\,1\,\mathrm{h}]{\text{againg}} +\mathrm{St},$$

hexane solvent, other conditions are the same as Table I.

Table VII. Conversion (%) data for the polymerization of styrene by Nd L_3–St–$\mathrm{Al(iso\text{-}Bu)_3}$ catalyst systems[a]

Nd L_3–St–$\mathrm{Al(iso\text{-}Bu)_3}$ / L	P_{507}	P_{204}	naph	acac
Conversion/%	73.9	77.9	30.0	8.1

[a] The catalyst preparation:

$$\mathrm{Nd+S+St+Al} \xrightarrow[60°\mathrm{C},\,1\,\mathrm{h}]{\text{aging}} +\mathrm{St};$$

Nd/St/Al = 1/4/8, (mol ratio), other conditions are the same as Table VI.

formed when CCl_4 or H_2O were added as third component into $\mathrm{Nd(naph)_3}$–$\mathrm{Al(iso\text{-}Bu)_3}$ catalyst system.

The effects of catalyst concentration, Al/Nd and CCl_4/Al mol ratio on the polymerization of styrene are summarized in Tables III, IV, V. The highest catalytic activity was obtained at a catalyst concentration of 7.5×10^{-3} mol l^{-1}; both above and below this concentration, activity decreased. The conversion for polymerization of styrene increases while decreasing PS molecular weight with increasing Al/Nd and CCl_4/Al mol ratios.

Besides neodymium naphthenate [$\mathrm{Nd(naph)_3}$], phosphonates [$\mathrm{Nd(P_{507})_3}$, $\mathrm{Nd(P_{204})_3}$], and acetylacetonate [$\mathrm{Nd(acac)_3 \cdot 3H_2O}$] combined with triisobutylaluminium also can form effective catalysts for the polymerization of

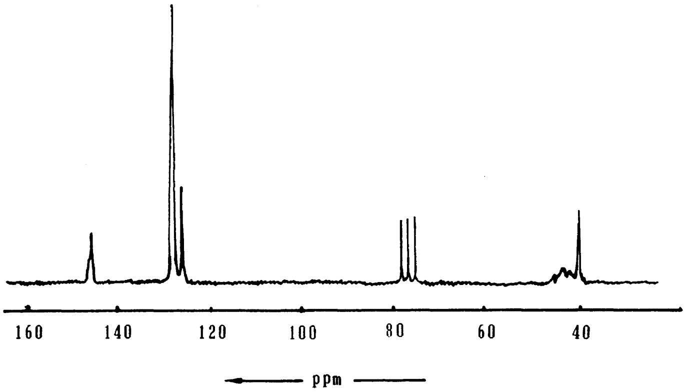

Figure 1. ^{13}C NMR spectrum of PS prepared with $Nd(naph)_3$–$Al(iso\text{-}Bu)_3$–H_2O catalyst system: Solvent, $CDCl_3$; reference, TMS.

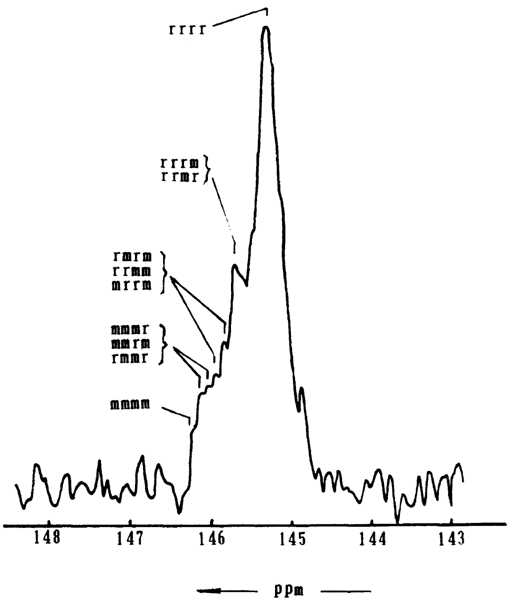

Figure 2. Enlarged ^{13}C NMR spectrum of the aromatic C1 carbon of PS prepared with $Nd(naph)_3$–$Al(iso\text{-}Bu)_3$–H_2O catalyst system: Solvent, $CDCl_3$; reference, TMS; r = racemic dyad; m = meso dyad.

styrene in hexane at 60°C, yet the catalytic activity of which is quite different (see Table VI). From the data in Table VI the activity of Nd catalysts with different ligands for styrene polymerization has the following order: $Nd\ (P_{507})_3 \sim Nd\ (P_{204})_3 > Nd(naph)_3 > Nd(acac)_3 \cdot 3H_2O$.

Table VII illustrates the activity of Nd coordination catalysts prepared in the presence of the monomer. From a comparison of the data of Tables VI and VII, the presence of the monomer during catalyst formation may increase the activity of the catalyst. It is worth noting that the activity of $Nd(P_{507})_3$ and $Nd(P_{204})_3$ catalyst systems in this situation showed great increase.

PS obtained with catalyst systems based on $Nd(naph)_3$, $Al(iso\text{-}Bu)_3$ and/or a third component in hexane at 60°C is a syndio-rich random polymer, which is confirmed by ^{13}C NMR (Figures 1 and 2). In Figure 2, the aromatic C1 spectrum of a syndiotactic-rich PS is shown, according to ref 8. It consists of seven peaks at 146.2, 146.1, 146.0, 145.9, 145.8, 145.7, and 145.3 ppm.

It is assumed in Figure 2 that C1 absorptions are split into Pentads which theoretically afford ten peaks. The peak at 145.3 ppm is assigned to an rrrr pentad and a peak at 146.2 ppm to a mmmm pentad.[8] Moreover, it is seen from Figure 2 that the relative amounts of the *rrrr*, *rrrm*, and *rrmr* pentads are much higher than those of other pentads in the PS obtained. Besides, a peak at the highest magnetic field (144.9 ppm) seems to be one which is longer than an *rrrr* pentad, and further investigation should perhaps be conducted.

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