

A Novel Catalytic System—NdCl₃·HMPA/Al(*i*-Bu)₃ for Copolymerization of Isoprene and Styrene

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Copolymerization of styrene (St) and isoprene (IP) was carried out with a catalyst system composed of anhydrous lanthanide chloride hexamethyl phosphoramidate complex (LnCl₃·HMPA) and aluminum organic compound (AOC). Among the catalysts examined, catalyst NdCl₃·HMPA/Al(*i*-Bu)₃ showed a high activity in the copolymerization under certain conditions giving copolymers (5%—15% St content) with high *cis*-1,4 microstructure in IP units (>95%). The effects of HMPA/Nd molar ratio, Al/Nd molar ratio, monomer/Nd molar ratio, St feed ratio, and the reaction time on copolymerization were examined with this catalytic system. The obtained copolymers were characterized by ¹H and ¹³C NMR spectroscopies and gel-permeation chromatography (GPC).

Keywords isoprene, styrene, copolymerization, lanthanide chloride

Introduction

Rare-earth coordination catalysts are known for their high activity and high stereospecificity in the polymerization of conjugated dienes.¹⁻⁵ The copolymerization of styrene (St) with butadiene using rare earth catalyst was followed with interest soon as the rare earth coordination catalyst appeared in the early 1960s.⁶⁻¹⁴ Copolymerization of isoprene (IP) and St using coordination catalysts was reported in a few papers,^{10,15-18} among them only Jin *et al.*¹⁰ and our group¹⁸ reported the use of rare earth catalysts for the copolymerization of IP and St.

Anhydrous lanthanide chloride is cheap and easily prepared chemicals. It is insoluble in organic solvent. But it can react with certain reagents, such as ethanol,² epoxide¹⁹ to form complex soluble in organic solvent and be used as effective catalyst compound for polymerizations. Recently, we have found that HMPA can react with anhydrous lanthanide chloride, forming complex. Thus, an effective catalytic system based on NdCl₃·HMPA and Al(*i*-Bu)₃ for isoprene polymerization and copolymerization of IP and St has been found. The characteristics of the copolymerization of isoprene and styrene with this new rare earth catalytic system are reported in this paper.

Experimental

Materials

Commercial IP, St and HMPA were purified by distillation under reduced pressure. Toluene and THF were dried by the conventional method. Anhydrous lantha-

nide chlorides were prepared from lanthanide oxides (Shanghai Yuelong Chemical Plant, 99.95%) as described in literature.²⁰ Al(*i*-Bu)₃, AlEt₃ and Al(*i*-Bu)₂H (AKZO Nobel) with purity of 99% were used without further purification. Al₂Et₃Cl₃ (provided by Zhenhai Petrochemicals Co.) was distilled before use.

Polymerization

Polymerization was carried out in a 50 mL ampoule under an atmosphere of dry argon. Catalyst was prepared by dissolving NdCl₃ in HMPA in a proper molar ratio firstly, then adding Al(*i*-Bu)₃ to the ampoule and aging at 50 °C for 0.5 h. Finally, IP and/or St were introduced using toluene as solvent, and polymerized for a certain time. The polymerization mixture was poured into a large quantity of ethanol containing 5% hydrochloric acid and a little amount of 2,6-di-*tert*-butyl-4-methyl phenol. The polymers were washed with ethanol and then dried in vacuum at 40 °C for 24 h and weighed to determine the copolymer yield.

Measurements

¹H and ¹³C NMR spectra were recorded on an Avance DMX 500 NMR in CDCl₃ using tetramethylsilane as the internal standard. Copolymer composition and the microstructure of IP units were determined by means of ¹H NMR spectroscopy.¹⁵ The intrinsic viscosities of the copolymer were measured in toluene with an Ubbelohde viscosimeter at 30 °C. The molecular weight and the molecular weight distribution (MWD) were determined by a WATERS 150C GPC with UV (WATERS 486UV) and RI (R401) detectors using THF as eluent and polystyrene as standard at 30 °C.

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Results and discussion

The copolymerization of isoprene and styrene with various rare earth complexes, cocatalyst—aluminum organic compound and solvents are summarized in Table 1. HMPA was added into the suspension of LnCl_3 in toluene and heated at 50 °C for 30 min. Polymerization active species containing Ln—C bond was probably formed when alkyl aluminum was added into above solutions. It can be seen that $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ is an effective catalyst for the IP polymerization (50 °C, 6 h, $[\text{IP}]/[\text{Nd}]=1000$, yield 98%, high *cis*-1,4 polyisoprene with rather high molecular weight of about 4.64×10^5). $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ is also a good catalyst for the copolymerization of IP and St (50 °C, 6 h, $[\text{M}]/[\text{Nd}]=1000$, 63% yield, high *cis*-1,4 IP unit of about 97% with 8.0% St content). ^1H and ^{13}C NMR spectra indicate that the obtained copolymer has high *cis*-1,4 microstructure with little 3,4 microstructure in IP unit, and the *cis*-1,4 content of IP unit calculated by means of ^1H NMR spectroscopy remains over 95% irrespective of the presence of styrene unit. In our previous paper, the *cis*-1,4 content of the IP units decreased little with increasing St content in the copolymer.¹⁸

The catalytic activities of anhydrous LaCl_3 , GdCl_3 or PrCl_3 are lower under the tested conditions and anhydrous TbCl_3 , YCl_3 or ErCl_3 has no activity for the co-

polymerization of isoprene and styrene. Among the co-catalyst alkyl aluminum used, the catalytic activity sequence is as follows: $\text{Al}(i\text{-Bu})_3 > \text{Al}(i\text{-Bu})_2\text{H} \gg \text{AlEt}_3 \sim \text{Al}_2\text{Et}_3\text{Cl}_3$. Solvent sort has great influence on copolymerization. It can be seen from Table 1 that, tetrahydrofuran (THF) and chloroform are not suitable for the copolymerization. Cyclohexane is another proper solvent for this copolymerization.

The effects of HMPA/Nd molar ratio, Al/Nd molar ratio, monomer/Nd molar ratio, St feed ratio, and the polymerization time on copolymerization were examined and summarized in Tables 2—5 and Figure 1, and it was found that the better molar ratio of HMPA to NdCl_3 is 3—5.

Figure 1 illustrated the influence of polymerization time on copolymer yield and St content. The yield increased with the polymerization time prolonged. The St content of copolymer was slightly decreased during the whole copolymerization process.

The molecular weight and yield of copolymer decreased with increasing molar percentage of St in the feed, on the contrary, St content in copolymer increased. It is worth noting that the *cis*-1,4 content of IP unit in copolymer was kept at a steady high value (about 97%) in spite of changes of the comonomer feed ratios (Table 3). The molar ratio of $\text{Al}(i\text{-Bu})_3$ to NdCl_3 affects the copolymerization obviously. Data in Table 4 showed

Table 1 Copolymerization of isoprene and styrene with $\text{LnCl}_3 \cdot \text{HMPA}/\text{AOC}$ catalyst system^a

Run	LnCl_3	Solvent	AOC	Yield/%	$[\eta]/(\text{dL} \cdot \text{g}^{-1})$	St content/mol%	Microstructure of the IP unit	
							<i>cis</i> -1,4/%	3,4/%
1	LaCl_3	toluene	$\text{Al}(i\text{-Bu})_3$	22	1.30	11.0	95.3	4.7
2	GdCl_3	toluene	$\text{Al}(i\text{-Bu})_3$	4.2	—	—	—	—
3	PrCl_3	toluene	$\text{Al}(i\text{-Bu})_3$	31	4.97	9.8	95.8	4.2
4	NdCl_3	toluene	$\text{Al}(i\text{-Bu})_3$	63	1.73	8.0	96.6	3.4
5 ^b	NdCl_3	toluene	$\text{Al}(i\text{-Bu})_3$	98	2.67	0	97.1	2.9
6	NdCl_3	toluene	$\text{Al}(i\text{-Bu})_2\text{H}$	32	1.60	6.6	91.2	8.8
7	NdCl_3	toluene	AlEt_3	7.2	—	—	—	—
8	NdCl_3	toluene	$\text{Al}_2\text{Et}_3\text{Cl}_3$	4.6	—	—	—	—
9	NdCl_3	THF	$\text{Al}(i\text{-Bu})_3$	1.1	—	—	—	—
10	NdCl_3	chloroform	$\text{Al}(i\text{-Bu})_3$	1.1	—	—	—	—
11	NdCl_3	cyclohexane	$\text{Al}(i\text{-Bu})_3$	50	1.67	7.49	97.7	2.3

^a $[\text{Ln}]=3.0 \times 10^{-3}$ mol/L, $[\text{HMPA}]/[\text{Ln}]=5$, $[\text{M}]=3.0$ mol/L, $[\text{IP}]/[\text{St}]=7/3$, $[\text{Al}]/[\text{Nd}]=30$, 50 °C, 6 h, in toluene. ^b Without styrene.

Table 2 Effect of molar ratio of $[\text{HMPA}]/[\text{Nd}]$ on copolymerization

HMPA/Nd molar ratio	Yield/%	$[\eta]/(\text{dL} \cdot \text{g}^{-1})$	St content/mol%	Microstructure of the IP unit	
				<i>cis</i> -1,4/%	3,4/%
1	no polymer	—	—	—	—
3	50	2.21	7.9	96.7	3.3
5	63	1.73	8.0	96.6	3.4
7	trace	—	—	—	—

Catalyst system: $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ in toluene, other conditions are the same as those in Table 1.

Table 3 Effect of St feed ratio on copolymerization

St in feed/mol%	$[\eta]/(\text{dL} \cdot \text{g}^{-1})$	Yield/%	St content/mol%	Microstructure of the IP unit	
				<i>cis</i> -1,4/%	3,4/%
0	2.67	98	0	97.1	2.9
10	2.34	96	4.2	97.0	3.0
30	1.73	63	8.0	96.6	3.4
50	1.53	39	11.5	96.8	3.2
70	1.09	20	15.0	96.8	3.2
90	—	3	—	—	—
100	—	0	—	—	—

Catalyst system: $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ in toluene, other conditions are the same as those in Table 1.

Table 4 Effect of molar ratio of Al/Nd on copolymerization

Al/Nd molar ratio	$[\eta]/(\text{dL} \cdot \text{g}^{-1})$	Yield/%	St content/mol%	Microstructure of the IP unit	
				<i>cis</i> -1,4/%	3,4/%
10	—	trace	—	—	—
20	2.05	45	6.9	96.1	3.9
30	1.73	63	8.0	96.6	3.4
40	1.04	65	7.6	97.1	2.9
50	0.93	67	6.3	96.8	3.2

Catalyst system: $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ in toluene, other conditions are the same as those in Table 1.

Table 5 Effect of different Monomer/Nd molar ratio on copolymerization

Monomer/Nd molar ratio	$[\eta]/(\text{dL} \cdot \text{g}^{-1})$	St content/mol%	Microstructure of the IP unit		Yield/%
			<i>cis</i> -1,4/%	3,4/%	
1000	1.73	8.0	96.6	3.4	63
1500	2.43	7.7	96.9	3.3	56
2000	3.03	7.9	97.1	2.9	49
2500	4.36	7.6	96.5	3.5	26

Catalyst system: $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ in toluene, $[\text{M}]=3.0$ mol/L, other conditions are the same as those in Table 1.

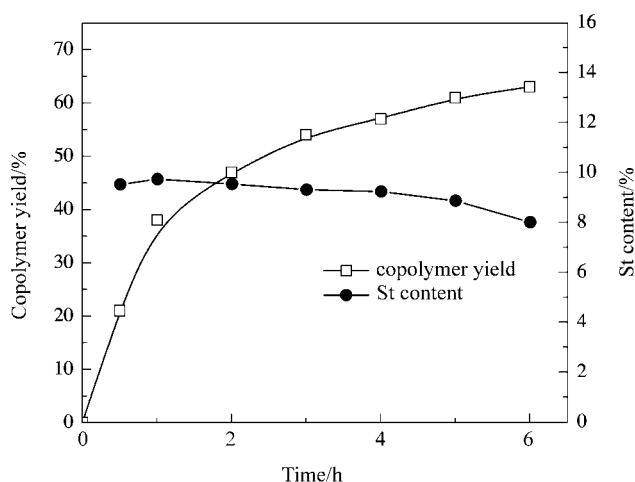


Figure 1 Effect of the copolymerization time on copolymer yield and St content. Catalyst system: $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ in toluene, other conditions are the same as those in Table 1.

that the molar ratio of St content decreased as the Al/Nd molar ratio increased. The polymer yield decreased and molecular weight increased with the increase of Monomer/Nd molar ratio. The ratio of monomer to NdCl_3 did not affect molar percentages of styrene content and *cis*-1,4 content of IP units in copolymer which were about 8% and 97% respectively, as shown in Table 5.

The GPC elution curves of the homopolymer and copolymer of isoprene and styrene obtained by $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ catalyst are shown in Figure 2. The molecular weight distribution of polyisoprene is relatively broad ($M_w/M_n=8.7$), while that of copolymer is relatively narrow ($M_w/M_n=5.9$). The copolymer also has a unimodal MWD curve, and the MWD curve by the UV detector ($\lambda=254$ nm), which is sensitive to the styrene unit, is in consistent with the MWD curve by the RI detector. Thus, it can be presumed that the obtained isoprene-styrene copolymer did not contain either homopolymer.

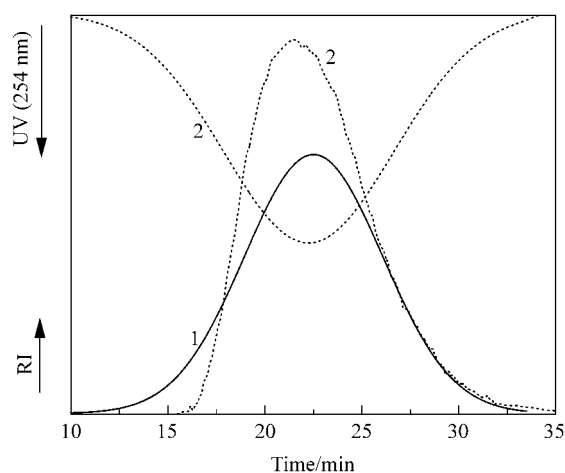


Figure 2 GPC elution curves of polyisoprene and copolymer of isoprene and styrene. 1: PIP (Table 1 run 4), 2: PIP-PSt (Table 1 run 5).

Conclusion

A novel catalyst composed of $\text{NdCl}_3 \cdot \text{HMPA}/\text{Al}(i\text{-Bu})_3$ has been found for the homopolymerization of IP and copolymerization of IP and St under certain conditions: IP/St = 7/3 (molar ratio), $[\text{Monomer}] = 3.0 \text{ mol/L}$, $[\text{Nd}] = 3.0 \times 10^{-3} \text{ mol/L}$, Al/Nd = 30, HMPA/Nd = 5 (molar ratio), copolymerization in toluene at $50 \text{ }^\circ\text{C}$ for 6 h. The unique point of this catalyst is high *cis*-1,4 content (95%) of IP unit in copolymer irrespective of the St content of the copolymerization (5%—15%).

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