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RESEARCH ARTICLE

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Polymerization of styrene catalyzed by rare earth Schiff base complexes

Abstract The rare earth Schiff base complex Nd $(H_2Salen)_2Cl_3 \cdot 2C_2H_5OH$ was synthesized by a simple and convenient method and characterized by IR and elemental analysis. The catalyst system composed of Nd $(H_2Salen)_2Cl_3 \cdot 2C_2H_5OH/Al(i\text{-}Bu)_3/CCl_4$ is effective for the polymerization of styrene (St). The optimum conditions are as follows: [St]/[Nd] = 1000, $[CCl_4]$/[Nd] = 9, [Al]/[Nd] = 30, and polymerization at 50°C for 20 h. The resulting polystyrene was characterized by NMR and GPC. The results of NMR show that the polymer obtained had a stereoregularity with 52.3% isotacticity and 47.7% syndiotacticity without any random structure.

Keywords rare earth Schiff base complex, styrene, polymerization

1 Introduction

Rare earth catalysts have been developed and used in polymer synthesis, and remarkable progress has been achieved in recent years in China [1]. These catalysts have been widely applied in the homo- and copolymerization of polar and nonpolar monomers and show unique catalytic properties. Synthesis and application of novel rare earth complexes is one of the main areas of this field, especially the exploration of new ligands and the resulting new catalyst. Recently, metal Schiff base complexes have been used as catalysts for polymerization [2,3], but rare earth Schiff base complexes as catalysts for polymerization were rarely reported. In this paper, the rare earth coordination catalyst system composed of a lanthanide Schiff base complex synthesized from the coordination of H_2Salen (*N*,*N*′-disalicylideneethylenediamine) and anhydrous lanthanide chlorides, combined with alkyl aluminum and other components, was used for the polymerization of styrene. The reactivity of the catalyst and the characteristics of polymerization are reported. It was found that the Nd $(H_2Salen)_2Cl_3 \cdot 2C_2H_5OH/Al(i\text{-}Bu)_3/CCl_4$ system can polymerize styrene to polystyrene with high molecular weight ($M_\eta = 17.5 \times 10^4$), and definite stereoregularity (52.3% isotactic, 47.7% syndiotactic) in toluene with over 50% yield.

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2 Experimental

2.1 Materials

Styrene (St) was purified by distillation over calcium hydride under reduced pressure. Toluene was distilled over sodium benzophenone ketyl. CCl_4 was dried by 4A molecular sieves. $Al(i\text{-}Bu)_3$(AKZO Nobel) with 99% purity was used as received.

2.2 Measurements

The intrinsic viscosity of the polymer was determined in THF at 25°C with an Ubbelohde viscometer. The viscosity average molecular weight (M_η) was calculated by the following equation: $[\eta] = 1.258 \times 10^{-4}[M_\eta]^{0.7155}$ [4]. The number average molecular weight (M_n) and molecular weight distribution (MWD) of polystyrene were determined in THF at 35°C by a Waters 150-C GPC with an IR detector against the polystyrene standards. The composition of rare earth Schiff base complexes was determined by elemental analysis (Cario Erba 1110), FT-IR spectrum (VECTOR 22), and coordination titration.

2.3 Preparation of rare earth Schiff base complexes

2.3.1 Synthesis of H_2Salen [5]

40.0 mL (0.38 mol) Salicylaldehyde and 13.0 mL (0.19 mol) ethylenediamine were refluxed in anhydrous alcohol for 15 min; yellow crystal was precipitated when

the reaction solution was cooled to room temperature. The resulting solid was purified by recrystallization and dried *in vacuo*. Yield:92%, ^{1}H NMR($CDCl_3$, 500 Hz, δ): 13.19(s, 2H, OH), 8.36(s, 2H, C<u>H</u>=N), 7.30(m, 2H, 3-<u>H</u>), 7.22(m, 2H, 6-<u>H</u>), 6.92(m, 2H, 2-<u>H</u>), 6.84(m, 2H, 5-<u>H</u>), 3.94 (s, 4H, N−C<u>H</u>$_2$−C<u>H</u>$_2$−N); IR, *v*: 1635 cm^{-1}, C=N.

2.3.2 Synthesis of rare earth Schiff base complexes [6]

1.651 g (0.00659 mol) anhydrous neodymium chloride and 3.560 g (0.0138 mol) H_2Salen were dissolved in 20 mL hot absolute alcohol individually. The solution containing a Schiff base ligand was added into the neodymium chloride solution under stirring, and a yellow powder precipitated immediately. After depositing for several hours, the solution was filtrated, and the resulting solid was washed with ethanol several times and dried *in vacuo*, yield: 88.0% (4.98 g). Lanthanum and dysprosium Schiff base complexes were synthesized similarly.

2.4 Characterization of the complex

The amounts of carbon, hydrogen, and nitrogen in the complex were determined by elemental analysis. Rare earth content was measured by coordination titration, and chlorine was titrated after precipitatation by silver nitrate. Anal. Calcd for $Nd(H_2Salen)_2Cl_3{\cdot}2C_2H_5OH$: C, 49.17; N, 6.37; H, 5.04; Nd, 16.4; Cl, 12.1. Found: C, 47.29; N, 6.34; H, 5.19; Nd, 16.7; Cl, 11.9.

From the IR spectra of H_2Salen and $Nd(H_2Salen)_2Cl_3{\cdot}2C_2H_5OH$ (Fig. 1), it can be seen that the peak of the C=N group was shifted from 1635 cm^{-1} to 1647 cm^{-1}, indicating that the group coordinated with neodymium.

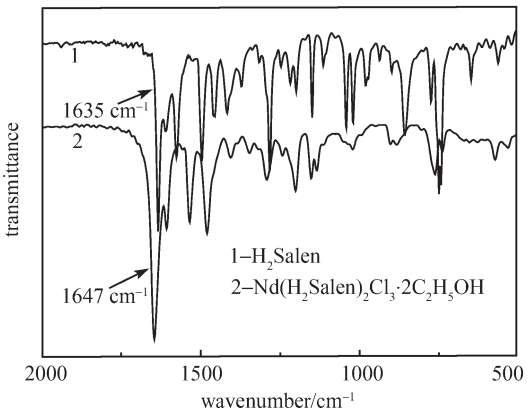

Fig. 1 IR spectra of H_2Salen (1) and $Nd(H_2Salen)_2Cl_3{\cdot}2C_2H_5OH$ (2)

2.5 Polymerization

All polymerizations were carried out under argon using Schlenk techniques. The catalyst components were added into a 20 mL ampoule sequentially. After aging the solvent for a certain period, a monomer was introduced into the ampoule and then polymerized at a certain temperature. Ethanol (containing 5% HCl) was added to terminate the polymerization. The polymer precipitate formed was collected by filtration, washed with ethanol three times, and then dried at room temperature at 30°C *in vacuo*.

3 Results and discussion

3.1 Effect of catalyst composition on the polymerization of styrene

The binary catalytic system created by the Neodymium Schiff base complex and Al(*i*-Bu)$_3$ shows low catalytic activity to the polymerization of styrene. It was found that polymerization activity was improved remarkably after adding a small amount of CCl_4 as the third component to form a ternary catalytic system. Tables 1 and 2 indicate that CCl_4 is more efficient than other alkane chlorides. When CCl_4/Nd = 9 (molar ratio), the polystyrene obtained had a 54.1% yield with viscosity average molecular weight of 17.5×10^4 g/mol. This means that CCl_4 participates in the formation of polymerization active species.

Table 1 Effect of the third component on polymerization

entry	third component	polymer yield/%	M_η ($\times 10^4$)
1	–	3.6	–
2	CH_2ClCH_2Cl	5.0	–
3	C_7H_7Cl	6.9	–
4	$CHCl_3$	11.4	2.8
5	CCl_4	54.1	17.5

Reaction conditions: [St]/[Nd] = 1000, [halide]/[Nd] = 9, [St] = 17.1 mol/L toluene as solvent
[Al]/[Nd] = 30, aging 1 h, polymerized at 50°C for 20 h

Table 2 Effect of CCl_4/Nd (molar ratio)on polymerization

entry	CCl_4/Nd (molar ratio)	polymer yield/%	$M\eta$ ($\times 10^4$)
1	0	3.6	–
2	3	15.6	2.4
3	5	17.2	2.6
4	7	18.3	19.3
5	9	54.1	17.5
6	11	41.0	3.2

Reaction conditions are the same as Table 1.

From Fig. 2 it can be seen that the conversion of polymerization increases with an increase of the Al/Nd molar ratio in the range of Al/Nd = 20–40; after that it decreases. The molecular weight of polystyrene decreases with an increase in the alkyl aluminum amount, indicating that the excess alkyl aluminum has a chain transfer effect to polymerization.

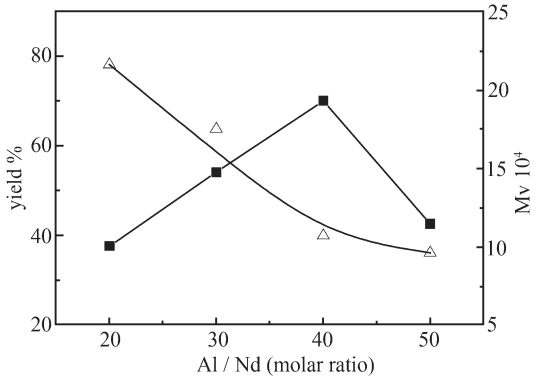

Fig. 2 Effect of Al/Nd molar ratio on the polymer yield (■) and M_v of polymer (△) Reaction conditions are the same as Table 1 except Al/Nd.

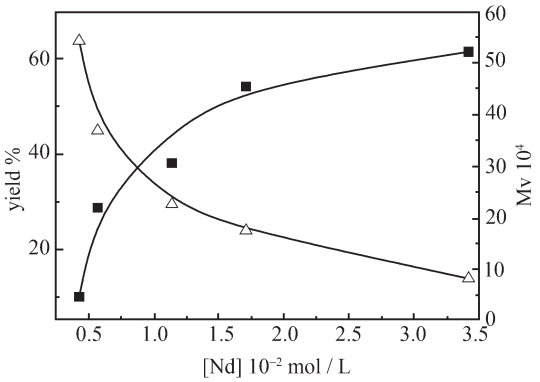

Fig. 3 Effect of the concentration of the catalyst on polymer yield (■) and M_v of polymer (△). Reaction conditions are the same as Table 1

The effect of light rare earth and heavy rare earth Schiff base complexes were compared. Results indicate that the neodymium complex has the highest catalytic activity, as shown in Table 3.

Table 3 Effect of rare earth on styrene polymerization

entry	ln	polymer yield/%	M_η ($\times 10^4$)
1	La	50.3	4.19
2	Nd	54.1	17.5
3	Dy	15.1	22.2

Conditions are the same as Table 1.

3.2 Effect of polymerization conditions on the polymerization of styrene

Figure 3 shows that under small amounts of the Nd complex ([M]/[Nd] = 4000, [Nd] = 0.43×10^{-2} mol/L), the catalyst system still has activity for the styrene polymerization. When [M]/[Nd] = 1000 ([Nd] = 1.71×10^{-2} mol/L), the polystyrene was prepared with high yield and moderate high molecular weight. As shown in Table 4, the conversion of polymerization increases with increasing reaction temperature, while the viscosity average molecular weight decreases at the same time. Table 5 indicates that the conversion increases as the polymerization time is prolonged, and the molecular weight reaches a maximum when polymerized for 20 h.

3.3 Characterization of polystyrene

The GPC curve of polystyrene obtained using Nd$(H_2Salen)_2Cl_3 \cdot 2C_2H_5OH$/Al(*i*-Bu)$_3$/$CCl_4$ system shows a unimodal elution curve with $M_n = 8.4 \times 10^4$ g/mol and MWD = 3.9. ^{1}H MNR spectrum indicates that there are only two α-H signals at 1.88 ppm and 2.18 ppm respectively, corresponding to the rr and mm units [7] calculated to be rr (47.7%), mm (52.3%).

Table 4 Effect of temperature on polymerization

enrty	temperature/°C	polymer yield/%	M_η ($\times 10^4$)
1	25	4.2	–
2	50	54.1	17.5
3	70	70.1	13.2
4	90	75.4	10.3

Conditions are the same as Table 1.

Table 5 Effect of polymerizing time on polymerization

entry	polymerization time/h	polymer yield/%	M_η ($\times 10^4$)
1	4	3.81	–
2	12	24.2	11.1
3	16	41.1	13.0
4	20	54.1	17.5

Conditions are the same as Table 1.

In conclusion, the Nd$(H_2Salen)_2Cl_3 \cdot 2C_2H_5OH$/Al(*i*-Bu)$_3$/$CCl_4$ system is an effective catalyst for the polymerization of styrene. The polystyrene can be prepared with over 50% yield and viscosity average molecular weight of 17.5×10^4 g/mol ($M_n = 8.4 \times 10^4$ g/mol, MWD = 3.9) without a random structure under the following conditions: [St]/[Nd] = 1000, [CCl_4]/[Nd] = 9, [Al]/[Nd] = 30, and polymerization at 50°C for 20 h.

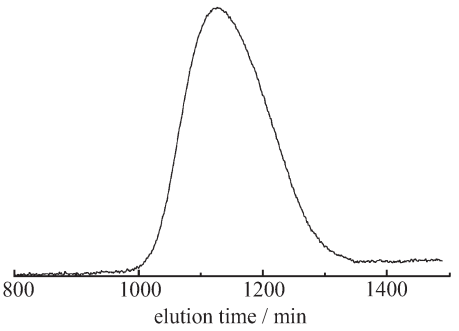

Fig. 4 GPC curve of PSt (entry 5 in Table 1)

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References

1. Huang B T, Shen Z Q. Progress of coordination polymerizations of olefins and diolefins. Beijing: Science Press, 1998, 227 (in Chinese)
2. Darensbourg D J, Macklewicy R M, Phelps A L, Billod D R. Copolymerization of CO_2 and epoxides catalyzed by metal salen complexes. Acc Chem Res, 2004, 37(11): 836–844
3. Yang J, Yu H, Li Q B, Li Y. Chemical synthesis of biodegradable aliphatic polyesters and polycarbonates catalyzed by novel versatile aluminum metal complexes bearing salen ligands. J Polym Sci Part A Polym Chem, 2005, 43(2): 373–384
4. Li Y M. Macromolecule physical experiment, Hangzhou: Zhejiang University Press, 1996, 319 (in Chinese)
5. Cameron P A. Jhurr D. Gibson V C. Controlled polymerization of lactides at ambient temperature using [5-Cl-salen] AlOMe. Macromol Rapid Commun, 1999, 20(12): 616–618
6. Bullok J I, Heidar A, Tajimir R. Schiff-base complexes of the lanthanoids and actinoids. Part1. lanthanoid III halide complexes with the un-ionised form of *N*,*N*′-disalicylideneethylenediamine and related bases. J C S Dalton, 1978, 36–39
7. Brownstein S, Bywater S. Worsfold D J. Proton resonance spectra and tacticity of polystyrene and deuteriopolstyrenes. J Phys Chem, 1962, 66: 2067–2068