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Polymerization of propylene oxide by a new neodymium complex of calixarene derivative

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Abstract

Polymerization of propylene oxide was performed in good yield and a high isotactic content of 58.0–70.6% by calixarene–neodymium complex **2**/Al(*i*-Bu)$_3$/H$_2$O catalyst system under the following conditions: [PO] = 4 mol/l; [PO]/[Al] = 300; Al/Nd = 6–16; temperature, 70°C; reaction time, 22 or 46 h and solvent, toluene.

Keywords: Calixarene–neodymium complex; Polymerization; Propylene oxide

1. Introduction

It has been found that rare earth metal compounds are a class of excellent catalysts for synthesis of poly(propylene oxide) (PPO) with high yield and high molecular weight [1–4]. But the isotactic content of PPO with rare earth metals is not high [3,4].

Calixarenes, a new class of macrocyclic compounds, have the ability to form complexes with almost all metals [5,6]. Due to their large steric hindrance, calixarene–metal complexes as catalyst should have good stereospecificity. For example, syndiotactic polystyrene was synthesized by calixarene–titanium complexes [7]. Here we report the polymerization of propylene oxide, which was performed in good yield and a high isotactic content of 58.0–70.6%, by the calixarene–neodymium complex **2**/Al(*i*-Bu)$_3$/H$_2$O catalyst system.

2. Experimental

2.1. Materials

Propylene oxide was distilled after drying over calcium hydride for several days. Toluene was distilled by refluxing with sodium and benzophenone.

All polymerization operations were carried out under dried nitrogen. To a glass vial, **2**, Al(*i*-Bu)$_3$, toluene and water were added in order. After the water was fully mixed by shaking, propylene oxide was added and the vial was heated in a water bath. The reaction solution was then poured into water. The separated organic phase was evaporated to dryness and a white polymer was obtained.

The resultant polymer was dissolved in boiling acetone. The cooled solution was stored at −15°C to precipitate isotactic PPO. The filtrate was evaporated to dryness to produce syndiotactic PPO.

The viscosity-average weight (M_v) was calculated according to the equation: $[\eta]\,(\mathrm{dl/g}) = 1.29 \times 10^{-4} M_v^{0.75}$ (in toluene at 25°C) [8].

The calixarene–neodymium complex was prepared according to the reaction shown in Scheme 1.

A solution of **1** [9] (0.10 g, 0.10 mmol) in dichloromethane (2 ml) was added to a solution of neodymium *p*-methylbenzenesulfonate (0.048 g, 0.10 mmol) in methanol (2 ml). Then two drops of triethylamine (about 0.2 mmol) were added to give a light yellow solution which was filtered and left to evaporate. The fine needles were collected by filtration to get a light red solid (0.069 g; yield, 51%). ^{1}H NMR: very wide peaks at about 7.2, 3.5 and 1.2 ppm. IR: 3350, 2950, 1600, 1500, 1460 cm^{-1}. Microanalysis for $C_{73}H_{79}O_9N_2SNd{\cdot}3H_2O$ (1358.736): Calcd (%): C, 64.52; H, 6.31; N, 2.06; S, 2.36; Found: C, 64.32; H, 6.34; N, 2.17; S, 2.38. Melting point, 220°C (dec).

3. Results and discussion

As shown in Table 1, the Al/Nd molar ratio has a marked

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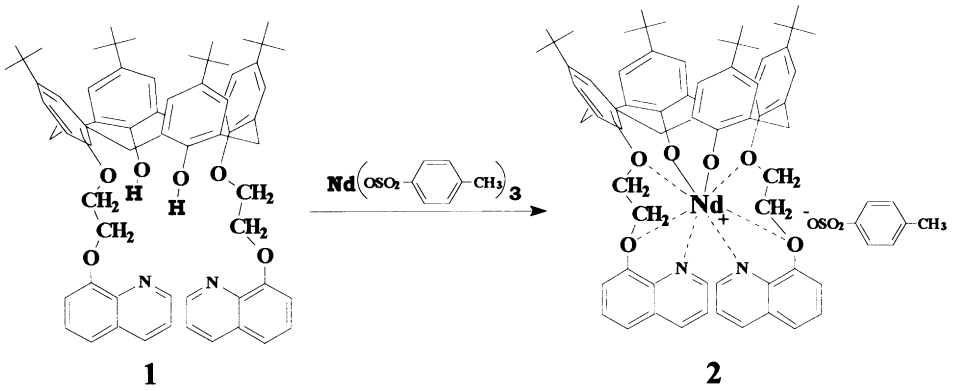

Scheme 1.

Table 1
Effect of Al/Nd ratio on polymerization of PO (conditions: $T = 70°C$, [PO] = 4 mol/l, [PO]/[Al] = 300, H_2O/Al = 0.5, toluene as solvent)

Al/Nd (molar ratio)	Duration (h)	Yield (%)	M_v ($\times 10^{-4}$)	Acetone-insoluble product
6	46	26	15.5	69.2
8	46	39	11.8	70.6
12	22	66	17.4	65.3
16	22	73	16.5	58.0

Table 2
Effect of concentration of PO on polymerization of PO (conditions: $T = 70°C$, Al/Nd = 12, [PO]/[Al] = 300, H_2O/Al = 0.5, toluene as solvent)

[PO] (mol/l)	Time (h)	Yield (%)	M_v ($\times 10^{-4}$)	Acetone-insoluble product
1	49	65	21.3	61.3
2	49	74	27.6	59.8
3	24	78	19.4	63.1
6	24	82	10.6	62.4

effect on the polymerization of PO. With increasing Al/Nd molar ratio the yield of PPO rapidly increases and the amount of acetone-insoluble product, i.e. isotactic content of PPO, generally decreases. The molecular weight of PPO has only a little change with the Al/Nd molar ratio increasing.

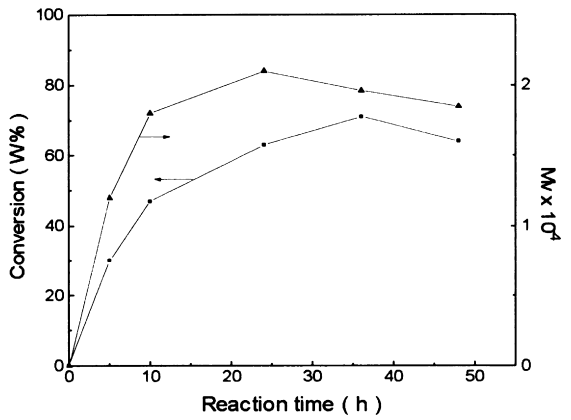

Fig. 1. Effect of reaction time on polymerization of PO. Reaction conditions: [PO] = 3 mol/l, [PO]/[Al] = 300, Al/Nd = 12, H_2O/Al = 0.5, $T = 70°C$, toluene as solvent.

The most remarkable is the high isotactic content of PPO (58.0–70.6%), which is the highest values in PPO with rare earth metals. It has been reported that the isotactic content is 33.2% with $Nd(P_{2O4})_3$ [3] and 45.7% with neodymium supported by chitosan [4]. The difference between the $Nd(P_{2O4})_3$ and the neodymium supported by chitosan may be due to the larger steric hindrance of chitosan in comparison to P_{2O4}(di(2-ethylhexyl)phosphate). Therefore the highest isotactic content obtained with the **2**/Al(*i*-Bu)$_3$/H_2O

Table 3
Effect of reaction temperature on polymerization of PO (conditions: [PO] = 3 mol/l, [PO]/[Al] = 300, Al/Nd = 12 H_2O/Al = 0.5, time 24 h, toluene as solvent)

Temperature (°C)	Yield (%)	M_v ($\times 10^{-4}$)	Acetone-insoluble product
30	26	10.3	63.7
50	46	17.8	62.4
70	78	19.4	63.1
80	64	16.7	56.8

catalyst system is probably ascribed to the larger steric hindrance of **2**. The fact that the isotactic content increases with **2** ($Al(i\text{-}Bu)_3$ being kept constant) demonstrates that the neodymium plays a key role in producing isotactic PPO.

The effect of concentration of PO on polymerization of PO is shown in Table 2. The conversion of PO increases with the increase in concentration of PO, but the molecular weight has the largest value at 2 mol/l of PO. The isotactic content of PPO is in the 59.8–63.1% range.

Fig. 1 demonstrates the effect of reaction time on the polymerization of PO. The conversion of PO and the molecular weight increase with the reaction time. But when the time is too long, not only the conversion but also the molecular weight decreases because of the degradation of resultant PPO. The optimum reaction time is in the range of 24–36 h.

The effect of reaction temperature on polymerization of PO is notable (see Table 3). When the temperature is low (at 30°C) both the conversion and the molecular weight are low. As the temperature is raised the conversion and the molecular weight rapidly increase. But if the temperature is too high (at 80°C), the conversion and the molecular weight become low. The optimum temperature is 70°C. The isotactic content of PPO is in the 56.8–63.7% range. At high temperature of 80°C the lowest isotactic content of PPO is obtained.

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