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Stereoregular Polymerization of (*R*,*S*)-Propylene Oxide by an Alumoxane−Propylene Oxide Complex[†]

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Introduction

After the discovery in 1955 of the iron(III) chloride catalyst for the stereoregular polymerization of (*R*,*S*)-propylene oxide (PO),[1] research on the preparation of this type of polymer from PO has continued sporadically for several decades. The primary focus of recent investigation has involved two general aspects: (1) the development of alternative catalytic systems aimed at the synthesis of a more highly stereoregular and crystalline poly(propylene oxide) (PPO) from the racemic monomer[2−4] and (2) the development of an understanding of the mechanisms of the steroregular polymerization as catalyzed by different metal species.[5−9]

Racemic PO can be polymerized in a stereoregular manner by a variety of transition and main group metal catalysts, including: $FeCl_3$−PO, $Al(^iBu)_3/H_2O$,[10] $AlEt_3/H_2O$,[11] ZnR_2/H_2O,[12] and (tetraphenylporphinato)aluminum chloride [AlCl(TPP)].[13] However, all of these catalysts suffer from the relatively low stereoregularities of the polymers obtained. Their isotactic diad contents are generally about 60−70%, even after removal of the atactic fraction by solvent fractionation. As part of our studies on the catalytic behavior of alkylalumoxanes,[14−16] we report herein the synthesis of a new type of catalyst that affords a highly isotactic poly(propylene oxide) with relatively high molecular weights from (*R*,*S*)-PO.

Experimental Section

To a solution of triisobutylaluminum $[Al(^iBu)_3]$ in heptane (20 mL of a 25% solution, 18 mmol), cooled to approximately −78 °C (liquid N_2 and ethanol mixture), was added dropwise distilled water (360 μL, 2.0 mmol). After the addition was completed, the temperature was maintained at −78 °C for about 1 h. The reaction was then allowed to warm to room temperature and subsequently heated to reflux for 8 h to yield a stock solution of isobutylalumoxane (IBAO). The IBAO solution was cooled by a mixture of liquid N_2 and ethanol to about −78 °C, and (*R*,*S*)-propylene oxide (2.5 mL, 36 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 4 h. The solvent was then removed under vacuum, leaving a yellowish fine powder which was stored and handled in a dry box. This IBAO−PO adduct may be used directly as prepared as a catalyst for the polymerization of propylene oxide.

The IBAO−PO adduct (1−10%) was added to liquid (*R*,*S*)-PO at 25 °C, in the absence of a solvent, with rapid stirring. The reaction was heated to 80 °C for 48 h, after which the polymerization bottle was opened and the polymeric product was dissolved in boiling acetone (5 mL g^{-1} PO), and an aliquot of 10% HCl in acetone was added. The precipitate thus formed was removed by filtration and washed with warm acetone to remove any polymer present. The acetone washings were added to the filtrate, and the mixture was cooled to −30 °C, at which point crystalline PPO precipitated. The remaining solution was decanted and evaporated to dryness to yield a waxy solid which represented as much as 70% by weight of the product. The crystalline polymer was redissolved in acetone, and the solution was filtered and dried under vacuum for 12 h to yield the pure polymer.

Molecular weights were determined by gel permeataion chromatography (GPC) using a Waters Model 6000A solvent delivery system with 10^6, 10^5, 10^4, 10^3, and 500-Å "Ultrastyragel" columns in series, and a model 401 refractive index detector. Calibration curves were based on polystyrene standards having low polydispersities. Chloroform was used as an eluent at a flow rate of 1.0 mL min^{-1}, the sample concentrations were 5−10 mg mL^{-1}, and injection volumes of 100 mL were used. A DuPont DSC-2000 analyzer was employed for thermal measurements with a typical sample weight of 5−10 mgand a heating rate of 10 °C min^{-1}, from −100 to 100 °C. Data used for T_g, T_m, and ΔH_m were taken from the thermogram of the first DSC scan. Indium was the standard used to calibrate the DSC thermogram.

Results and Discussion

In early work by others on the ring-opening polymerization of (*R*,*S*)-PO using the product of the reaction of triethylaluminum with water, ethylalumoxane, as a coordination catalyst,[10] the yields of crystalline and high molecular weight PPO were extremely low (e.g. 1.5% based on monomer). In our observation, when the polymerization was carried out in solution using the product of the reaction of triisobutylaluminum with water, isobutylalumoxane (IBAO), as the catalyst, the polymers so obtained were waxy and low molecular weight, and no crystalline polymer could be isolated. When the polymerization was carried out in bulk with this catalyst, overheating was observed due to the violent side reactions between PO and IBAO, and again in this case no crystalline polymer was obtained. However, when 2 molar equiv of PO were added to IBAO slowly at very low temperature (−78 °C), the overheating was avoided, and a solid adduct was collected. This IBAO−PO adduct was not stable in air, and it was not soluble in most nonreactive solvents. As a result, we have not been able to determine the structure of this adduct as yet, but that is not too surprising because the structure of solid IBAO has not been determined either. Nevertheless, while we have no specific information on the structure of the IBAO−PO complex, based on our isolation and characterization of a crystalline complex between a tert-butylaluminoxane and β-butyrolactone (see Conclusions), we propose that the IBAO−PO complex is formed by the ring opening reaction of PO and IBAO to yield the adduct. A cage opening of aluminoxanes with adduct formation is well documented.[16,20]

The IBAO−PO solid adduct was used as the catalyst for the ring-opening polymerization of (*R*,*S*)-PO, and it showed a much different catalytic ability than IBAO itself. While, in our studies, IBAO was not capable of polymerizing racemic PO into crystalline and stereoregular polymers (as mentioned above), the IBAO−PO complex catalyzed the polymerization of PO to yield crystalline, high molecular weight polymers, that could be isolated by solvent fractionation. Furthermore, the IBAO−PO adduct is a solid which can be accurately

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[†] We are pleased to dedicate this publication to Prof. Dr. Dieter Seebach on the occasion of his 60th birthday.

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Table 1. Yield and Properties of the Crystalline Polymer Fraction Obtained from the Polymerization of (*R*,*S*)-PO Catalyzed by IBAO−PO Complex[a]

cat. amount[b] (mol %)	yield[c] (%)	molecular weights M_n	M_w (10^3)	M_w/M_n	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})
2	7	90	163	1.8	−67	64	72
5	10	84	140	1.8	-67	64	69
8	15	60	105	1.8	−68	62	48
10	35	15	25	1.7	−67	63	31

[a] All polymerization reactions were carried out at 80 °C for 48 h. [b] Mole percent of IBAO−PO complex based on PO monomer. [c] Based on monomer.

weighed under an inert atmosphere for use in the polymerization reaction and which redissolves in the monomer at 25 °C without a violent reaction. Another advantage of this adduct is that it does not contain any unreacted triisobutylaluminum, which is not necessarily the case with IBAO itself.[27]

It is not unusual that a catalyst−monomer complex can serve as the true catalyst for a polymerization reaction. The "Pruitt−Baggett catalyst" is a good example. In their work,[1] instead of using $FeCl_3$ as the catalyst, Pruitt et al. first prepared a complex by reacting 2 molar equiv of PO with $FeCl_3$. Indeed, it may be a common feature of coordination ring-opening polymerization reactions that the first and critical step of the polymerization is the complexation between the catalyst and the monomer.

Table 1 summarizes the polymer yields and characterization data for the crystalline polymer fractions obtained at different polymerization conditions using IBAO−PO as catalysts. In this study all polymerization reactions were carried out in pressure-resistant bottles at 80 °C for 48 h, but the ratio of IBAO−PO catalyst to monomer was varied, and the crystalline polymer yields were clearly dependent on the relative amount of the catalyst added. Similarly, the molecular weights of these polymers (Table 1) as determined by GPC analysis varied as a function of the monomer-to-catalyst ratio. At the highest catalyst ratios the number average molecular weight, M_n, was 15 000 while at the lowest catalyst ratio an M_n of 90 000 was obtained.

The glass transition (T_g) temperatures, melting temperatures (T_m), and heats of fusion (ΔH_m) of the crystalline polymer fractions were determined by differential scanning calorimetry (DSC), with the results shown in Table 1. Representative thermograms of the crystalline polymers produced with 2% and 10% IBAO−PO catalyst are shown in parts a and b of Figure 1, respectively. From Figure 1b a glass transition at approximately −67 °C[17] may be estimated in addition to a sharp melting endotherm with a peak at approximately 63 °C. However, the crystalline polymer prepared with the lower catalyst concentration (Figure 1a) had a significantly sharper melting transition and higher degree of crystallinity, as indicated by ΔH_m, than that prepared with a higher catalyst concentration. The sharp melting transitions observed for all of the polymers are consistent with the higher degrees of crystallinity of these polymers than those previously reported. The crystalline nature of the polymers was also confirmed by X-ray diffraction. The *d*-spacings calculated from the diffraction pattern in Figure 2 show that the crystalline PPO obtained using the IBAO−PO catalyst is identical to that reported by Stanley and Litt,[18] although they did not describe the method of preparation of their polymer.

The ^{1}H and ^{13}C NMR spectra of the crystalline polymers prepared with the IBAO−PO catalyst are consistent with those expected for highly isotactic PPO. Figure 3 shows an expanded ^{1}H NMR spectrum of the methyl signal for 10% IBAO−PO. The larger peak at δ = 17.42 ppm is assigned to the isotactic diads, −RR− and −SS−, while the smaller peak at δ = 17.32 ppm is assigned to the syndiotactic diads, −RS− and −SR−. Integration of the two peaks gave the percentage of each diad and the tacticity of the polymer. All of the fractionated polymer had isotactic diad contents in the range of 90−100%. Similarly, the ^{13}C NMR spectrum of polymers prepared using 2% IBAO−PO catalyst showed only a single resonance (d = 17.5 ppm) suggesting that the polymer has close to 100% isotactic diads. We believe, therefore, that the PPO prepared with the IBAO−PO complex in this study has the highest isotactic content of any previously reported polymer prepared by the polymerization of racemic PO polymerization.

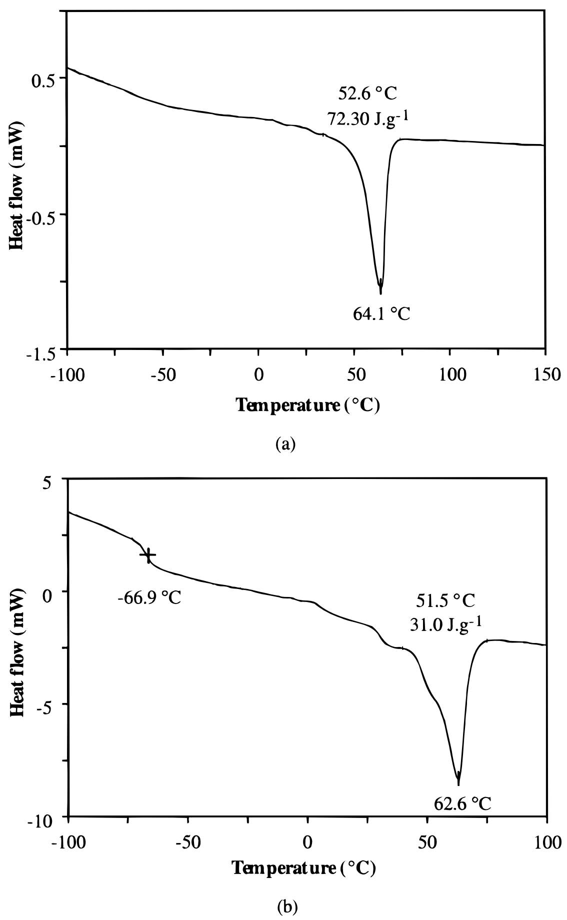

Figure 1. DSC thermograms of the crystalline PPO fraction obtained from the polymerization reactions with (a) 2% and (b) 10% IBAO−PO catalyst.

Conclusions

Previous studies have used the ^{13}C NMR spectra to determine the tacticity of PPO for samples prepared with different catalysts, and in those studies the isotactic diad contents of the crystalline polymer were only in the range of 60−70%. All of those polymers, and the polymers reported here, too, either could have a stereoblock structure (i.e., copolymers with blocks of −*RRRRR*− and −*SSSSS*− connected by −*RS*− or −*SR*− unit) or the highly isotactic fraction could be a 1:1 mixture of isotactic *R*- and *S*-polymers. If the isotactic fraction was obtained from two different asym-

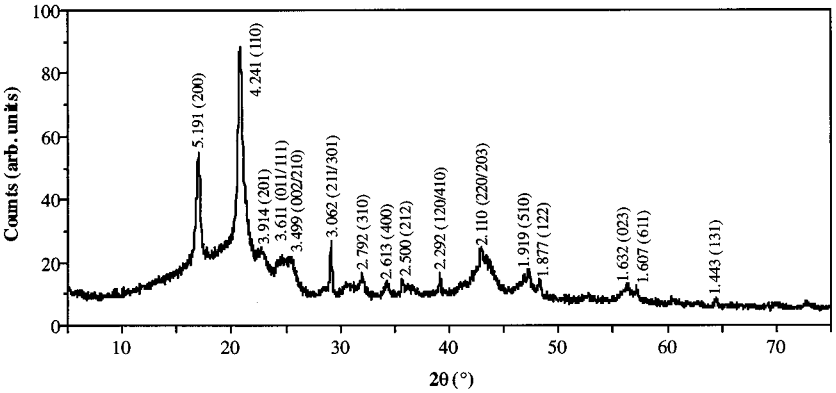

Figure 2. Powder X-ray diffraction pattern of the crystalline PPO fraction obtained with 2% IBAO−PO catalyst; the crystalline regions form an orthorhombic cell with $a = 10.40$, $b = 4.64$, $c = 6.92$ Å; space group $P2_12_12_1$.

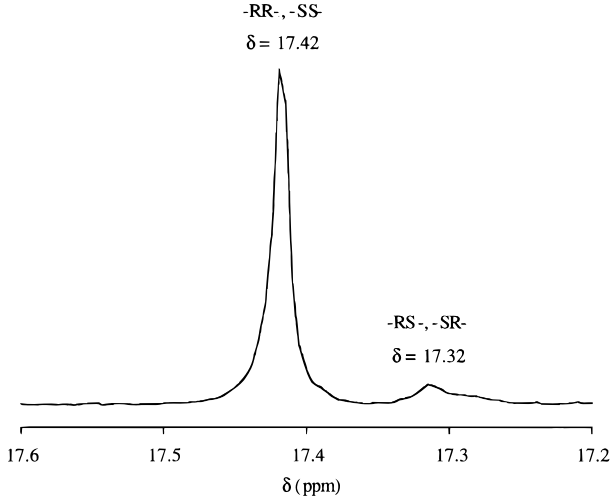

Figure 3. ^{13}C NMR spectrum ($CDCl_3$) of the crystalline PPO fraction prepared with 10% IBAO−PO catalyst.

metric catalyst sites (i.e., from *R*- and *S*-IBAO−PO sites), each of which had a highly preferential reactivity for propylene oxide of one particular configuration, then the latter could be obtained.

Which of these two possible types of stereoregular polymers and polymerization reactions applies here is unknown at present. It may be of significance, however, that we have prepared an optically active, crystalline complex by the reaction of the *tert*-butylalumoxane hexamer with racemic β-butyrolactone[19] (BL), and this complex was found to be a very active catalyst for the polymerization of (*R*,*S*)-BL.[15] In that case, both isotactic and syndiotactic polymer fractions were formed. Nevertheless, for chiral monomers such as PO or BL, this type of complex could be responsible for the coordination polymerization of the [*R*] and [*S*] monomers by the action of separate active sites in the catalyst to yield a mixture of highly optically pure [*R*] and [*S*] homopolymers. Additional studies are in progress to attempt to differentiate between these possibilities, that is, between either end group control of the propagation step to form the stereoblock copolymer or by catalyst control to form the [*R*] and [*S*] homopolymers.

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