Macromolecules **1998,** *31,* 3473−3477

Stereoregular Polymerization of [*R*,*S*]-3-Butyrolactone Catalyzed by Alumoxane−Monomer Adducts

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Received December 3, 1997; Revised Manuscript Received March 23, 1998

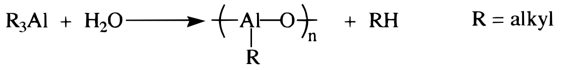
ABSTRACT: The reaction between 2 molar equiv of 3-butyrolactone (BL) and either methylalumoxane (MAO) or isobutylalumoxane (IBAO) yielded an adduct, either MAO−BL or IBAO−BL. Both MAO−BL and IBAO−BL were found to be much more effective catalysts for the ring-opening polymerization of the racemic monomer, [*R*,*S*]-BL, than either MAO or IBAO alone in having much higher reaction rates and forming higher yields of crystalline polymer. The polymerization of [*R*,*S*]-BL in bulk catalyzed by 10 mol % MAO−BL at 80 °C went to near completion within 20 min, while use of the equivalent amount of MAO alone as the catalyst required many hours or days to obtain the same results. The crude polymeric products obtained from the polymerization reaction using 10 mol % MAO−BL contained 60 wt % of a crystalline, isotactic polymer, as compared to only 30−40% with MAO alone. The polymers obtained were characterized by GPC, DSC, and NMR. No difference was found between the catalytic behavior of the complex formed between either [*R*]-BL and MAO or [*R*,*S*]-BL and MAO. The structures of MAO−BL and IBAO−BL could not be determined because of their instability and insolubility. A procedure for removing the catalyst residue from the polymeric products was developed so that nearly complete removal of Al residue could be realized in short contact times without loss of atactic polymers.

Introduction

Alumoxane catalysts can be used to polymerize racemic 3-butyrolactone, [*R*,*S*]-BL, to stereoregular, crystalline polymers[1−3] including both isotactic and syndiotactic poly-3-hydroxybutyrate, PHB. An atactic polymer fraction is also obtained in all cases, and these different types of polymers can be separated by solution fractionation.[1−5] The isotactic, crystalline polymer has a melting temperature of 160−170 °C and a heat of fusion of approximately 45 J/g, depending on the degree of isotacticity.[6] ^{13}C NMR spectroscopy reveals that this polymer generally has an isotactic diad percentage of between 75 and 90%, depending on the catalyst and polymerization conditions.[7] Initially, it was proposed that this crystalline polymer consisted of a physical mixture of P-[*R*]-HB and P-[*S*]-HB,[1,2,3,8] but it is more likely, although never demonstrated unequivocally, that the polymers are stereoblock in structure and contain numerous blocks of both [*R*]-HB and [*S*]-HB unit sequences which are sufficiently long to permit phase separation and crystallization.[9] One observation that supports this concept is that the isotactic polymers obtained in the polymerization of [*R*,*S*]-BL are completely biodegradable by a bacterial PHB depolymerase,[10] and it is known that such enzymes, which are secreted by microorganisms for the degradation of bacterial PHB, only recognize and hydrolyze polymers with [*R*]-HB units.[10] Therefore, with such enzymes a physical mixture of P-[*R*]-HB and P-[*S*]-HB would be only partially degradable as a solid while a block copolymer could be degraded to molecular fragments.

With alumoxane catalysts the crystalline fraction is generally isotactic in structure, but in some cases,[11−13] a third fraction, which is also partially crystalline, can be isolated from P-[*R*,*S*]-HB. NMR analysis revealed that this polymer fraction has a relatively high percentage of syndiotactic diads,[12,13] and the syndiotactic polymer has a melting temperature of 70−100 °C.[12] Biodegradation tests show that the highly syndiotactic polymer degrades much more slowly than either the atactic or isotactic polymers, although in time it will degrade completely.[14]

Alumoxanes are the reaction products of a trialkylaluminum with water as shown in the general reaction equation



$$R_3Al + H_2O \longrightarrow \left(\underset{R}{Al} - O \right)_n + RH \qquad R = \text{alkyl}$$

The specific structures of the alumoxanes are not known, but there is generally no simple formula of the type shown that can be used to represent the real structure of alumoxanes because the products of the hydrolysis can consist of many different types of oligomeric compounds, which may have linear, cyclic, or even cage structures.[15,16] Furthermore, the compositions and structures are sensitive to the hydrolysis conditions, including the ratio of water to aluminum, temperature, and solvent,[15] and also to subsequent reaction conditions.

There are several important deficiencies in the application of alumoxane catalysts to the preparation of isotactic P-[*R*,*S*]-HB from [*R*,*S*]-BL, including the following: (1) polymerization reactions are very slow and for some alumoxanes it can take as long as 5 days to reach completion; (2) isotactic polymer formation is generally less than 50 wt % of the product; (3) since the active center in alumoxane catalyst is unknown, and apparently constitutes only a small portion of the catalyst material, it is difficult to optimize the formation of the stereoregular polymers, so large amounts of catalyst are required; (4) the alumoxanes can readily rearrange in solution.

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S0024-9297(97)01769-5 CCC: $15.00

We have studied the effects of reaction solvent, types of alkyl group in the alumoxane catalyst, and the ratio of [H_2O]/[Al] in the preparation of alumoxanes on polymer tacticity.[17,18,19] The following results were obtained: (1) polar solvents favored the formation of atactic polymers; (2) a large alkyl group in the alumoxane (*tert*-butyl) favored the formation of syndiotactic polymers whereas smaller alkyl groups (methyl, ethyl, and isobutyl) favored the formation of isotactic polymers; (3) a [H_2O]/[Al] ratio of 1.0 in the preparation of methylalumoxane or isobutylalumoxane gave the best polymerization results in terms of reaction rate and polymer tacticity. In addition, the preparation of a highly crystalline polymer in acceptably high molecular weights was best attained by carrying out the polymerization of [*R*,*S*]-BL in bulk, although, even under the best conditions, the polymerization reaction took 5 days to complete and the crystalline polymer yields were less than 50%.[17,18,19]

The mechanism of the ring-opening polymerization of BL catalyzed by alumoxanes is still unknown. Aluminum alkoxides can catalyze the polymerization of lactones and lactides by an ester interchange reaction, which involves only acyl−oxygen bond breaking with complete retention of the configuration of the chiral center in the monomer, but this simple mechanism cannot be the case for alumoxanes-catalyzed polymerization reaction of [*R*,*S*]-BL because previous studies have shown that alkyl−oxygen bond cleavage at the 3-position could occur in such reactions. That is, Zhang and co-workers,[2,20,21] in their studies on the polymerization of [*S*]-BL catalyzed by ethylalumoxane (EAO), found that, depending on the procedure for the preparation of EAO, either retention or inversion of configuration or racemization could occur.

The main goals of this study, therefore, were to develop a catalyst system capable of catalyzing the polymerization of [*R*,*S*]-BL at a much higher rate to form a more highly crystalline, isotactic polymer. For this purpose, the preparation and activity of a new type of alumoxane catalyst was investigated. This catalyst was prepared by an initial low-temperature reaction of either methylalumoxane, MAO, or isobutylalumoxane, IBAO, with [*R*,*S*]-BL. The development of a facile purification procedure for removing Al residue in the polymer products, without the loss of atactic polymer fraction, was also studied.

Experimental Section

Chemicals. [*R*,*S*]-BL was purchased from Aldrich, dried over CaH_2 for 24 h and distilled under reduced pressure. [*R*]-BL (88% EE) was obtained from Dr. Lee Schechtman of the Procter and Gamble Co. and purified as above. Trimethylaluminum (TMA) and triisobutylaluminum (TIBA) were purchased from Akzo Chemicals, Inc., in heptane or toluene solution. Hexane, heptane, and toluene used for the catalyst synthesis and polymerization reaction were each refluxed with sodium for at least 48 h and distilled before use. The procedure for the preparation of the catalyst adducts of MAO, MAO−BL, and IBAO, IBAO−BL, at low temperature were essentially identical, so only that for IBAO−BL is described below.

Preparation of Alumoxanes. The hydrolysis of triisobutylaluminum, TIBA, was carried out in a 50-mL Schlenk tube. All the glassware was cleaned with distilled water, oven dried at 250 °C, and flame dried under vacuum with argon purge. The Schlenk tube was charged with 0.0182 mol of TIBA in 20 mL of toluene and was cooled to −78 °C with a liquid N_2/ethanol bath. A 360 μL (0.02 mol) aliquot of distilled water was added dropwise with a syringe to the TIBA solution (*Caution*! exothermic reaction!). The resulting mixture was stirred while the temperature was maintained at −78 °C for about 30 min, and then the mixture was allowed to warm gradually to room temperature. During the course of warming the solution was monitored to avoid overheating, which could be observed by the violent bubbling. The reaction mixture was then stirred at room temperature for an hour, heated, and refluxed for 12 h. At the end of the reaction, the solvent was evaporated under vacuum, leaving 4 g of a powderlike solid.

Preparation of IBAO−BL Complex. A 2 g sample of the IBAO prepared as above (containing 0.009 mol of Al) was transferred in a drybox under an argon atmosphere to a 50-mL Schlenk tube. Then, 20 mL of predried heptane was added to the IBAO. The resulting solution (a suspension in the case of MAO) was cooled to −78 °C with a liquid N_2−ethanol bath, at which point 1.55 g (0.018 mol) of [*R*,*S*]-BL (or [*R*]-BL) was added dropwise from a syringe. The reaction mixture was stirred at −78 °C for an hour and allowed to warm slowly to room temperature. The stirring was continued for another hour at room temperature, and after heptane was evaporated off, a white (MAO−BL) or a yellowish (IBAO−BL) powder was obtained. The yields were quantitative in both cases.

Polymerization of [*R*,*S*]-BL. To a 30-mL Schlenk tube charged with an appropriate amount of the above MAO−BL or the IBAO−BL complex was added 5 g (0.058 mol) of [*R*,*S*]-BL at room temperature with vigorous stirring. The mixture was heated to 80 °C with an oil bath, and the polymerization was continued for 48 h to ensure completion.

Polymer Isolation and Fractionation. When the polymerization reaction was completed, the Schlenk tube was opened to air, and 0.5 mL of 10% aqueous HCl solution was added to quench the polymerization reaction. The polymeric product was dissolved in a minimum amount of chloroform. The chloroform solution was poured slowly into a mixture of equal volumes of hexane and ethyl ether (5 mL per mL of chloroform) to form a flocculant precipitate of the polymer. After filtration, a white or yellowish solid, referred to as the crude polymer, was obtained. For the solvent fractionation, 1 g of the crude polymer was stirred with 6 mL acetylacetone (AcAc) at room temperature for 24 h, and the resulting solution was filtered and added dropwise into methanol (10 mL per mL of AcAc). The methanol-insoluble fraction was filtered, washed with methanol, and dried in a vacuum oven. The methanol-soluble polymer fraction was recovered by precipitation in the hexane/ether (1/1) mixture.

Procedure for Removing Al Residue. A 0.5 g sample of the crude polymer was dissolved in 25 mL of chloroform, and 5 drops of concentrated HCl was added to the chloroform solution. The solution was stirred for 5 min, and 2 g of anhydrous $CaCl_2$ was added to the chloroform solution. After filtration, the same procedure was repeated three times, and the final filtrate was concentrated to maximum concentration. The purified polymer was recovered by precipitation in ethyl ether. The amount of the aluminum residue in the polymer was determined by elemental analysis.

Polymer Characterization. Molecular weights were determined by GPC analysis. Polystyrene samples with low polydispersities were used as the standards to generate calibration curves. The instrument used was a Waters Model 6000A solvent delivery system with 10^6, 10^5, 10^4, 10^3, and 500-A “Ultrastyragel” columns in series and a model 401 refractive index detector. Chloroform was used as the eluant at a flow rate of 1.0 mL/min. Sample concentrations were 5−10 mg/mL, and injection volumes of 100 μL were used.

Thermal analysis was carried out with a Du Pont DSC-2000. The polymer samples were heated at a rate of 20 °C/min to determine the glass transition temperatures (T_g), melting temperatures (T_m) and the heats of fusion (ΔH_m). The thermogram of the first heating cycle was used to determine T_m and ΔH_m, but the thermogram of the second heating cycle was used for the determination of T_g.

^1H NMR spectra were recorded at 200 MHz on a Bruker 200 AC spectrometer; $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) as the internal reference. ^{13}C NMR spectra were recorded on a Brucker 300 MSL spectrometer at 75.4 MHz; $CDCl_3$ was used as the solvent and the internal reference at 77.00 ppm. NMR spectral data (ppm) for the polymer are as follows. ^1H NMR: 1.25 (3H, CH_3), 2.50 (2H, CH_2−CO−), 5.25 (H, −O−C*H*) ppm. ^{13}C NMR: 21.0 (CH_3), 42.0 (CH−CH_2−CO), 68.0 (*C*H−CH_2−CO), 169.5(*C*O) ppm.

Results and Discussion

Complex Catalyst Preparation. In previous studies it was found that an atactic polymer was obtained when the polymerization of [*R*,*S*]-BL catalyzed by MAO and IBAO was carried out in a homogeneous system using dichloroethane as the solvent, but polymerization in bulk gave a highly isotactic polymer.[17] However, it was observed in the latter case that when [*R*,*S*]-BL was combined with MAO at room temperature in the absence of a solvent, a violently exothermic reaction occurred. In that case, both the catalyst and monomer were decomposed, most likely because of overheating caused by a very fast polymerization reaction. However, the fast reaction could be avoided even in the bulk system by initially reacting alumoxane with the monomer at a low temperature (−78 °C) in heptane or hexane to prepare a more effective catalyst, so in the present study, this low-temperature reaction and the catalyst obtained were studied in some detail. It was found that two molar equiv of the monomer reacted with either MAO or IBAO to form a reproducible solid product, which could be obtained quantitatively. This solid is assumed to be an adduct of either MAO or IBAO and [*R*,*S*]-BL (for reasons discussed below), and because the yields of these adducts were quantitative, the following general formulas are applied to their compositions: $(BL)_2(MAO)$ and $(BL)_2(IBAO)$.

Stoichiometry was found to be very important in forming the adducts. When more than 2 molar equiv of the monomer were added to either MAO or IBAO at −78 °C, a slow polymerization took place and the 2:1 adducts could not be isolated. When less than 2 molar equiv of the monomer were added to either MAO or IBAO, the reaction was not complete, so that when more monomer was added to the complexes at room temperature, a rapid polymerization and overheating occurred again. Therefore, 2 molar equiv of the monomer were required for the formation of the adducts, and in that case, the yields of the adducts were quantitative. However, these adducts are insoluble in nonpolar solvents and are unstable at room temperature, so their characterization was very difficult. In contrast, it was found in a separate study that a stable crystalline 2:1 adduct of *tert*-butylalumoxane and BL could be prepared and isolated, and the crystalline and molecular structure of this adduct was determined.[22] In the latter study the adduct was obtained by reacting 2 molar equiv of BL with the *tert*-butylalumoxane hexamer, $[(^tBu)Al(\mu_3\text{-}O)]_6$ (which is a well-defined cage compound[9,16]), and ^1H NMR, ^{13}C NMR, ^{27}Al NMR, and X-ray crystallography could be used to fully characterize the structure of the adduct.

Catalysis of the Complexes. When the MAO−BL and IBAO−BL adducts were added to BL monomer, either [*R*,*S*]-BL or [*R*]-BL, at ambient temperature in the absence of solvent, a controlled polymerization reaction occurred and no overheating was observed. When 5 mol % or more of MAO-[*R*,*S*]-BL was used with [*R*,*S*]-BL the viscosity of the reaction mixture increased rapidly, and within 20 min the polymerization system formed a gel. The polymerization reaction with 10 mol % MAO−BL was stopped after 20 min, and the crude polymer yield was found to be 80% based on monomer weight. However, to ensure the complete conversion of BL with different catalyst amounts, reaction times of 48 h were used for all the polymerization reactions reported in Table 1.

Table 1. Yields and Molecular Weights of the Polymers Obtained from the Polymerization of [*R*,*S*]-BL with MAO−BL and IBAO−BL Adducts as Catalysts[a]

reaction no.	catal	catal amount (mol %)[b]	yield (wt %)[c] crude	insol. fraction[d]	10^3M_w[e]	10^3M_n[e]
1	MAO−BL	1	10	4	43	6
2	MAO−BL	5	80	45	94	14
3	MAO−BL	10	100	60	116	20
4	MAO-[*R*]-BL	5	82	46	101	18
5	MAO-[*R*]-BL	10	100	58	117	23
6	IBAO−BL	1	25	8	40	7
7	IBAO−BL	5	60	25	74	7
8	IBAO−BL	10	100	45	94	6

[a] Polymerization reactions were carried out in bulk at 80 °C for 48 h. [b] Catalyst amount based on moles of monomer. [c] Based on weight of monomer. The crude polymer yield = total weight of reaction product × 95%, assuming that 5 wt % of the product is the catalyst residue. [d] Methanol-insoluble polymer fraction. [e] Weight, M_w, and number, M_n, average molecular weights as determined by GPC analysis of chloroform solutions relative to polystyrene standards.

The polymer obtained was fractionated by partially dissolving the product in acetyacetone (AcAc) and precipitating in methanol (see Experimental Section). The methanol-insoluble fraction was crystalline, while the methanol-soluble fraction was an amorphous, rubbery polymer.

At a constant reaction time of 48 h, both the crude polymer yield and the methanol-insoluble polymer yield increased with increasing amount of the catalyst complex (Table 1). When 10 mol % of MAO−[*R*,*S*]-BL adduct was used, the crude polymer yield was 100%, and the crystalline polymer yield of 60% was the highest ever obtained in our studies.[17]

It should be noted that when 10 mol % of MAO−[*R*,*S*]-BL was employed and if all of BL was converted to polymer, the crude polymer yield should be 120% based on monomer weight since each mole of the complex contained 2 mol of BL. The fact that the crude polymer yield was 100% instead of 120% probably indicates that even after the quantitative conversion of the monomer, the catalyst still contains unreacted BL, possibly in the form of ligands.

From Table 1, It can be seen that there is no difference between the catalytic abilities of MAO−[*R*]-BL and MAO−[*R*,*S*]-BL when they were used as the catalyst for [*R*,*S*]-BL polymerization, respectively.

Polymer Characterization. From the data in Table 1, it can be seen that the molecular weight of the unfractionated polymer also generally increased with increasing amount of the adduct catalyst. With MAO−[*R*,*S*]-BL, both the weight average molecular weight, M_w, and number average molecular weight, M_n, increased with increasing amount of catalyst, but in the case of IBAO−BL, when the catalyst amount was increased, only M_w increased considerably while M_n remained relatively unchanged.

Table 2 lists the glass transition temperatures, melting temperatures, and heats of fusion of the crude polymers obtained using MAO−BL and IBAO−BL as the catalysts. It can be seen from the data in Table 2

Table 2. Thermal Properties of Crude P-[*R,S*]-BL Prepared with MAO−BL and IBAO−BL Adducts

reaction no.	$T_g{}^a$ (°C)	$T_{m1}{}^b$ (°C)	$\Delta H_{m1}{}^b$ (J/g)	$T_{m2}{}^b$ (°C)	$\Delta H_{m2}{}^b$ (J/g)
1	−6	77[c]	10	155	1
2	2	70	2	158	11
3	6			160	12
4	5	74	4	159	12
5	6			161	13
6	−18	104[c]	18		
7	2			154	14
8	0	67[c]	6	159	7

[a] Glass transition temperatures determined by DSC from the second cycle thermogram. [b] Melting temperature, T_m, and heat of fusion, ΔH_m, from the first cycle thermogram. [c] Very broad endothermic peak.

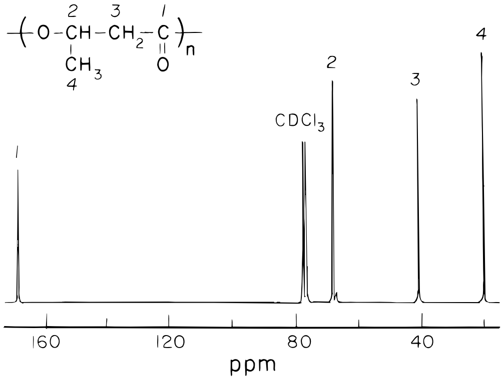

Figure 1. 75-MHz ^{13}C NMR spectrum of P[*R,S*]-BL.

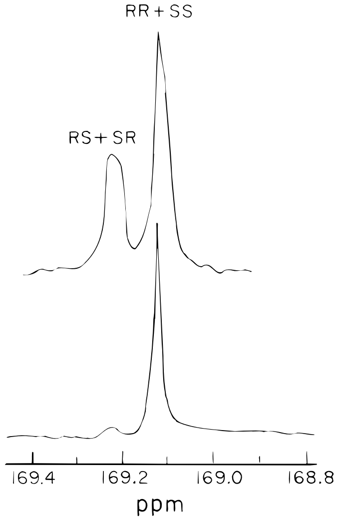

Figure 2. Expanded spectra of the carbonyl peaks of (A) crude polymer and (B) methanol-insoluble polymer.

that when the amount of MAO−BL was lower than 10 mol %, or when IBAO−BL was used, there was a second melting peak in the range 67−105 °C. This peak was attributed to the presence of a syndiotactic polymer fraction.[12,13] When 10 mol % or more MAO−BL was used as the catalyst, no syndiotactic melting peak was found (see entry 3 in Table 2).

Figure 1 shows the ^{13}C NMR spectrum of a polymer obtained with the MAO−BL catalyst. The assignment of each peak is indicated in the figure. Figure 2 shows the expanded carbonyl peak of the crude (A) and the methanol-insoluble (B) polymers, respectively. The peak at 169.23 ppm was assigned to the syndiotactic diads (i.e., *RS* or *SR* diads), and the peak at 169.51 ppm was assigned to the isotactic diads (i.e., *RR* or *SS* diads).[2] Integration of these two signals gave the approximate isotacticity of the polymers. From the figure it can be seen that the methanol-insoluble polymers had much higher isotactic diad contents. Integration of the spectra indicated that the crude polymers had diad isotacticity contents of about 60%, and after AcAc−methanol fractionation, the isotactic diad contents increased to about 90% (see Table 3).

Table 3. Properties of Methanol-insoluble Polymers Obtained from the Polymerization of [*R,S*]-BL with MAO−BL and IBAO−BL Catalysts[a]

			isotactic diad content (%)[b]	
reaction no.[a]	$T_m{}^a$ (°C)	$\Delta H_m{}^a$ (J/g)	crude	insoluble fraction
1	161	35	60	85
2	162	32	63	83
3	163	31	65	78
4	161	33	63	79
5	162	36	65	90
6	156	37	61	87
7	153	42	62	88
8	163	49	64	91

[a] See Table 1. [b] Isotactic diad content as estimated by ^{13}C NMR analysis of carbonyl region.

Table 4. Molecular Weights of Methanol-insoluble Polymers Obtained from the Polymerization of [*R,S*]-BL with MAO−BL and IBAO−BL Catalysts[a]

reaction no.[a]	$M_w{}^a$	$M_n{}^a$	M_w/M_n
1	254 000	53 000	4.8
2	109 000	15 000	7.2
3	145 000	29 100	5.0
4	156 000	33 000	4.7
5	168 000	31 000	5.4
6	120 000	20 100	6.0
7	281 000	34 000	8.3
8	358 000	44 000	8.1

[a] See Table 1.

Table 3 lists the thermal properties of the methanol-insoluble polymer and the isotacticities of both crude and methanol-insoluble polymer fractions. A comparison of the data in Tables 2 and 3 shows that methanol-insoluble polymers had much higher values of heat of fusion than the crude polymers and, therefore, much higher degrees of crystallinity, as would be expected because of the much higher isotactic diad contents of the former. The molecular weights of the methanol-insoluble polymers, obtained from GPC analysis, are included in Table 4.

Removal of Catalyst Residues. It was found that an Al residue remained in the polymer even after fractionation. Because so much alumoxane catalyst was required to obtain high yields (1−10 mol %), the amount of Al in the polymer was very high, and so it was desirable to remove it from the polymer. The method generally used in our past studies for removing the aluminum catalyst residue was to treat the crude polymer with an Al complexing agent such as AcAc, but this procedure also removes a large amount of both atactic and isotactic polymer. When hydrochloric acid in methanol was used for that purpose, the atactic portion of the polymer product was also removed, so in order to retain this fraction in the crude polymer (which may be desirable for practical applications), another procedure was evaluated in which the crude polymer was extracted with dilute aqueous hydrochloric acid. However, in that method the recovered polymer had a lower molecular weight and a much broader molecular

Table 5. Removal of Al Residue from a Crude Polymer Sample[a]

	before treatment	extraction by AcAc	extraction by $HCl-CHCl_3$
sample weight (g)	1.00	0.60	0.85
Al content (wt %)	2.40	0.10	0.20
M_w ($\times 10^{-3}$)	116	145	114
M_n ($\times 10^{-3}$)	20	29	19
M_w/M_n	5.7	5.0	5.9
T_m (°C)	160	163	162
ΔH_m (J/g)	12	31	15
isotactic diad content (%)	65	78	68

[a] See Experimental Section for method.

weight distribution,[23] presumably because of hydrolytic degradation, so further studies were required to find a method free of these disadvantages.

The method developed in the present study using a chloroform solution of hydrochloric acid, as described in the Experimental Section, had the advantage of short contact times between the polymer and the acid and small amounts of acid used. Table 5 shows the results obtained for removal of the Al residue from a typical crude polymer sample. As the data show, the Al residue was largely removed, while the polymer weight loss was only 15%, and the molecular weight did not decrease measurably from the treatment. Apparently the acid−polymer contact time was short enough so that the polymer was not degraded. The T_m of the polymer remained unchanged, but ΔH_m increased slightly, presumably because of the slight increase in isotactic diad content of the polymer that resulted from the use of this procedure. That is, some of the atactic polymer was solubilized, and this resulted in the 15% weight loss observed. In Table 5 the effectiveness of this method ($HCl-CHCl_3$) was also compared with that of the previous one (AcAc). Preliminary results indicated that this crude polymer had enhanced biodegradability compared to the isotactic fraction.[17]

Monomer−Catalyst Adducts. A previous example of a polymerization reaction catalyzed by a monomer-catalyst adduct, which was prepared by a low-temperature reaction of the two, is that of the ferric chloride-propylene oxide catalyst.[24,25] In that system propylene oxide (PO) was added gradually to anhydrous ferric chloride at low temperatures, and the resulting PO−$FeCl_3$ adduct was also an effective catalyst for the polymerization of [*R*,*S*]-PO to form a highly isotactic polymer. A chiral PO monomer was also polymerized to the isotactic polymer with this monomer-catalyst adduct.[26] We recently reported[27] on the stereoregular ring-opening polymerization of [*R*,*S*]-PO catalyzed by a similar alumoxane−PO adduct. In these cases, the metal compound itself ($FeCl_3$ of IBAO) could initiate a polymerization reaction of PO, but the product was an atactic polymer, and for the stereoregular polymerization reaction the monomer−catalyst adduct was apparently the true catalyst.

Acknowledgment. Financial support for this work was provided by Zeneca Ltd. and the Materials Research Laboratory of the University of Massachusetts, which is funded by the National Science Foundation.

References and Notes

(1) Shelton, J. R.; Agostini, D. E.; Lando, J. B. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 2789.
(2) Zhang, Y,; Gross, R. A.; Lenz, R. W. *Macromolecules* **1990**, *23*, 3206.
(3) Tanahashi, N.; Doi, Y. *Macromolecules* **1991**, *24*, 5732.
(4) Ohta, T.; Miyaje, T.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1725.
(5) Tani, H.; Yamashita, S.; Teranishi, K. *Polym. J.* **1972**, *3*, 417.
(6) Teranishi, K.; Araki, T.; Tani, H. *Macromolecules* **1972**, *5*, 660.
(7) Bloembergen, S.; Holden, D. A.; Bluhm, T. L.; Hammer, G. K.; Marchessault, R. H. *Macromolecules* **1989**, *22*, 1656.
(8) Agostini, D. E.; Lando, J. B.; Shelton, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **1971**, *9*, 2775.
(9) Lenz, R. W.; Yang, J.; Wu, B.; Harlan, J.; Barron, A. R. *Can. J. Microbiol.* **1995**, *Suppl. Vol. 1*, 274.
(10) Timmins, M. R.; Lenz, R. W.; Hocking, P. J.; Marchessault, R. H.; Fuller, R. C. *Markromol. Chem. Phys.* **1996**, *197*, 1193.
(11) Hocking, P. J.; Marchessault, R. H. *Polym Bull.* **1993**, *30*, 163.
(12) Kemnitzer, J. E., McCarthy, S. P., Gross, R. A. *Macromolecules* **1993**, *26*, 1221.
(13) Kemnitzer, J. E.; McCarthy, S. P.; Gross, R. A. *Macromolecules* **1993**, *26*, 6143.
(14) Hocking, P. J.; Marchessault, R. H.; Timmins, M. R.; Scherer, T. M.; Lenz, R. W.; Fuller, R. C. *Makromol. Chem. Rapid Commun.* **1994**, *15*, 447.
(15) Pasynkiewicz, S. *Polyhydron* **1990**, *9*, 429.
(16) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.
(17) Wu, B. Ph.D. Thesis, University of Massachusetts, 1996.
(18) Benvenuti, M.; Lenz, R. W. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1991**, *29*, 793.
(19) Pajerski, A. D.; Lenz, R. W. *Makromol. Chem. Macromol. Symp.* **1993**, *73*, 7.
(20) Zhang, Y.; Gross, R. A.; Lenz, R. W. *Macromolecules* **1990**, *23*, 3206.
(21) Gross, R. A.; Zhang, Y.; Konrad, G.; Lenz, R. W. *Macromolecules* **1988**, *21*, 2657.
(22) Harlan, C. J.; Barron, A. R.; Wu, B.; Lenz, R. W. *J. Chem. Soc., Chem. Commun.* **1997**, 2183.
(23) Wu, B.; Lenz, R. W. Unpublished results.
(24) (a) Pruitt, M. E.; Jackson, L.; Baggett, J. M. US Patent, 1955, 2,706,181. (b) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286 and references therein.
(25) Pruitt, M. E.; Jackson, L.; Baggett, J. M.; Freeport, R. J.; Bloomfield, L. J.; Templeton, J. H. US Patent, 1955, 2,706,182.
(26) (a) Sato, A.; Hirano, T.; Tsuruta, T. *Makromol. Chem.* **1975**, *176*, 1187. (b) Tsuruta, T. In *Ring-Opening Polymerization*; Saegusa, T., Goethals, E. J., Eds.; ACS Symposium Series 59; 1977; American Chemical Society: Washington, DC, p 178. (c) Brode, G. L.; Koleske, J. V. *J. Macromol. Sci.—Chem.* **1972**, *A6*, 1109.
(27) Wu, B., Harlan, C. J., Lenz, R. W., Barron, A. R. *Macromolecules* **1997**, *30*, 316.

MA9717698