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(16) The homopolymerization Ia was attempted with anionic (*n*-butyllithium), cationic (titanium tetrachloride), and radical (AIBN; benzoyl peroxide; benzoin methyl ether, $h\nu$) initiators. In each case, no polymer was obtained and the monomer was recovered.

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Polymerization of β-Monosubstituted-β-propiolactones Using Trialkylaluminum–Water Catalytic Systems and Polymer Characterization

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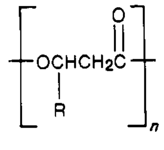
ABSTRACT: The catalysts ethylaluminoxane (EAO), methylaluminoxane (MAO), and a crude in situ catalyst preparation from the reaction of Et_3Al with water were used to synthesize poly([*R*,*S*]-benzyl malolactonate), PBML, and poly([*R*,*S*]-β-hydroxybutyrate), P([*R*,*S*]-HB). Studies of stereoregularity, crystallinity, and molecular weight were carried out on these homopolymers and their product fractions by 75.4-MHz ^{13}C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and gel-permeation chromatography (GPC), respectively. PBML and P([*R*,*S*]-HB) were fractionated into an acetone-soluble portion of comparatively lower molecular weight and low stereoregularity and an acetone-insoluble crystalline fraction with a higher molecular weight ($\bar{M}_w$ greater than 300 000 for PBML and P([*R*,*S*]-HB)) and with high degrees of stereoregularity (up to 88% isotactic diads for P([*R*,*S*]-HB)). The three catalysts were all capable of synthesizing an acetone-insoluble PBML and P([*R*,*S*]-HB) fraction of similarly high crystallinity. Measurements of the enthalpy of fusion (ΔH_m) by DSC for this fraction were usually between 6 and 8 cal/g for PBML and 14 and 16 cal/g for P([*R*,*S*]-HB), while their stereoregular isomers have ΔH_m values of 12.5 and 22 cal/g, respectively. The high peak melting temperatures observed by DSC for these fractions suggest the formation of crystalline regions which show essentially complete exclusion of the noncrystallizable monomer stereochemistry. Racemic benzyl malolactonate (BML) and β-butyrolactone (BL) monomers were copolymerized by using EAO and MAO catalysts. Analysis of these copolymers by ^1H and ^{13}C NMR allowed evaluation of the comonomer diad sequence distribution and showed that the copolymer composition was nearly identical with the monomer feed. The use of the in situ catalyst preparation to perform the above copolymerization resulted in lower yields and extreme sample heterogeneity.

Introduction

The class of β-monoalkyl-substituted poly(β-hydroxyalkanoates) (PHA) are found in a wide variety of bacterial microorganisms throughout nature[1] and function as carbon and energy storage materials.[2] Bacterial PHA commonly contains large amounts of ester units derived from β-hydroxybutyrate (HB), but units derived from β-hydroxyvalerate (HV) and even those with longer n-alkyl pendant groups are also found, as shown below.[1] These polymers are 100% isotactic because the chain chiral centers have only the *R* stereochemical configuration.[2,3]

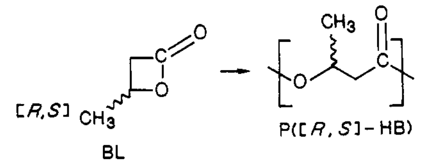


$$\left[-OCH(R)CH_2C(=O)- \right]_n$$

$R = (CH_2)_xCH_3$
$X = 0-7$
PHA

The bacterial polyesters, when carefully isolated, can have viscosity molecular weight averages above 500 000 and a heterogeneity index of approximately 2.[4,5] The bacterial polyester containing primarily HB units is normally stored within the cell and subsequently degraded enzymatically to β-hydroxybutyric acid, which is a metabolite in the fatty acid β-oxidation cycle. This polymer is also biodegradable in environments such as soil, anaerobic sewage, and seawater.[6]

The polymerization of racemic β-butyrolactone (BL) to form poly([*R*,*S*]-β-hydroxybutyrate), P([*R*,*S*]-HB), as shown below, has previously been carried out by using the catalysts obtained by the reaction of Et_3Al or Et_2Zn and H_2O.[7-9] The aluminum-based catalyst produced a highly stereoregular, crystalline polymer fraction,[7-9] while the zinc catalyst produced only atactic, amorphous P([*R*,*S*]-HB). P([*R*,*S*]-HB) synthesized from the racemic β-lactone BL has, of course, a diastereomeric relationship to the optically pure polymer produced by bacteria from β-hydroxybutyric acid.



The aluminum-based catalyst most often used for the polymerization of β-substituted-β-propiolactones is that obtained directly from the reaction of Et_3Al and H_2O in toluene.[7,8] The use of additives, such as epichlorohydrin, in the formation of the catalyst has been investigated as well.[8] More recently, attention has been directed toward the catalyst ethylaluminoxane (EAO), which is claimed to be polymeric ($([-AlEt-O]_n-)$) in nature.[9] This catalyst is believed to be more stereoregulating, have better catalytic activity, and improved reproducibility for the polymerization of BL. EAO have also been used to polymerize a

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variety of β-alkyl- and β-chloroalkyl-β-propiolactones[9] and even monomers in which the β-substituent was an ester functionality.[10] The catalyst referred to as methylaluminoxane (MAO) is believed to be an oligomer of the structure $[-\mathrm{AlMe-O}]_n-$ with n = 6-20. This catalyst has been used in combination with metallocene compounds and is of interest for the polymerization of ethylene to linear polyethylene and for the stereospecific polymerization of propylene.[11]

The polymerization of benzyl malolactonate (BML) (R = $COOCH_2C_6H_5$ in the structure above) in both racemic[12] and enantiomerically pure forms[13,14] has been previously carried out in this laboratory by using anionic catalysts. Poly(benzyl malolactonate) (PBML) is of interest because it can readily be debenzylated without degradation to poly(malic acid) (PMA).[12-14] The hydrolysis product of PMA is malic acid (MA), which is a Krebs cycle intermediate and, consequently, nontoxic. For example, PMA prepared from the racemic monomer given to mice intraperitoneally has a high LD_{50} of 3300 mg/kg of body weight and, therefore, a low acute toxicity.[15] PBML synthesized by anionic polymerization reactions yields an amorphous polymer ($\bar{M}_w$ approximately 20 000) from a racemic monomer[12,14] and a crystalline polymer ($\bar{M}_w$ approximately 100 000) from the enantiomerically pure monomer.[13,14] However, the polymerization of racemic BML using $Et_3Al{\cdot}H_2O$ as catalyst was previously reported to produce less than 2% of a crystalline polymer.[12]

In this work we report on the use of EAO, MAO, and a crude in situ catalyst, which was prepared from the reaction of Et_3Al with H_2O, to synthesize crystalline P([*R*,*S*]-HB) and PBML from their racemic monomers, as well as a copolymer of α-benzylmalate (BM) and HB, P(BM-*co*-HB). All of the polymeric products from these reactions were fractionated, and the fractions were characterized to determine the relative abilities of these aluminum-based catalysts to synthesize stereoregular polymers and to form random copolymers, P(BM-*co*-HB), from monomers which are functionally quite different. The copolymer P(BM-*co*-HB), like PBML itself, should be easily converted to P(MA-*co*-HB) by catalytic hydrogenation.[12-14] P(MA-*co*-HB) will have variable degrees of carboxylic acid functionality, and therefore hydrophilicity, according to the monomer feed and the relative reactivities of BL and BML.

Experimental Section

Polymer Characterization. All molecular weight data reported in the tables were obtained by GPC. The instruments used included a Waters Model 6000A solvent delivery system and a Model 401 refractive index detector with 10^6, 10^5, 10^4, 10^3, and 500-Å ultrastyragel columns in series. Chloroform was used as eluant at a flow rate of 1.4 mL/min. Sample concentrations of 0.1-0.2% wt/vol and injection volumes of 300 μL were used. Polystyrene standards with a low polydispersity were purchased from Polysciences and used to generate a calibration curve.

The ^{13}C NMR measurements were recorded at 75.4 MHz on a Varian XL-300 NMR spectrometer. The ^1H NMR measurements were recorded either at 200 or 300 MHz on Varian XL-200 and XL-300 NMR spectrometers, respectively. The sample concentrations employed for ^{13}C NMR measurements were typically 3.8% wt/vol, and a total of 1500-5000 scans were accumulated. All spectra were recorded at 25-30 °C by using $CDCl_3$ as solvent. The solvent $CDCl_3$ and tetramethylsilane (TMS) were used as internal references for ^{13}C and ^1H NMR spectra, respectively. The delay time between sampling pulses for both ^{13}C and ^1H NMR measurements was 3.0 s. Quantitative data for copolymer composition were obtained from ^1H NMR measurements carried out as described above.

The heat of fusion (ΔH_m) and melting temperatures (T_m) for all polymer samples were determined by using a Perkin-Elmer Model DSC-4. The weight of each sample was typically 4-8 mg. Samples were heated at a rate of 20 °C/min from approximately 5 to 200 °C, quickly cooled, and then scanned a second time by using the same heating rate and temperature range as the first scan. Data used for ΔH_m and T_m were taken from the first scan. T_m was taken as the peak of the melting endotherm. When multiple endotherms were observed, the T_m from the higher temperature endotherm is reported.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer.

Aluminum and C,H analyses were carried out by the Microanalysis Laboratory at the University of Massachusetts, Amherst, MA.

Determination of Et_3Al Concentration. Triethylaluminum solutions in toluene at 1.9 M concentration were purchased from Aldrich Chemical Co. The solutions were packaged under nitrogen in Aldrich Sure/Pac metal cylinders. Samples from each were reacted with water and the amount of ethane gas evolution was measured. The reaction was carried out in glassware which had been flame-dried while flushing with vacuum and argon. All transfers were carried out either by cannulation or with a syringe under an argon atmosphere. The procedure used was as follows: a solution of 1.0 mL of the commercial Et_3Al solution was added to 49 mL of THF, which had been dried by reflux followed by distillation over lithium aluminum hydride. This solution (10 mL) was transfered into a 50-mL three-neck flask and 5 mL of water was added to an attached equalizing dropping funnel. One neck of this flask was attached to a volume graduated cylinder containing mineral oil. After pressure equilibration was achieved, water was added dropwise while cooling the reaction flask with an external ice-water bath and the volume of gas evolution was measured by the displacement of the mineral oil. The final volume measurement (approximately 30 mL) along with room temperature and pressure values were observed after proper time for temperature equilibration. This procedure was carried out three times for each triethylaluminum solution purchased. The calculated molarity, from the average for the three determinations, had values of 1.9 ± 0.1 M. These measured values were used when calculating quantities for the catalyst preparations.

Catalyst Preparations. All catalyst preparations were conducted in glassware which had been flame dried while being alternately flushed with argon and evacuated and finally maintained under a positive pressure of argon. Transfers were carried out by cannulation or with a syringe, under an argon atmosphere. Transfers of the catalyst powders were carried out in a drybox under inert atmosphere.

Reagent grade toluene, purchased from Fisher Scientific, was dried by reflux over sodium metal for 16 h followed by fractional distillation under an argon atmosphere.

The in situ catalyst[7,8] was prepared directly in the polymerization ampule by first adding the solution of Et_3Al in toluene (approximately 1.9 M), cooling to −78 °C, adding a known volume of water, and finally stirring this mixture magnetically while warming to room temperature for 30 min. After this period of time, the catalyst solution contained both gel-like translucent and white particles in a clear and colorless solution.

The polymeric EAO catalyst was prepared by a procedure very similar to that described previously.[9] Toluene (86 mL) and 2.0 M Et_3Al in toluene (30 mL, 0.06 mol) were transferred into a flask, the solution was cooled with an external bath at −78 °C, and deionized water (1.06 mL, 0.059 mol) was added with vigorous magnetic stirring. The stirring was continued for 40 min, while maintaining the external bath temperature at −78 °C, and for 30 min thereafter in an external bath at 0 °C. The particulate matter was allowed to settle while the reaction contents warmed to room temperature for 40 min with no stirring. The clear liquid supernatent was transferred into a distilling flask and the toluene removed at 10^{-1} Torr. Anhydrous decahydronaphthalene (decalin) commercially obtained from Aldrich Chemical Co. (100 mL) was added to the residue and the decalin distilled away at 10^{-3} Torr by using an external silicone oil bath at 60 °C. The residue was then heated to 180-190 °C for 30 min at 10^{-3} Torr and cooled to room temperature; decalin (100 mL) was added to the residue and distilled away as above. The residue was heated once again to 180-190 °C as above and cooled to room temperature; decalin (100 mL) was added and removed as described above. After this

Table I
Polymerization Conditions and Yields for the Homopolymerization of [*R*,*S*]-Butyrolactone (BL) Using Catalysts Derived from the Reaction of R_3Al[a] with Water

polym	polymerztn time, days	molar ratio H_2O/R_3Al[a]	mol % Al/monomer	cat.[b]	yield crude, %	yield after AcAc treatment, %	yield of acetone-insol fractn: from monomer, %	yield of acetone-insol fractn: from crude prod, %
1	7	1.45	6.0	in situ	55	17	11	20
2	7	1.45	6.0	in situ	31	13	10	20
3	7	1.0	4.0	in situ	63	3	2.2	4
4	14	1.0	4.0	EAO	51	31	20	40
5	14	1.0	4.0	MAO	22	20	16	74

[a] Samples 1–4, R = Et, sample 5, R = Me. [b] The in situ catalyst was prepared directly in the polymerization ampule; EAO is ethylaluminoxane ($([-AlEt-O]_n-)$); MAO is methylaluminoxane ($([-AlMe-O]_n-)$). [c] AcAc is acetylacetone.

Table II
Characterization of the Product Fractions in Table I from the Homopolymerization of [*R*,*S*]-Butyrolactone (BL)

polym	molecular weight determination (GPC)[a]: AcAc[b]-treated prod[c] $\bar{M}_w/\bar{M}_n$	acetone-sol fractn $\bar{M}_w/\bar{M}_n$	acetone-insol fractn $\bar{M}_w/\bar{M}_n$	ΔH_m,[d] cal/g: AcAc treated	acetone insol	peak melting temp, °C: AcAc treated	acetone insol
1	380 000/36 000 (11)	80 000/22 000 (3.6)	290 000/39 000 (7.4)	9.8	16.0	162	166
2	730 000/43 000 (17)	30 000/9500 (3.2)	440 000/80 000 (5.5)	9.0	14.0	159	165
3	410 000/32 000 (13)	160 000/18 000 (8.9)	300 000/47 000 (6.4)	14.3	19.6	163	165
4	650 000/43 000 (15)	100 000/27 000 (3.7)	880 000/110 000 (8.0)	8.3	13.6	161	163
5	310 000/35 000 (8.9)	99 000/22 000 (4.5)	620 000/100 000 (6.2)	12.9	15.9	160	164

[a] Eluted with chloroform at 25 °C; the molecular weight averages were calculated on the basis of polystyrene standards. [b] AcAc is acetylacetone. [c] Partially fractionated product which remained after AcAc treatment. [d] Determined by DSC during the first heating scan.

distillation was visually complete, the residue was left for an additional 90 min at 10^{-3} Torr and heated with an external oil bath at 60 °C. Hexane (100 mL) dried by reflux followed by distillation over sodium metal was added to the residue, which had the appearance of an opaque gel. This suspension was stirred for 120 min at room temperature, then for 10 min at 40 °C. It was filtered through a 4–8 μm scintered glass funnel to yield a clear, colorless hexane solution. The hexane was distilled off, first at ambient pressure and then at 10^{-3} Torr, leaving 2.2 g (52% yield) of a white powder. Anal. Calcd for C_2H_5AlO: C, 33.3; H, 6.9; Al, 37.5. Exptl: C, 29.2; H, 6.9; Al, 39.2. A catalyst solution of EAO was prepared by dissolving this solid in toluene (33 mg/mL), giving a colorless clear solution.

The oligomeric MAO catalyst was prepared in the laboratory of Prof. James C. W. Chien at the University of Massachusetts.[16] Other synthetic routes to MAO have been described as well.[17] Anal. Calcd for CH_3AlO: C, 20.9; H, 5.2; Al, 46.6. Exptl: C, 23.7; H, 7.1; Al, 46.5. A catalyst solution of MAO was prepared by dissolving this solid in toluene (26.6 mg/mL) to form a colorless clear solution.

Both the EAO and MAO catalysts were stored in flasks as solids at 5 °C under an argon atmosphere in a desiccator, using drierite as desiccant. They were used within three weeks of their preparation. The catalyst solutions, once prepared, were used within a 24-h period.

Monomer Preparation. [*R*,*S*]-BL was obtained commercially from Aldrich Chemical Co., dried over CaH_2 at 80 °C for 2 h under an argon atmosphere, and then fractionally distilled (70 °C vapor temperature, 30 mm). The procedure used to synthesize [*R*,*S*]-BML was that described in the literature.[12–14] The ^1H NMR and IR spectra of these two compounds were consistent with their structures.

Polymer Preparation. An ampule to be used for the polymerization was flame dried while flushing with vacuum and argon. All reactants added to these ampules were transferred with a syringe under an argon atmosphere. Either the catalyst was prepared directly in the ampule (see in situ catalyst preparation) or the appropriate catalyst solution (see preparation of the EAO and MAO catalysts) was transferred into the ampule. The catalyst solution was cooled to −78 °C, and the monomer(s) were added. The contents of the ampule were degassed during three freeze–thaw cycles and finally sealed under vacuum. Polymerization reactions were carried out at 60 °C for time periods ranging from 7 to 14 days for homopolymerizations and as long as 27 days for copolymerizations.

At the end of the polymerization periods the products were yellow to light brown in color and gellike in consistency, exhibiting variable fluidity. After the ampules were opened, their contents were triturated and dispersed with a magnetic stirrer in ether (about 100 mL/g of initial monomer) containing 1% water. The undissolved solid was vacuum filtered and added to chloroform (about 100 mL/g of initial monomer) and the suspension was stirred for 16 h at 25 °C and refluxed for 10 min. The hot chloroform suspension was passed through a 25–50-μm scintered glass filter funnel containing a 1-cm layer of Celite. The clear chloroform solution so obtained was concentrated to about 10 mL of chloroform per gram of initial monomer. This solution was precipitated into ether and the solid vacuum filtered and washed with ether to give the crude product. The crude product was treated with acetylacetone (AcAc) purchased from Aldrich Chemical Co. (7.5 mL/g of crude product) for the removal of aluminum.[9] The crude product suspension in AcAc was stirred for 24 h at room temperature after which time 7.5 mL of methanol per milliliter of AcAc was added. The insoluble material was vacuum filtered and washed with methanol and the solvent was removed to yield the AcAc-treated product.

The AcAc-treated product was separated into acetone-soluble and acetone-insoluble fractions using a Soxhlet extractor. Polymer samples to be fractionated were ground in a mortar, placed into the extractor thimbles, and extracted for 16 h with hot acetone, using glasswool and aluminum foil to insulate the apparatus. The acetone-insoluble fraction remained in the thimble while the acetone-soluble fraction was the residue obtained after solvent removal.

The ^1H and ^{13}C NMR as well as IR spectra of the polymer product fractions were consistent with the expected structures.

Results and Discussion

Homopolymerization of BL. The homopolymerization of BL was carried out with three different catalysts, including the in situ catalyst and the preprepared EAO and MAO (see Experimental Section). The results for all three catalysts are summarized in Tables I and II.

Treatment of the crude, yellow colored polymer products with AcAc, which was originally suggested by Tani and

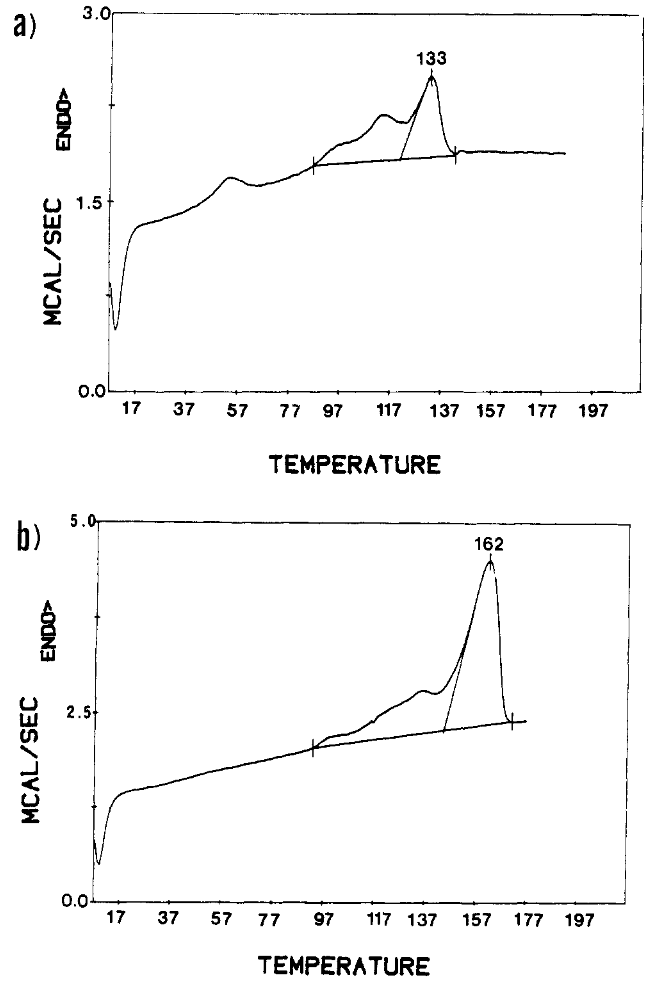

Figure 1. DSC thermograms during the first heating scan of polymer 5: (a) the acetone-soluble fraction; (b) the acetone-insoluble fraction.

co-workers for the removal of aluminum,[9] was found to greatly decrease the aluminum content of the product and markedly increase its solubility so that a partial fractionation was achieved to yield a polymer with higher crystallinity. The treatment removed all colored impurities to yield white samples. In the case of the crude sample of polymer **3**, for example, the crude polymer had a weight-average molecular weight, $\bar{M}_w$, of 150 000, a number-average molecular weight, $\bar{M}_n$, of 10 000, and an enthalpy of fusion, ΔH_m, as measured by DSC of 1.3 cal/g. In contrast, after the AcAc treatment, the sample had an $\bar{M}_w$ of 410 000, an $\bar{M}_n$ of 32 000, and a ΔH_m of 14.3 cal/g. Similarly, polymer **4** prior to AcAc treatment had a ΔH_m of 2.3 cal/g as compared to 8.3 cal/g after treatment. For polymer **3**, the percent aluminum content found in the crude product compared to the product obtained after AcAc treatment were 2.2% and 0.05%, respectively. For polymer **5**, the values were 0.8% and 0.05%, respectively.

All of the catalysts produced acetone-insoluble fractions which had high degrees of stereoregularity and high molecular weights and acetone-soluble fractions which had much lower degrees of stereoregularity and molecular weights (see Table II). Similar results were previously observed by Araki and co-workers.[9] ΔH_m values for the acetone-insoluble fractions ranged from 13.6 to 19.6 cal/g while the enantiomerically pure polymer produced by bacteria, which, therefore, is completely isotactic in structure, has a ΔH_m of approximately 22 cal/g.[18]

The DSC thermograms of the acetone-soluble and acetone-insoluble fractions of polymer **5** are shown in parts a and b of Figure 1, respectively. These thermograms are very similar to those obtained for the other samples studied, which include the acetone-insoluble fractions of polymers **1**–**4** and the acetone-soluble fraction of polymer **3**. All of these polymers had high degrees of crystallinity in their acetone-insoluble fraction and a relatively lower enthalpy of fusion (generally about 6.6 cal/g) in their acetone-soluble fraction. The peak melting temperatures of the acetone-soluble fractions were approximately 130 °C. The depression in the peak melting temperature by approximately 31 °C, in combination with the lower values of enthalpy of fusion for the acetone-soluble fractions, suggests lower degrees of stereoregularity for these fractions.

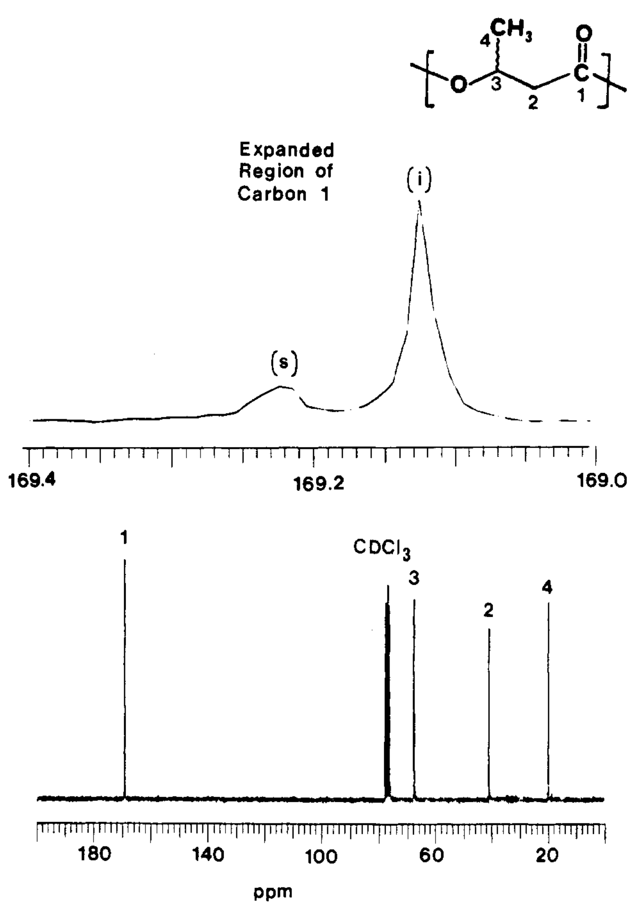

Figure 2. 75.4-MHz ^{13}C NMR spectrum of the acetone-insoluble fraction of polymer **4**, recorded at 25 °C in $CDCl_3$, along with an expansion of the region containing the carbonyl carbon 1 signals.

The ^{13}C NMR spectrum of amorphous P([*R*,*S*]-HB), which was previously reported by Araki and co-workers, had carbonyl carbon atom shifts and methylene carbon atom shifts which were sensitive to tacticity.[19] Diad sequences are clearly seen in the carbonyl carbon region, where two peaks appear.[19] The upfield and downfield peaks correspond to isotactic, (i), and syndiotactic, (s), stereochemical sequences respectively.[19,20] The (i) sequences (*R*–*R* and *S*–*S*) are NMR equivalent while the (s) sequences (*R*–*S* and *S*–*R*) are not because of directionality effects. Both of the (s) diad sequences can be assigned to the downfield signal due to the equality of the integrated areas of the upfield and downfield signals for an atactic sample and from positive identification of the upfield signal obtained by mixing P([*R*,*S*]-HB) with natural origin P([*R*]-HB).[21] An expansion of the ^{13}C NMR spectrum of polymer **4** in the carbonyl region is shown in Figure 2. From integrated areas of the (i) and (s) signals for the carbonyl carbons, values of 88% and 82% (i) diads for

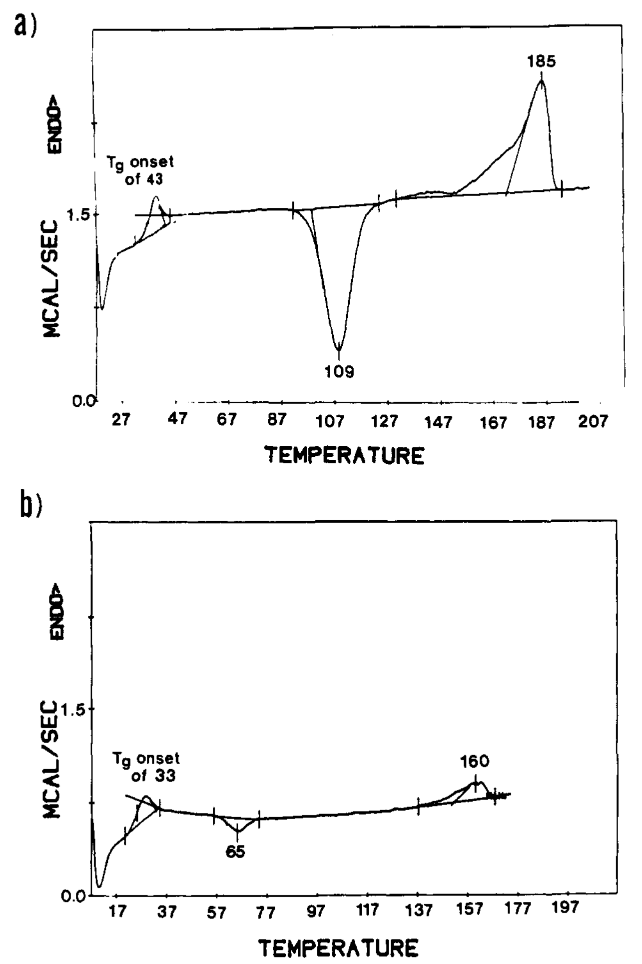

Figure 3. DSC thermograms during the second heating scan of (a) the acetone-insoluble fraction of polymer 11 and (b) polymer 19, unfractionated, after AcAc treatment.

polymers 1 and 4 were obtained, respectively. The higher fraction of isotactic diads in polymer 1 relative to 4 is in agreement with their comparative heats of fusion (16.0 versus 13.6 cal/g, respectively). A higher fraction of isotactic diads in these samples suggests that the polymer contains longer sequences with the same stereochemical configuration, that is, isotactic blocks. The acetone-soluble fractions of polymers 1 and 5 have 67% and 60% (i) diads, respectively, which is consistent with the melting transition observed in the DSC thermograms of this fraction for polymers 3 and 5. An atactic poly(β-monosubstituted-β-propiolactone) should not exhibit a melting transition.[22]

It is evident from the DSC and ^{13}C NMR results that perfect stereoregulation was not observed in the acetone-insoluble fractions by any of the catalysts under any of the polymerization conditions investigated in this work. This result is in contradiction to the observation of Araki and co-workers,[19] who reported that the acetone-insoluble fraction of P([*R*,*S*]-HB), which was synthesized under identical conditions to those for polymer 4, had a ^{13}C NMR spectrum indistinguishable from that of natural origin P([*R*]-HB).

The catalyst MAO produced a relatively low yield of crude product, of which 80% remained in the highly crystalline acetone-insoluble fraction (see Table I). The catalyst EAO and the in situ catalyst gave higher crude yields, but a smaller fraction of these crude products remained after fractionation. The highest overall yield of the acetone-insoluble fraction was achieved by using the catalyst and polymerization conditions originally reported by Araki and co-workers,[9] but the yield obtained, 20%, was considerably lower than that reported by them, 52%.[9] This difference is likely due to changes in the workup procedure, which, in our work, most likely produced an acetone-insoluble fraction with a higher molecular weight and degree of stereoregularity relative to their acetone-insoluble fraction. The acetone-insoluble fractions were bimodal and had large polydispersities ($\bar{M}_w/\bar{M}_n$) with values which ranged from 5 to 9.

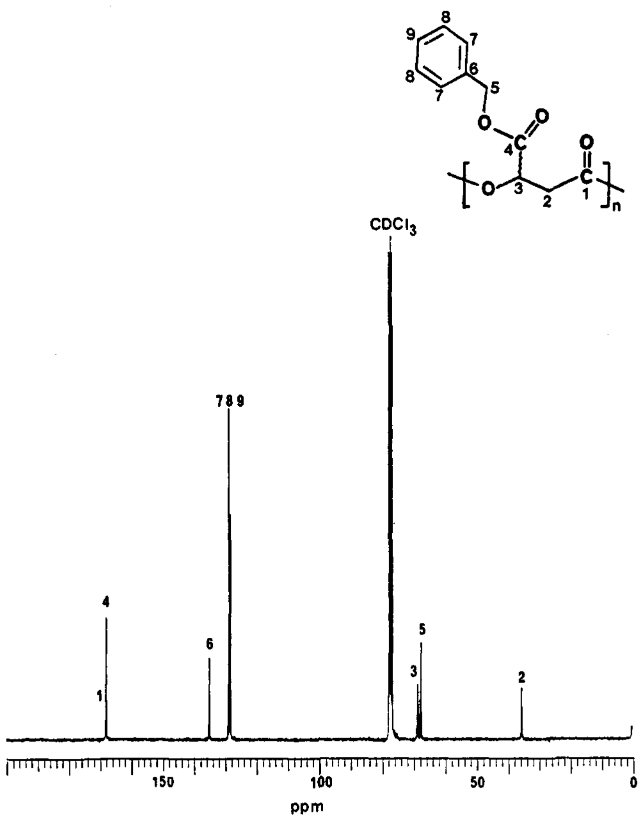

Figure 4. 75.4-MHz ^{13}C NMR spectrum, recorded at 25 °C in CDCl$_3$, of polymer 6 (PBML), unfractionated, after AcAc treatment.

Homopolymerization of BML. In earlier work carried out in our laboratories, PBML was synthesized by using the anionic initiator tetraethylammonium benzoate, in bulk, at 60 °C.[12-14] The polymer that was synthesized, as above, from racemic monomer was obtained in about 60% yield and was amorphous.[12,14] Molecular weight determinations by GPC (see Experimental Section), gave values for $\bar{M}_w$ of approximately 20 000 and for $\bar{M}_w/\bar{M}_n$ of approximately 1.1.[12,14] The polymer formed by using the above initiator, from enantiomerically pure *R*-configuration BML, was obtained in about 85% yield and was crystalline.[13,14] From the DSC thermogram (during the first heating scan) this polymer had a ΔH_m of 12.5 cal/g and a peak melting temperature of 190 °C.[13,14] The molecular weight determinations by GPC (see Experimental Section) for this optically active polymer gave values for $\bar{M}_w$ of approximately 100 000 and for $\bar{M}_w/\bar{M}_n$ of approximately 2.1.[13,14]

Guerin et al. characterized PBML stereoisomers for tacticity effects by ^{13}C NMR (75.4 MHz).[23] The polymers were prepared, with triethylamine as initiator, by using different ratios of [*R*]- and [*S*]-BML. The PBML samples were believed to have a random placement of [*R*]- and [*S*]-BM monomer units. The peak assigned to the methine carbon 3 (see Figure 4), when expanded, showed three major peaks which were attributed to triad tacticity effects.[23] When PBML was synthesized by using a high enantiomeric excess of either the *R* or the *S* enantiomer,

Table III
Polymerization Conditions and Yields for the Homopolymerization of [*R*,*S*]-Benzyl Malolactonate (BML) Using Catalysts Derived from the Reaction of R_3Al^a with Water

							yield of acetone-insol fractn, %	
polym	polymerztn time, days	molar ratio H_2O/R_3Al^a	mole % Al/monomer	cat.[b]	yield crude, %	yield after AcAc[c] treatment, %	from monomer	from crude prod
6	7	1.45	6.0	in situ	24	18	12	50
7	7	1.46	6.7	in situ	23	17	12	52
8	7	1.0	4.0	in situ	8	6	3	38
9	7	1.0	5.6	in situ	4	3	2	50
10	14	1.0	4.1	EAO	11	10	8	73
11	14	1.0	3.4	EAO	17	14	8	47
12	14	1.0	4.0	MAO	16	14	8	50
13	14	1.0	4.3	MAO	20	16	8	40

[a] Samples 6–11 R = Et; samples 12 and 13 R = Me. [b] The in situ catalyst was prepared directly in the polymerization ampule: EAO is ethylaluminoxane ($[-AlEt-O]_n-$); MAO is methylaluminoxane ($[-AlMe-O]_n-$). [c] AcAc is acetylacetone.

Table IV
Characterization of the Product Fractions in Table III from the Homopolymerization of [*R*,*S*]-Benzyl Malolactonate (BML)

	molecular weight determination (GPC)[a]			ΔH_m,[d] cal/g		peak melting temp, °C	
polym	AcAc[b]-treated prod[c] $\bar{M}_w/\bar{M}_n$	acetone-sol fractn $\bar{M}_w/\bar{M}_n$	acetone-insol fractn $\bar{M}_w/\bar{M}_n$	AcAc-treated prod	acetone-insol fractn	AcAc-treated prod	acetone-insol fractn
6	540 000/36 000 (15)	87 000/14 000 (6.2)	680 000/69 000 (9.9)	4.0	8.3	183	189
7	230 000/41 000 (5.6)	64 000/16 000 (4.0)	360 000/28 000 (13)	4.2	5.4	185	189
8	310 000/21 000 (15)	45 000/8000 (5.6)	350 000/27 000 (13)	4.3	5.6	181	186
9	250 000/29 000 (8.6)	32 000/7200 (4.4)	130 000/21 000 (6.2)	4.7	5.5	185	187
10	270 000/31 000 (8.7)		360 000/47 000 (7.7)	4.9	7.1	188	190
11	300 000/15 000 (20)	30 000/7500 (4.0)	310 000/33 000 (9.4)	4.5	6.9	184	186
12	450 000/19 000 (24)	36 000/4000 (9.0)	310 000/23 000 (13)	3.6	6.2	176	180
13	196 000/15 000 (13)	41 000/9000 (4.6)	390 000/35 000 (11)	4.1	7.8	182	184

[a] Eluted with chloroform at 25 °C; the molecular weight averages were calculated on the basis of polystyrene standards. [b] AcAc is acetylacetone. [c] Partially fractionated product which remained after AcAc treatment. [d] Determined by DSC during the first heating scan.

the peak from the methine carbon at highest field increased relative to the others, and it was therefore assigned as being due to an isotactic (I) triad arrangement.[23]

It was previously reported by Araki and co-workers, from ^{13}C NMR studies (25.2 MHz) on poly(β-alkylpropiolactones), that the methine carbon of poly(β-esters) was insensitive to tacticity effects.[19] It is clear from the work of Guerin et al.,[23] as well as from similar observations in the present study on analogous PBML stereoisomers, that the methine carbon signal for the ^{13}C NMR spectrum of a poly(β-monosubstituted-propiolactone) can show sensitivity to tacticity effects.

Observations of tacticity effects in the ^{13}C NMR spectra of PBML stereoisomers allowed us to evaluate qualitatively the stereoregularity of PBML samples, synthesized from racemic monomer, using the prepared catalysts MAO and EAO and the in situ catalyst preparations (see Experimental Section).

The results from aluminum catalyst homopolymerizations of BML are summarized in Tables III and IV. The acetone-insoluble fractions from these polymerizations contained high molecular weight crystalline PBML. From observation of Table IV it is seen that the acetone-insoluble fractions of polymers 6–13 had values of $\bar{M}_w$ usually from 300 000 to 400 000. These samples were highly polydisperse, with values of $\bar{M}_w/\bar{M}_n$ ranging from 6.2 to 13. DSC thermograms were carried out on these acetone-insoluble fractions and gave values for ΔH_m of generally between 6 and 8 cal/g. The DSC thermogram recorded during the second heating scan (see Experimental Section) of polymer 11 (the acetone-insoluble fraction) is displayed in Figure 3a. This figure clearly shows the glass transition, the exotherm due to crystallization, and the endotherm due to melting.

From previous work, it is known from the DSC thermograms of racemic and enantiomerically pure PBML, which were polymerized by using the initiator tetraethylammonium benzoate, that the former polymer was amorphous while the latter had a ΔH_m of 12.5 cal/g with a peak melting temperature (T_m) at 190 °C. It is clear, therefore, that the acetone-insoluble fractions of polymers 6–13 have a degree of stereoregularity high enough to allow crystallization.

The T_m values for the nonfractionated AcAc-treated PBML samples were from 2 to 6 °C lower than those of their corresponding acetone-insoluble fractions (see Table IV). The T_m values of the acetone-insoluble fractions in Table IV were slightly depressed from the value of 190 °C for P([*R*]-BML)[13,14] with the exception of polymer 11, which had the identical value. The above results are likely due to the effect of stereoirregular chain segments acting as crystalline impurities.

Earlier studies were carried out by Guerin et al. on PBML which contained an [*S*]-BM/[*R*]-BM (70/30) monomer composition with the stereochemical configurations randomly arranged along the chains.[23] This polymer had a 50 °C depression in T_m relative to isotactic PBML.[23] Examples of other poly(β-substituted-β-propiolactones) which show this type of behavior have been given,[22] and theoretical treatments such as Flory's law applied to stereocopolymers[24] agree with the above results. The high values of T_m for the acetone-insoluble fractions of PBML and P([*R*,*S*]-HB) suggest, therefore, that these samples contain chain segments or blocks which closely approximate or have perfect stereoregularity over a sufficiently long length to allow the formation of crystalline regions which show essentially complete exclusion of the noncrystallizable monomer stereochemistry.

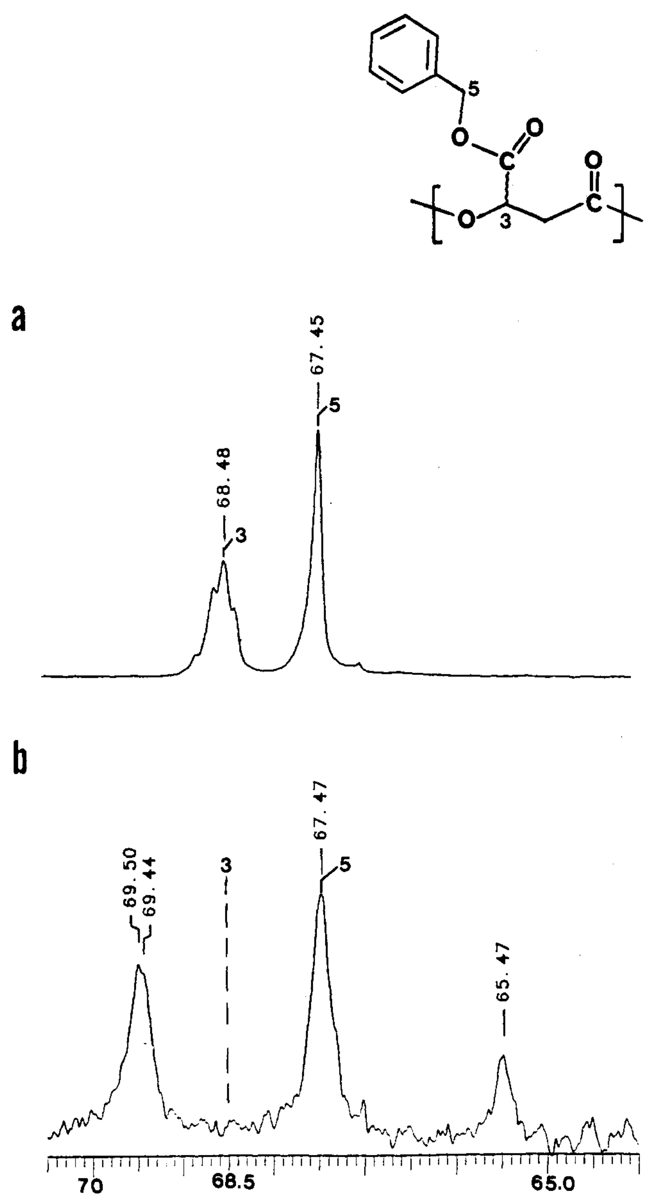

Figure 5. Expanded regions of the methine (carbon 3) and benzyl (carbon 5) carbons from the ^{13}C NMR spectrum recorded at 25 °C in $CDCl_3$ of an atactic PBML sample: (a) proton decoupled; (b) proton coupled and nuclear Overhauser effect enhanced.

The ^{13}C NMR spectra of the acetone-soluble and acetone-insoluble fractions of polymers **6**, **8**, **10**, and **12** were taken, and appeared almost identical with that of the AcAc-treated unfractionated polymer **6** shown in Figure 4, without observing expansions of various regions.

The assignments of the chemical shifts for the methine and benzyl carbons 3 and 5, respectively, were confirmed by obtaining the proton-decoupled ^{13}C NMR spectrum of an atactic PBML sample[12] and comparing it with the nuclear Overhauser enhanced proton-coupled ^{13}C NMR spectrum of the same sample (parts a and b of Figure 5, respectively). The downfield signal in 5a appears as a doublet in Figure 5b which corresponds to a carbon with one hydrogen attached (carbon 3), while the upfield signal in Figure 5a appears as a triplet in Figure 5b which corresponds to a carbon with two hydrogens attached (carbon 5). The doublet from carbon 3 overlaps with the two downfield peaks from the triplet of carbon 5 (see Figure 5b).

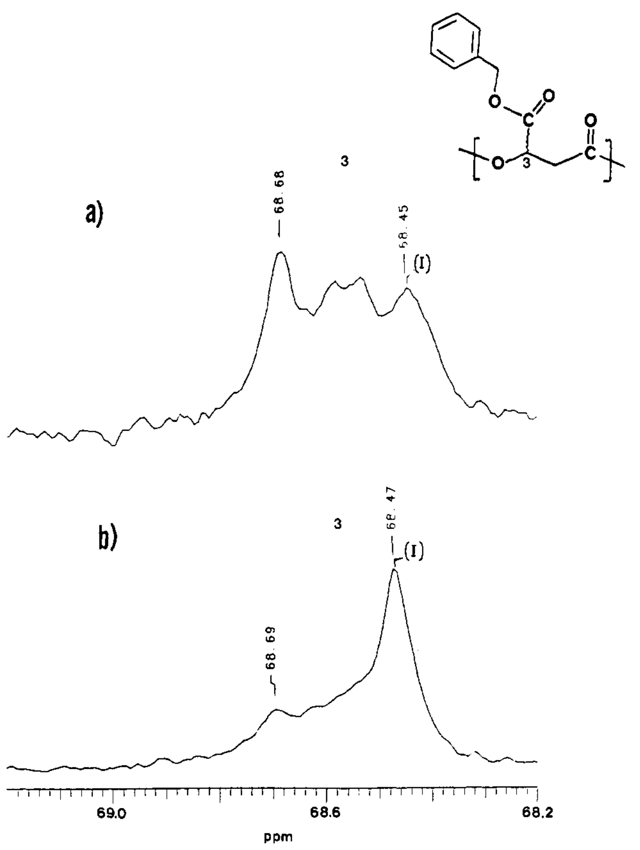

Figure 6. Expanded regions of the methine carbon 3 from the 75.4-MHz ^{13}C NMR spectra, recorded at 25 °C in $CDCl_3$, of polymer **6**: (a) the acetone-soluble fraction; (b) the acetone-insoluble fraction.

The expanded region of the methine carbon 3 signals for the acetone-soluble and acetone-insoluble fractions of polymer **6** are shown in parts a and b of Figure 6, respectively. For the acetone-insoluble fraction, the peak corresponding to the (I) triads becomes very much increased in intensity relative to the peaks from the other respective triads. The acetone-soluble fraction does not show this characteristic. The expanded regions of the methine carbon 3 signals for the acetone-soluble and acetone-insoluble fractions of polymers **8**, **10**, and **12** appeared almost identical with those displayed in Figure 6. This observation, along with the DSC thermogram results discussed above, demonstrates the ability of the in situ prepared catalysts, along with the preprepared catalysts EAO and MAO (see Experimental Section), to synthesize an acetone-insoluble fraction of PBML from a racemic monomer which has a high degree of stereoregularity.

Investigations on the acetone-soluble fractions of polymers **6**, **8**, **10**, and **12** by DSC did not show a melting transition from 147 to 187 °C. A small endothermic transition was often seen for these samples at approximately 100 °C having a ΔH of approximately 0.5 cal/g. This result may be associated with the crystallization of chain segments having low degrees of stereoregularity. From the ^{13}C NMR and DSC data on this product fraction, it is clear that the monomer stereochemical sequence distribution closely approximates an atactic arrangement.

The GPC chromatograms of the acetone-soluble and acetone-insoluble fractions of polymers **6**–**13** consistently showed the higher relative molecular weight of the acetone-insoluble fraction (see Table IV). This result is a characteristic which is common to both P([*R*,*S*]-HB) and PBML.

Treatment of crude PBML samples with AcAc effected the removal of yellow impurities along with aluminum. For example, the aluminum content of the crude sample of polymer **8** was 1.4%, but after AcAc treatment the sample contained 0.12% aluminum and was colorless. The other

Table V

Polymerization Conditions and Yields for the Attempted Copolymerization of [*R*,*S*]-Butyrolactone (BL) and [*R*,*S*]-Benzyl Malolactonate (BML) by Using Catalysts Derived from the Reaction of R_3Al[a] with Water

polym	polymeriztn time, days	molar ratio H_2O/R_3Al[a]	mol % Al/monomer	cat.[b]	monomer feed[c] BL:BML; polym compstn[c] HB:BM	yield crude, %	yield after AcAc[d] treatment, %	yield of acetone-sol fractn, %
14	27	1.45	6.0	in situ	50:50; 22:78	17	5	
15	7	1.48	5.7	in situ	50:50; 38:62	9	6	
16	7	1.0	4.0	in situ	80:20; 70:30	17	3	
17	27	1.0	2.0	in situ	50:50; 44:56	9	6	
18	27	1.0	4.0	EAO	50:50; 54:46	15	10	
19	27	1.0	4.1	EAO	50:50; 45:55	15	10	9.2
20	27	1.0	3.6	EAO	32:68; 36:64	27	23	19
21	27	1.0	3.8	MAO	54:46; 50:50	26	21	19
22	27	1.0	4.0	MAO	28:72; 28:72	32	27	23

[a] Samples 14–20, R = Et; samples 21, 22, R = Me. [b] The in situ catalyst was prepared directly in the polymerization ampule: EAO is ethyl aluminoxane ($[-AlEt-O]_n-$); MAO is methylaluminoxane ($[-AlMe-O]_n-$). [c] Data presented in mole percent of each monomer. [d] AcAc is acetylacetone.

Table VI

Characterization of the Product Fractions in Table V from the Attempted Copolymerization of [*R*,*S*]-Butyrolactone (BL) and [*R*,*S*]-Benzyl Malolactonate (BML)

	molecular weight determination (GPC)[a]					composition[e]	
polym	AcAc[b]-treated prod[c] $\bar{M}_w/\bar{M}_n$	acetone-sol fractn $\bar{M}_w/\bar{M}_n$	acetone-insol fractn $\bar{M}_w/\bar{M}_n$	ΔH_m[d] after AcAc treatment, cal/g	peak melting temp after AcAc treatment, °C	acetone-sol fractn HB:BM	acetone-insol fractn HB:BM
14	67 000/15 000 (4.5)			1.1	161		
15	130 000/12 000 (11)			1.7	163		
16	240 000/37 000 (6.5)			2.1	153		
17	220 000/19 000 (12)			1.4	158		
18	300 000/24 000 (13)			0.3	153		
19	200 000/17 000 (12)	70 000/16 000 (4.3)	600 000/68 000 (8.8)	0.6	150	44:56	
20	270 000/16 000 (17)	210 000/11 000 (19)	840 000/120 000 (7.0)	0.6	153	32:68	48:52
21	400 000/34 000 (12)	350 000/29 000 (12)	690 000/52 000 (13)	0.5	159	44:56	50:50
22	300 000/14 000 (21)	140 000/13 000 (11)	860 000/85 000 (10)	0.0		28:72	33:67

[a] Eluted with chloroform at 25 °C; the molecular weight averages were calculated on the basis of polystyrene standards. [b] AcAc is acetylacetone. [c] Partially fractionated product which remained after AcAc treatment. [d] Determined by DSC during the first heating scan. [e] Data presented in mole percent of comonomer units.

crude and AcAc-treated samples in Table III are assumed to contain similar quantities of aluminum. As was observed with P([*R*,*S*]-HB), the removal of aluminum with AcAc from crude PBML samples markedly increased sample solubilities and therefore allowed for a more complete fractionation using hot acetone (see Experimental Section).

When the crude PBML samples in Table III were fractionated, a large weight fraction of these polymer samples was found to be acetone insoluble (40–74%) but yields of the crude samples were low (less than or equal to 24%). An in situ catalyst preparation gave the highest yield of the acetone-insoluble fraction (12%) where the molar ratio of H_2O/Et_3Al used was 1.45 (see Table III). The extreme sensitivity of the product formed to the molar ratio of H_2O/Et_3Al used is well documented[8,9] and was demonstrated, as well, in this work where the yield of the acetone-insoluble fraction fell to approximately 2.5% when the H_2O/Et_3Al molar ratio used was 1.0 (see Table III). Studies to determine the optimal H_2O/Et_3Al molar ratio for the in situ catalyst preparation were not undertaken.

In summary, the racemic β-propiolactone BML, which has a carbobenzoxy β-substituted ring and, therefore, a carbonyl electron-withdrawing group attached to the ring at the β position, could be successfully polymerized with a high degree of stereoregulation by using an in situ catalyst preparation as well as with the preprepared catalysts EAO and MAO (see Experimental Section) to give a crystalline polymer with an $\bar{M}_w$ greater than 300 000. Use of the anionic initiator tetraethylammonium benzoate to polymerize racemic BML produced an amorphous polymer with an $\bar{M}_w$ of approximately 20 000.

Copolymerization of Racemic BML and BL. The anionic catalysts tetraethylammonium benzoate, sodium methoxide, and *n*-butyllithium were all reported by Araki and co-workers to be unsuitable initiators for the homopolymerization of BL.[8,9] Optimistic from results that an in situ catalyst preparation, as well as the preprepared catalyst EAO and MAO, was capable of homopolymerizing both BML and BL, the investigation of the copolymerization of these two monomers with the aluminum-based catalysts above was encouraged. This copolymerization was studied so that polymers with variable degrees of carboxylic acid functionality could be obtained, depending on the monomer feed and the relative reactivities of the monomers BL and BML, after the catalytic hydrogenation of the benzyl ester protecting groups.

The results of the attempted copolymerizations are summarized in Tables V and VI. Longer reaction times were used for these polymerizations relative to the homopolymerizations of BML and BL carried out in this work, due to the visually slower progress of the polymerization (by observation of sample flow). The yields for polymers **14–17** synthesized by using an in situ catalyst preparation (see Experimental Section) were low, less than 6% after AcAc treatment. These samples were not fractionated.

When the preprepared catalyst EAO was used for polymers **18–20**, yields for these samples after AcAc treatment ranged from 10 to 23%. Polymers **19** and **20** were fractionated with hot acetone (see Experimental

Section) after which greater than 82% of the AcAc-treated samples were acetone-soluble. The yields obtained were identical for the 50:50 comonomer feeds (polymers **18** and **19**) but more than doubled when the comonomer feed of BML was increased to 68% (polymer **20**).

Polymers **21** and **22**, for which the preprepared catalyst MAO was used, were obtained in similar yields of 19% and 23% of the acetone-soluble fractions, respectively, even though different comonomer feeds were used for these two polymer samples (see Table V). The acetone-soluble fractions of polymers **21** and **22** account for greater than 84% of the mass of their respective AcAc-treated samples.

The composition of the acetone-soluble fractions for polymers **19–22** closely approached, or were identical with, the monomer feed ratios used (see Tables V and VI). These acetone-soluble samples above were found to be slightly enriched in BM relative to the unfractionated AcAc-treated samples.[25] The similarity between the monomer feed and the polymer composition for polymers **18–22** was not anticipated due to the steric and electronic differences between the β-substituents of BL and BML.

The unfractionated AcAc-treated samples of polymers **18–22** were studied by DSC which showed peak melting temperatures ranging from 150 to 160 °C with ΔH_m values of less than or equal to 0.6 cal/g. The DSC thermogram of polymer **19** (unfractionated, after AcAc treatment) recorded during the second heating scan (see Experimental Section) is shown in Figure 3b. Observation of the DSC thermograms for the acetone-soluble fraction of polymer **19**, recorded during the first and second heating scans, did not show any transitions due to melting or recrystallization.

The low ΔH_m values observed for polymers **18–22** (unfractionated, after AcAc treatment) suggest that they do not consist primarily of blocks containing BM and HB which have high degrees of stereoregularity[26] but in fact are copolymers which contain a somewhat random comonomer distribution. The comonomer units have very different pendant group structures which are likely to impede crystallization.

The peak melting temperature for polymers **18–21**, when observed by DSC, were on average 9 and 31 °C lower than those of the acetone-insoluble fractions of P([*R*,*S*]-HB) and PBML, respectively (see Tables II, IV, and VI). The minima observed in the DSC thermograms of polymers **18–21**, which are most likely due to the crystallization exotherm, occur at approximately 65 °C. The minima corresponding to the crystallization exotherm for P([*R*,*S*]-HB) and PBML ranges from 47 to 75 °C and 103 to 130 °C, respectively (where less crystalline samples show transitions at higher temperatures). We see, then, that the melting endotherm and crystallization exotherm for polymers **18–21** correspond quite well with the melting and crystallization transitions observed in the DSC thermograms for the acetone-insoluble fractions of P([*R*,*S*]-HB) (see Table II).

The above results from studies by DSC suggest, therefore, that the melting and crystallization transitions observed for samples **18–21** may arise from polymer chain segments which contain somewhat stereoregular blocks of HB. The weight fraction of stereoregular blocks of HB should be decreased in the acetone-soluble fractions of polymers **18–22**. This assumption is supported by the absence of both melting and crystallization thermal transitions in the acetone-soluble fraction of polymer **19**, while these thermal transitions were observed for the AcAc-treated sample of polymer **19**. The possibility that highly stereoregular copolymer chain segments give rise to the thermal transitions observed by DSC cannot be excluded. This latter explanation, though, is unlikely due to the very different structure of the comonomer pendant groups.

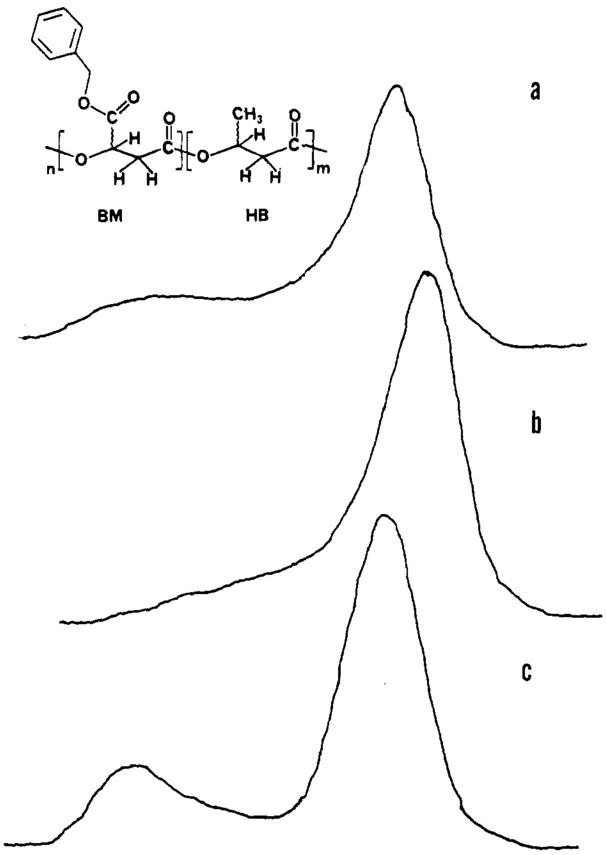

Figure 7. GPC chromatograms drawn so that equivalent elution volumes overlap: (a) polymer **19**, unfractionated, after AcAc treatment; (b) polymer **19**, the acetone-soluble fraction; (c) polymer **17**, unfractionated, after AcAc treatment.

In parts a and b of Figure 7 are shown the GPC chromatographs for polymer **19**, unfractionated after AcAc treatment and the acetone-soluble fraction, respectively. By comparison of these two chromatograms, we see that the acetone-soluble fraction contains lower molecular weight material with a corresponding decrease in the high molecular weight tail. These two GPC chromatograms are representative for what was observed from the chromatograms of polymers **18–22**. The acetone-soluble fractions of polymers **19–22** have values for $\bar{M}_w$ ranging from 70000 to 350000 and polydispersity $\bar{M}_w/\bar{M}_n$ values from 4.3 to 19 (see Table VI).

An investigation by ^{13}C NMR of the samples obtained from the attempted copolymerizations was carried out. The ^{13}C NMR spectrum of polymer **21** (the acetone-soluble fraction) is shown in Figure 8. Expanded regions of the ^{13}C NMR spectrum from Figure 8 are displayed in Figure 9. In Figure 9b is shown an expansion of the methylene regions for BM and HB monomer units along with peak assignments for the comonomer diad sequences shown in Figure 10. These assignments were made by observation of the ^{13}C NMR spectra of the sample from Figure 8 mixed with PBML and natural origin P([*R*]-HB). In the first case, there was an increase in the upfield signal in Figure 9b, allowing the assignment of the BM–BM comonomer diad sequence, while in the latter mixing experiment the downfield signal increased in intensity, allowing the assignment of the HB–HB comonomer diad sequence. Assignment of BM–HB and HB–BM comonomer diad sequences was made assuming a relatively small chemical shift change between BM–BM and BM–HB and between HB–HB and HB–BM (see Figure 9b). The above assign-

Table VII
Experimental[a] and Calculated[b] Comonomer Diad Fractions for Poly([*R*,*S*]-benzyl malolactonate-*co*-[*R*,*S*]-butyrolactone), P(BM-*co*-HB)

		diad sequence			
polym	polym comp[c] HB:BM	HB-HB obsd[a] (calcd)[b]	HB-BM obsd[a] (calcd)[b]	BM-HB obsd[a] (calcd)[b]	BM-BM obsd[a] (calcd)[b]
17, after AcAc[d] treatment	44:56	0.38 (0.19)	0.06 (0.25)	0.12 (0.25)	0.44 (0.31)
18, after AcAc[d] treatment	54:46	0.43 (0.29)	0.11 (0.25)	0.17 (0.25)	0.29 (0.21)
19, acetone-sol fractn	44:56	0.27 (0.19)	0.16 (0.25)	0.20 (0.25)	0.36 (0.31)
20, acetone-sol fractn	32:68	0.18 (0.10)	0.14 (0.22)	0.23 (0.22)	0.45 (0.46)
20, acetone-insol fractn	49:51	0.40 (0.24)	0.09 (0.25)	0.19 (0.25)	0.32 (0.26)
22, after AcAc[d] treatment	28:72	0.14 (0.08)	0.14 (0.20)	0.14 (0.20)	0.58 (0.52)
22, acetone-sol fractn	28:72	0.14 (0.08)	0.14 (0.20)	0.23 (0.20)	0.49 (0.52)

[a] Relative peak areas of the methylene carbon (2) for the comonomer diad sequences described in Figures 9b and 10. [b] Calculated values from eq 1–3, assuming a perfectly random distribution. [c] Data presented in mole percent of comonomer units. [d] AcAc is acetylacetone.

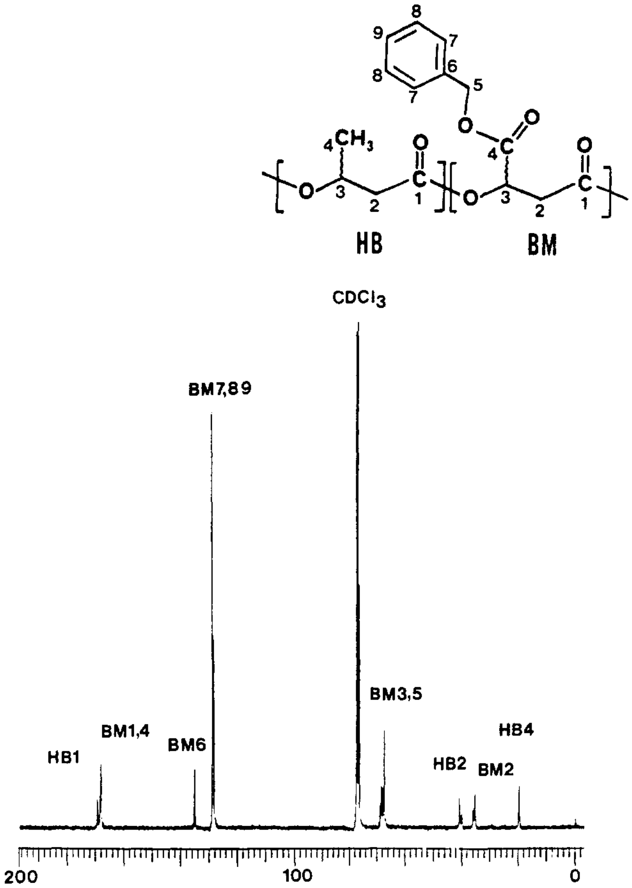

Figure 8. 75.4-MHz ^{13}C NMR spectrum, recorded at 25 °C in $CDCl_3$, of the acetone-soluble fraction of polymer **19**.

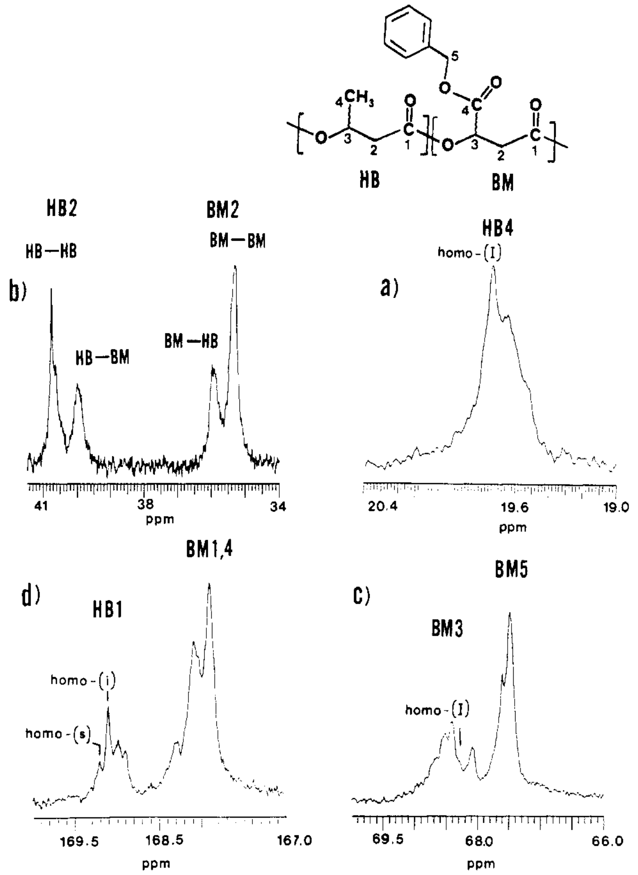

Figure 9. Expanded regions of the ^{13}C NMR spectrum from Figure 8 showing (a) the methyl carbons 4 of HB; (b) the methylene carbons 2 of both HB and BM; (c) the methine and benzyl carbons, C-3 and C-5 respectively, of BM; and (d) the carbonyl carbon 1 of HB along with the carbonyl carbons 1 and 4 of BM.

ments allowed quantitation of the relative fractions of comonomer diad sequences shown in Figure 10. If one assumes a Bernoullian or random statistical copolymerization of BML and BL, the calculation of the comonomer diad fractions above can be carried out with knowledge of F_{HB} (defined as the mole fraction of HB units in the polymer) by using the following equations:[27]

$$[HB\text{-}HB] = F_{HB}^2 \tag{1}$$

$$[HB\text{-}BM] = [BM\text{-}HB] = F_{HB}(1 - F_{HB}) \tag{2}$$

$$[BM\text{-}BM] = (1 - F_{HB})^2 \tag{3}$$

The value of F_{HB} was determined by ^{1}H NMR spectroscopy.[25] Table VII lists the calculated comonomer diad sequence fractions, using eq 1–3 along with observed values for selected samples from Table V. The observed comonomer diad fractions were obtained by cutting and weighing the respective comonomer diad peaks for the BM2 and HB2 signals. The total areas obtained as described above for BM2 comonomer diads relative to HB2 comonomer diads were corrected by using the monomer composition data from ^{1}H NMR spectrometer integration.[25]

Comparison of the observed and calculated values in Table VII for the acetone-soluble fractions of polymers **19**, **20**, and **22** shows excellent agreement for BM–HB and BM–BM diads but poorer agreement for HB–BM and HB–HB diads. It can be concluded from these results that when a BM monomer unit is at the growing chain terminus, it will add with a probability approaching equality a BM or HB unit, but when an HB unit is at the growing chain terminus, it will preferably add another HB unit (the HB–HB diad fraction observed was considerably larger

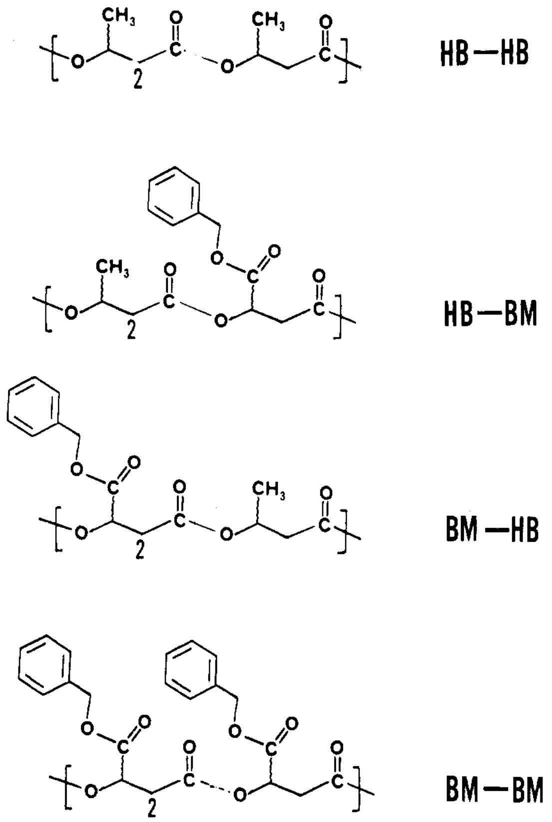

Figure 10. Comonomer diad sequences for P(BM-*co*-HB) are shown, where the methylene carbon 2 is assigned, which we observed by ^{13}C NMR in Figure 9b.

than the calculated value). The observed and calculated comonomer diad fractions showed better agreement for the acetone-soluble fractions of polymers **22** and **24** than for their corresponding acetone-insoluble fraction and unfractionated AcAc-treated sample, respectively (see Table VII).

It is clear from the results presented above that copolymers of BM and HB monomer units may be formed, using catalysts EAO and MAO, in yields of approximately 20% after fractionation of acetone-soluble copolymer.

Attempts to copolymerize BML and BL by using the in situ catalyst preparation (see Experimental Section) proved much less successful. The GPC chromatograms of polymers **16–19**, unfractionated, after AcAc treatment, all showed bimodal distributions where the high and low molecular weight peaks were both approximately bell shaped. This result suggests extreme sample heterogeneity. The GPC of polymer **17**, unfractionated, after AcAc treatment, is shown in Figure 7c and demonstrates these characteristics. Analysis of polymer **17**, unfractionated, after AcAc treatment by ^{13}C NMR, showed that this sample consists of mainly HB–HB and BM–BM diads as is clearly seen by comparison of the observed and calculated comonomer diad fractions (see Table VII).

The in situ catalyst preparation (see Experimental Section) was therefore considered to be a poor catalyst for the synthesis of P(BM-*co*-HB) copolyesters which approach a statistically random distribution.

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Registry No. [*R*,*S*]-BL (homopolymer), 36521-53-6; [*R*,*S*]-BL (SRU), 35038-21-2; [*R*,*S*]-BML (homopolymer), 88849-68-7; [*R*,*S*]-BML (SRU), 88849-76-7; [*R*,*S*]-((BML)(BL)) (copolymer), 115227-39-9.

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Chain Propagation/Step Propagation Polymerization. 4. A DSC Study of Phase Separation in Regular Poly(oxyethylene)-*block*-Poly(pivalolactone) Telechelomers

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ABSTRACT: Anionic chain polymerization coupled with step polymerization is being used to prepare segmented copolymers containing soft poly(oxyethylene) (POE) and hard poly(pivalolactone) (PPVL) segments each having narrow molecular weight distributions (MWD). The chain polymerization results in formation of a telechelomer (a high molecular weight monomer capable of self-polymerization via a step propagation mechanism) wherein the telechelomer contains one POE segment and one PPVL segment. The phase separation of four telechelomers containing 17, 33, 37, and 54 wt % poly(pivalolactone) was investigated by using differential scanning calorimetry (DSC). The crystalline melting temperature (T_m) of the segments was used as a criterion for phase separation, and the approach used was first to adjust the T_m's to take into account such variables as molecular weight, end groups, and copolymerization and then to observe the variation of T_m's with increasing poly(pivalolactone) content. It was found that both segments are phase mixed to some extent.

Introduction

The field of multiphase segmented copolymers, although some 30-years old, remains quite active[1,2] in part due to the possibility of obtaining a variety of useful meterials ranging from impact-resistant plastics to elastomers. Poly(urethane ethers) and particularly poly(ester ethers) lend themselves to melt extrusion such that these polymers can be shaped easily, an extremely valuable feature. As true elastomers, however, these copolymers lack the physical properties that are demanded in many applications, particularly when they are melt processed.[3] Specifically, the elastic properties that are deficient in melt-extruded segmented copolymers are stress and recovery related, like immediate elastic recovery (often less than 95%), stress decay (often greater than 15%), and compression set (more than 10%). These properties are direct manifestations of the inefficiency of the physical cross-links in the copolymer, which in turn is a function of how well the phase separation in the copolymer is achieved.

Phase mixing can be attributed partly to the irregularity of the copolymer chain. In the case of poly(ester ether) copolymers, synthesized by normal step polymerization reactions, the hard segment has a polydispersity ratio approaching 2, and this distribution of chain lengths within the hard segment adversely affects phase separation.[4] Droescher and co-workers support the hypothesis that high regularity within segments, i.e., monodispersity within each segment, leads to enhanced phase separation and crystallization phenomena.[5] Their investigations involved monodisperse aromatic poly(ester ether) copolymers synthesized in a multistep scheme of nucleophilic substitution reactions.[5] Inoue and co-workers,[6] also have prepared low molecular weight versions of poly(ester ether) block copolymers having monodisperse segments using porphyrin catalysts. The molecular weights of these polymers are about 5000.

Our goal is to synthesize highly regular poly(ester ether) segmented copolymers, to investigate their phase separation behavior, and to see how the phase separation behavior affects mechanical and surface properties. Our strategy involves synthesizing a highly regular telechelomer[7] and then converting it to high molecular weight polymer. In order to obtain narrow molecular weight distributions for both segments, the telechelomer has been prepared by anionic polymerization; the telechelomer then can be converted to high molecular weight copolymer by step polymerization. Figure 1 shows this strategy applied to the synthesis of poly(oxyethylene-*co*-pivalolactone) segmented copolymers. Since the soft poly(oxyethylene) (POE) segment is incompatible with the hard poly(pivalolactone) (PPVL) segment, these regular copolymers will exhibit enhanced phase separation. A high molecular weight poly(pivalolactone-*b*-dimethylsiloxane) diblock copolymer has been prepared, and its phase separation behavior has been investigated in the past.[8]

Differential scanning calorimetry (DSC) has been used to study phase separation in a number of multiphase polymer systems.[9] A few excellent quantitative DSC investigations appeared in the literature,[10,11] and many other qualitative investigations[12] were quite adequate to determine the presence of phase mixing. In the qualitative studies, the phase mixing was determined by monitoring the glass transition temperature (T_g) of the soft segment (which was completely amorphous) and the crystalline melting point (T_m) of the hard segment. An increase in T_g of the soft segment and a decrease in T_m of the hard segment, with increasing hard segment content in the copolymer, indicated phase mixing. When the soft segment

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