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Synthesis and Polymerization of Racemic and Optically Active β-Monosubstituted β-Propiolactones

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ABSTRACT: The reaction of ketene with chloral and 2,2-dichloropropanal leads, respectively, to the synthesis of β-(trichloromethyl)-β-propiolactone (CCl_3-PL) and β-(1,1-dichloroethyl)-β-propiolactone (CH_3CCl_2-PL). Both monomers were prepared in the optically active form with enantiomeric excesses of 100% and 95% for CCl_3-PL and CH_3CCl_2-PL, respectively, using quinidine as a catalyst, and an enantiomeric excess of 100% for CH_3CCl_2-PL using brucine as a catalyst. Both monomers were also prepared in the racemic form. Enantiomeric excesses were determined from optical rotation (CCl_3-PL) or ^{1}H NMR spectroscopy (CH_3CCl_2-PL and CCl_3-PL) after complexation of the lactone with a europium chiral shift reagent. Polymerization was carried out in bulk and toluene solution, under vacuum, using mainly triethylaluminum as initiator. Solution characterization of the polymers was conducted by viscometry, osmometry, and gel permeation chromatography. The polymers prepared from optically active monomers are less soluble in organic solvents than those prepared from racemic monomers. In addition, the former polymers are crystalline and exhibit a high-temperature melting peak (T_m = 275 °C for poly(CCl_3-PL) and 235 °C for poly(CH_3CCl_2-PL)) whereas the latter polymers are amorphous and decompose at about 200 °C.

Introduction

The synthesis of high optical purity β-lactones and polylactones is a difficult task. However, interesting results have been obtained with α-substituted β-propiolactones. For example, D'Hondt and Lenz[1] and Carrière and Eisenbach[2] prepared α-phenyl-α-ethyl-β-propiolactones having enantiomeric excesses of 80% and 95%, respectively. They showed that the polymers synthesized from these optically active monomers have a melting point of about 130 °C higher than the melting point of the polymer prepared from the corresponding racemic monomer.

More recently, Grenier et al. have prepared optically active poly(α-methyl-α-ethyl-β-propiolactones) from monomers having enantiomeric excesses of 97% and 99%.[3] They have shown that these polymers have higher equilibrium melting points, enthalpies of fusion, and crystallization rates than those of the corresponding racemic polymers.[4] Moreover, the change in properties is not a linear function of the enantiomeric excess of the polymer: most properties remain almost constant for enantiomeric excesses between 0% and 60%; between 60% and 100%, they increase linearly. This general behavior of the optically active α-substituted poly(β-propiolactones) is therefore similar to that of the optically active polyamides, prepared by Schmidt[5] from β-lactams containing one or two asymmetric centers.

With β-substituted β-propiolactones, the results obtained so far are less convincing. An interesting[6,7] attempt was reported by Agostini et al., who prepared D-(+)-β-butyrolactone from β-bromobutyric acid having an enantiomeric excess of 90%. Unfortunately, some racemization occurred during the closure of the lactone whose enantiomeric excess dropped to 73%. From this lactone, poly(β-methyl-β-propiolactone), also called poly(β-hydroxybutyrate) (PHB), was synthesized and compared with the naturally occurring, high optical purity PHB. The enantiomeric excess of the PHB could not be measured but it is presumably low. An attempt to prepare optically active PHB's, using stereoselective[8] initiators, led to polymers with moderate enantiomeric enrichments.

A series of β-monosubstituted poly(β-propiolactones) was prepared from the corresponding racemic monomers by using achiral organoaluminum or organozinc initiators (substituents = methyl, ethyl, isopropyl, *tert*-butyl, chloromethyl, dichloromethyl, trichloromethyl),[9-11] solid-state polymerization upon γ- and X-ray irradiation (substituents = dichloromethyl and trichloromethyl),[12] and cationic polymerization (substituent = trichloromethyl).[13] After fractionation, a crystalline and tactic fraction is usually obtained.[14]

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The reaction between ketene and aldehydes normally leads to racemic β-lactones.[9-11,15] When chiral bases are used, optically active lactones have been obtained.[16-18] Wynberg and Staring[18] have recently reported details for the preparation of β-(trichloromethyl)-β-propiolactone (CCl_3-PL) from the addition of ketene to chloral in 100% optical purity using a chiral base.

We have repeated this preparation, and, using similar conditions, we have also prepared β-(1,1-dichloroethyl)-β-propiolactone (CH_3CCl_2-PL) in excellent optical yields. These two monomers were polymerized with various initiators: triethylaluminum, triethylaluminum/H_2O, aluminum chloride, and $ZnEt_2$/(*R*)-(−)-3,3-dimethyl-1,2-butanediol. The polymers were characterized by viscometry, osmometry, gel permeation chromatography, X-ray scattering, and differential scanning calorimetry.

Experimental Section

Materials. All chemicals used in this study were obtained commercially, except ketene and 2,2-dichloropropanal.

Triethylamine and chloral were purified by distillation; quinidine was purified by successive crystallizations in benzene; cinchonine was purified by sublimation at 200 °C under high vacuum.

Gaseous ketene was prepared by pyrolysis of acetone vapors.[19] Residual acetone vapors were eliminated with an acetonitrile–dry ice trap, maintained at −40 °C. The ketene yield was determined by the method described by Vogel.[19] Our generator produced 0.05 mol/h.

In some instances, it was preferred to prepare the ketene in situ by reacting acetyl chloride with triethylamine.[16] This method is safer than the previous one, ketene being a highly toxic gas, but it cannot be used to prepare the optically active lactones.

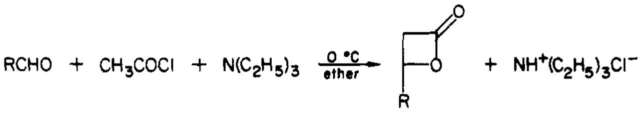
2,2-Dichloropropanal was prepared by using the method described by Dick.[20]

Methods. In order to verify the purity of the chemicals used, the following apparatuses were used: a Beckman IR-4250 spectrophotometer and Varian EM-360A and Bruker HX-90 ^{1}H NMR spectrometers. Carl Zeiss and Perkin-Elmer P-241 polarimeters were used for measurements of optical rotation; Ubbelohde capillary viscometers were used for intrinsic viscosity measurements, in toluene or chlorobenzene at 24.0 ± 0.1 °C.

For molecular weight measurements, we used a Mechrolab 501 osmometer and a Waters, Model 502, GPC apparatus equipped with a Data Module and μ-Styragel columns. In the osmometry experiments, the polymers prepared from racemic monomers were dissolved in toluene, and the measurements were done at 24.0 ± 0.1 °C. In the GPC experiments, tetrahydrofuran was the solvent and the temperature was 27 °C. Low-polydispersity polystyrene standards were used for calibration.

A Philips generator, equipped with a Cu target and a Warhus–Statton camera,[21] was used for X-ray measurements. The incident radiation was nickel filtered. A Perkin-Elmer DSC-4 apparatus, equipped with a 3600 TADS computer, was used for calorimetry measurements. The apparatus was calibrated with indium, and the measurements were run at a heating rate of 20 °C/min.

Synthesis of *rac*-β-(Trichloromethyl)-β-propiolactone (CCl_3-PL). The reaction was carried out by following eq 1 where R = CCl_3:

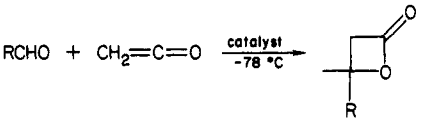


(1)

In a three-necked round-bottom flask equipped with a thermometer, a dropping funnel, a condenser and a magnetic stirrer, 14.7 g (0.1 mol) of chloral and 15.8 g (0.2 mol) of acetyl chloride were dissolved in 100 mL of anhydrous ether. A total of 20.2 g (0.2 mol) of triethylamine, dissolved in 50 mL of anhydrous ether, was added dropwise in order to maintain the temperature of the mixture between 0 and 10 °C. The reacting mixture was stirred for 1 h and vacuum filtered with a Büchner funnel to eliminate the ammonium salt. The solution was dried over $MgSO_4$. After removal of $MgSO_4$ by filtration, the ether was evaporated and the lactone distilled under vacuum. A total of 17.5 g of lactone (92%) was recovered which crystallized spontaneously. The lactone was recrystallized in hexane.

CCl_3-PL: T_b = 64 °C/0.1 mmHg; T_m = 39 °C; IR (KBr), ν_{max} 1855 cm^{-1} (C═O); ^{1}H NMR (90 MHz, $CDCl_3$) δ_1 3.46 (dd, J_{ab} = 16 Hz, J_{ac} = 4.5 Hz, CH_2), δ_2 3.68 (dd, J_{ab} = 16 Hz, J_{bc} = 5 Hz, CH_2), δ_3 4.88 (dd, J_{ac} = 4.5 Hz, J_{bc} = 5 Hz, CH).

Synthesis of Optically Active β-(Trichloromethyl)-β-propiolactone (CCl_3-PL). The reaction was carried out by following eq 2, where R = CCl_3



(2)

according to the method described by Wynberg and Staring.[18] Quinidine was used as a chiral base catalyst. The lactone was recrystallized in methylcyclohexane (yield 89%).

CCl_3-PL: T_b = 120 °C/0.5 mmHg; T_m = 51–52 °C; $[\alpha]^{20}_{578}$ −15.3° (lit.[18] $[\alpha]^{20}_{578}$ −15.3° (*c* 1, cyclohexane), ee 98%); the IR and ^{1}H NMR spectra are identical with those of the racemic CCl_3-PL.

Synthesis of *rac*-β-(1,1-Dichloroethyl)-β-propiolactone (CH_3CCl_2-PL). The reaction was carried out by following eq 1 where R = CH_3CCl_2. The method already described for the racemic CCl_3-PL was followed (yield 5%).

CH_3CCl_2-PL: T_b = 90–92 °C/7 mmHg; T_m = 30–32 °C; IR (CCl_4), ν_{max} 1863 cm^{-1} (C═O); ^{1}H NMR (90 MHz, $CDCl_3$) δ_1 2.24 (s, CH_3), δ_2 3.65 (d, *J* = 5 Hz, CH_2), δ_3 4.75 (t, *J* = 5 Hz, CH).

Synthesis of Optically Active β-(1,1-Dichloroethyl)-β-propiolactone (CH_3CCl_2-PL). The reaction was carried out by following eq 2 where R = CH_3CCl_2 and by using quinidine or brucine as the chiral base catalyst. The method already described for the optically active CCl_3-PL was followed[18] (yield 42% and 15% using quinidine and brucine, respectively).

CH_3CCl_2-PL: T_b = 90 °C/7 mmHg; T_m = 49–50 °C; $[\alpha]^{27}_D$ 17.5° (*c* 1, cyclohexane) with the quinidine catalyst and $[\alpha]^{27}_D$ −18.5° (*c* 1, cyclohexane) with the brucine catalyst; the IR and ^{1}H NMR spectra are identical with those of the racemic CH_3CCl_2-PL.

Polymerization. The polymerization of the racemic and optically active monomers using triethylaluminum as initiator was conducted in anhydrous toluene, under vacuum, in a sealed tube at 55 °C. The monomer solution was degassed by successive freeze–pump–thaw cycles. The initiator was introduced at −78 °C, under an argon current, using a microsyringe. The mixture was again degassed and the tube sealed. After the polymerization, the tube was opened and chloroform added. The resulting solution or suspension (the polymers prepared from optically active monomers are insoluble in chloroform) was poured in pentane and stirred for 30 min. The resulting polymer suspension was centrifuged at 10 000 rpm and 0 °C for 10 min, and the polymer was dried before its characterization.

Other polymerizations were carried out in high-vacuum-sealed apparatuses. $AlCl_3$ was sublimated under vacuum. The $AlEt_3$/H_2O and $ZnEt_2$/(*R*)-(−)-DMBD ((*R*)-(−)-3,3-dimethyl-1,2-butanediol) initiators were prepared by reacting, in toluene and at room temperature, the organometallic derivative with the corresponding hydroxyl compound in a 1/1 ratio. After 2 h of reaction, the volatile species were removed and the initiator was dried 2 h at room temperature before adding the monomer. Polymerizations were carried out in bulk at 60 °C. The resulting polymers were dissolved in chloroform and poured in methanol. The resulting polymer suspension was centrifuged and dried before its characterization.

Results and Discussion

Monomer Synthesis. Table I lists the monomers which have been synthesized and their yields. Racemic lactones were obtained by using triethylamine as a catalyst, optically active CCl_3-PL using quinidine and optically active CH_3CCl_2-PL using quinidine and brucine. The yields of CCl_3-PL are excellent in both cases; the yields of CH_3CCl_2-PL are lower, particularly with triethylamine.

Table I
Synthesis of Racemic and Optically Active Monomers

	CCl_3-PL			CH_3CCl_2-PL		
catalyst	yield, %	$[\alpha]^{20}_{578}$,[a] deg	ee, %	yield, %	$[\alpha]^{27}_{D}$,[a] deg	ee, %
quinidine	89	−15.3	98 (*S*)	42	17.5	95
brucine			68[b] (*R*)	15	−18.5	100
cinchonine[b]		−13.1	84 (*S*)			
quinine[b]		11.9	76 (*R*)			
$N(C_2H_5)_3$	92	0	0	5	0	0

[a] Measured in cyclohexane, *c* 1. [b] Taken from ref 18.

Optical Purity. Table I also gives the specific rotation and the enantiomeric excess (ee) of the lactones. The enantiomeric excess is defined by

$$ee = 100|[R] - [S]|/([R] + [S]) \qquad (3)$$

where [*R*] and [*S*] are the amounts of each isomer in the mixture and ee is expressed in percent.

For CCl_3-PL, we have calculated the enantiomeric excess from

$$ee = 100[\alpha]/[\alpha_0] \qquad (4)$$

where $[\alpha]$ is the specific rotation of the mixture and $[\alpha_0]$ that of the pure isomer. Wynberg and Staring have determined an $[\alpha_0]^{20}_{578}$ of 15.6° (*c* 1, cyclohexane) for CCl_3-PL.[18] Our $[\alpha]$ value leads to an enantiomeric excess of 98% for the CCl_3-PL prepared by using the quinidine catalyst which is in agreement with the results reported by these authors using the same catalyst. They also reported an *S* configuration for the levorotatory lactone, as indicated in Table I. Some additional results obtained by Wynberg and Staring, using brucine, cinchonine, and quinine catalysts, are also included in Table I for comparison purposes.

For CH_3CCl_2-PL, $[\alpha_0]$ is not known and eq 4 could not be used readily to calculate the enantiomeric excess. Calorimetric methods such as those described by Jacques, Collet, and Wilen[22] were tried on similar lactones but found to be of insufficient accuracy.[23]

We have then attempted to form a diastereoisomer complex between CH_3CCl_2-PL and (*S*)-2,2,2-trifluoro(9-anthryl)-1-ethanol as suggested by Pirkle et al., since it gave satisfactory results with other substituted β-propiolactones.[23,24] Unfortunately, the 90-MHz ^1H NMR spectra of these complexes could not be resolved.

However, a satisfactory answer was obtained by forming a complex between CH_3CCl_2-PL and a europium shift reagent, tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III), with a 90-MHz ^1H NMR apparatus. The NMR spectra of the racemic CH_3CCl_2-PL, of the racemic CH_3CCl_2-PL complexed with the europium reagent, and of the optically active CH_3CCl_2-PL prepared with the brucine catalyst and complexed with the europium reagent are shown in Figure 1. All spectra were taken in CCl_4, at a molar concentration of 0.7, and with 0.32 equiv of the europium reagent. It is seen that the methyl group of CH_3CCl_2-PL appears at 2.24 ppm without the europium reagent and is shifted to about 3 ppm in the presence of the europium reagent. Moreover, the 3 ppm signal appears as a doublet, with peaks separated by 0.067 ppm and corresponding to the two isomers. For the optically active CH_3CCl_2-PL, within experimental error, only one peak is observed which may indicate that this monomer is optically pure. Using eq 3 and assuming that the [*R*] and [*S*] values are given by the area under the methyl NMR peaks allowed an enantiomeric excess of 100% to be calculated (Table I). Using eq 4 and $[\alpha_0]$ = 18.5° allowed an enantiomeric excess of 95% to be calculated for the CH_3CCl_2-PL prepared with the quinidine catalyst (Table I). One should note that the NMR spectra of the lactone–europium complex do not allow the determination of the configuration of the lactone since a small variation of the concentration of the lactone and/or of the shift reagent usually leads to an important change of the NMR chemical shifts.

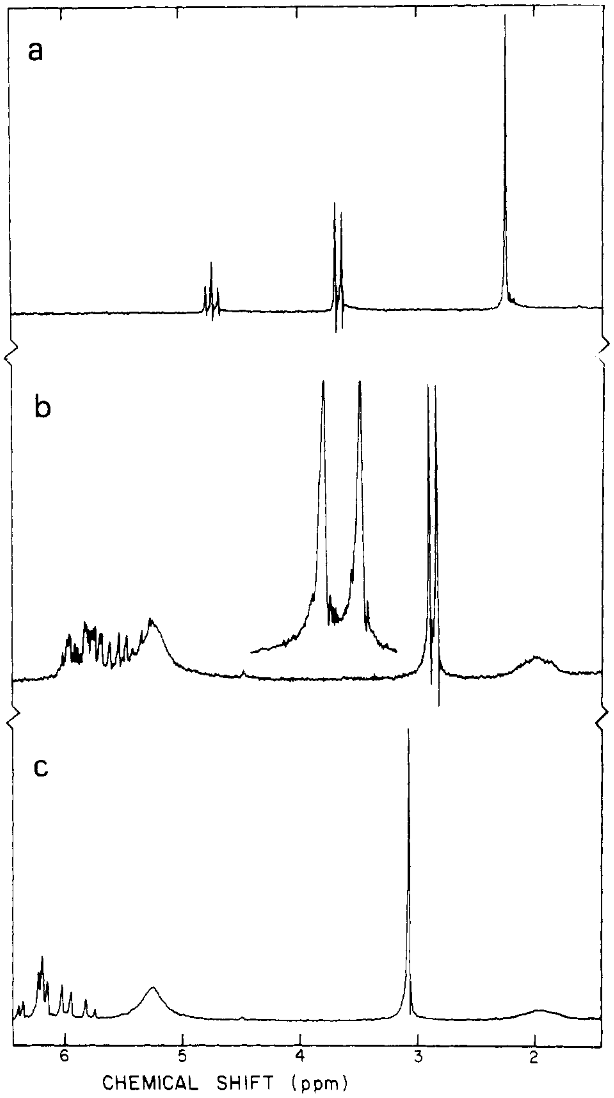


Figure 1. 90-MHz ^1H NMR spectra: (a) *rac*-CH_3CCl_2-PL; (b) *rac*-CH_3CCl_2-PL complexed with the europium chiral reagent; (c) optically active CH_3CCl_2-PL prepared with the brucine catalyst and complexed with the europium chiral reagent.

Table I indicates that using a quinidine catalyst allows a dextrorotatory CH_3CCl_2-PL and a levorotatory CCl_3-PL to be synthesized. In contrast, using the brucine catalyst, one obtains a levorotatory CH_3CCl_2-PL. In each case, high enantiomeric excesses are obtained. However, cinchonine and quinine proved to be less effective with CCl_3-PL[18] and

Table II
Polymerization of Racemic and Optically Active CCl_3-PL and CH_3CCl_2-PL in Toluene, at 55 °C, Using $AlEt_3$ as Initiator

monomer	expt	monomer ee, %	monomer concn, M	[init]/[monomer], 10^2	polymn time, days	yield, %	[η], dL/g
CCl_3-PL	58-J	98	10.6	5.4	7	90	0.85[a]
	83-Z	98	11.7	1.3	7	50	1.00[a]
	59-N	0	11.7	5.4	7	65	0.074
	68-Q	0	5.9	4.5	6	70	0.068
	66-P	0	10.6	2.5	7	75	
	72-S	0	5.9	2.3	8	75	0.094
	80-T	0	11.6	2.0	7	65	0.095
	81-U	0	12.1	1.6	7	70	0.105
	81-X	0	11.1	1.4	7	60	0.126
	81-W	0	11.1	1.0	7	60	0.115 (0.105)[a]
	81-V	0	11.5	0.7	13	5	
CH_3CCl_2-PL	101-C	0	5.3	1.8	31	40	0.044
	102-D	0	6.3	2.8	9	35	0.032
	97-A	95	6.2	1.8	7	60	0.095[a]
	100-B	95	4.9	1.0	28	80	0.51[a]

[a] In chlorobenzene.

Table III
Polymerization of Racemic and Optically Active CCl_3-PL Using Different Initiators

expt	monomer ee, %	init	monomer concn in toluene, M	[init]/[monomer], 10^2	polymn time, days	polymn temp, °C	yield, %	M_n[b] × 10^{-3}
10-AL	0	$AlCl_3$	bulk	0.6	1	60	32.5	10.8
11-AL	0	$AlCl_3$	5.3	0.15	7	22	45	8.1
12-AL	0	$AlEt_3/H_2O$ (1/1)	bulk	4.0	3	60	72.6	40
81-W	0	$AlEt_3$	11.1	1.0	7	55	60	14[c]
13-AL	0	$ZnEt_2$/(*R*)-(−)-DMBD[a] (1/1)	bulk	8.0	1	60	18	17
14-AL	95	$AlEt_3/H_2O$ (1/1)	bulk	8.1	1	60	61	
83-Z	98	$AlEt_3$	11.7	1.3	7	55	50	
56-H	0	AcOK/18-crown-6	5.3	2.0	25	55	0	
57-I	98	AcOK/18-crown-6	5.3	6.0	20	55	0	

[a] DMBD = 3,3-dimethyl-1,2-butanediol. [b] Osmometry analysis, in toluene. [c] GPC analysis (relative to polystyrene standards).

with disubstituted β-propiolactones.[23] It is believed that the efficiency of the chiral base catalysts depends strongly on the nature of the chiral base and of the aldehyde or ketone used in the reaction. The exact nature of the complex formed, however, is unknown at the present time.

Polymerization. Table II gives the experimental conditions used in the polymerization of racemic and optically active CCl_3-PL and CH_3CCl_2-PL with triethylaluminum as initiator. It indicates that four polymers can be synthesized in good yields with triethylaluminum. The yields are, however, slightly larger with the optically active monomers and slightly larger with CCl_3-PL as compared to those of CH_3CCl_2-PL.

In addition, under the polymerization conditions used, the monomer concentration and the ratio of the initiator to monomer concentration seem to have little influence upon the yields of the polymers and their intrinsic viscosity.

The intrinsic viscosities of the poly(CCl_3-PL)'s prepared from optically active monomers are both of the order of 1.0 dL/g whereas those of the poly(CCl_3-PL)'s prepared from racemic monomers are of the order of 0.1 dL/g. This difference is very significant and it does not depend upon the use of different solvents for the measurement of the viscosity of both series of polymers. Indeed, for sample 81-W, intrinsic viscosities of 0.115 and 0.105 dL/g were measured in toluene and chlorobenzene, respectively. A similar trend was observed in the measurement of the intrinsic viscosity of poly(CH_3CCl_2-PL): values of the order of 0.04 dL/g were determined for the polymers prepared from racemic monomers and larger values were obtained for the others.

Important differences in solubility were also observed between the polylactones prepared from racemic and those prepared from optically active monomers. The poly(CCl_3-PL)'s prepared from optically active monomers are insoluble in toluene, tetrahydrofuran, and chloroform whereas those prepared from racemic monomers are soluble. This difference may be due in part to the higher molecular weights of the polymers prepared from optically active monomers, as indicated by their higher intrinsic viscosities, and in part to the stereoregularity of their chains.

The results obtained with various initiators ($AlCl_3$, $AlEt_3/H_2O$, $ZnEt_2$/(*R*)-(−)-DMBD) are given in Table III. Two runs made with $AlEt_3$ are included for comparison purposes. The initiator system $AlEt_3/H_2O$ gives polymers with higher molecular weights than those of the other initiators investigated. The stereoelective initiator $ZnEt_2$/(*R*)-(−)DMBD leads to an optically active polymer ($[\alpha]^{25}_D$ −1°, $CHCl_3$, *c* 1) whose optical purity is unknown.

Experiments 56-H and 57-I were conducted with an anionic initiator: potassium acetate/dicyclohexyl-18-crown-6. In these two cases, the initiator was added to the monomer solution at room temperature and no polymer was formed after 20 and 25 days of reaction.

Molecular Weight Analysis. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of most of the polylactones prepared in Table II from racemic monomers are reported in Table IV. For poly(CCl_3-PL), M_n is of the order of 12 kg/mol and M_w of the order of 15 kg/mol. For poly(CH_3CCl_2-PL), the numbers are slightly lower. In both cases, there is a good correlation between the intrinsic viscosity and the molecular weight, and the polydispersity index is low.

The molecular weights of the polylactones prepared from optically active monomers could not be determined because these polymers were not soluble in the solvents which

Table IV
Molecular Weight of Poly(CCl_3-PL) and Poly(CH_3CCl_2-PL) Prepared from Racemic Monomers by Gel Permeation Chromatography[a]

monomer	expt	[η], dL/g	M_w × 10^{-3}	M_n × 10^{-3}	M_w/M_n
CCl_3-PL	68-Q	0.068	11.5	7	1.6
	66-P		13	9	1.4
	72-S	0.094	16	14	1.1
	80-T	0.095	15	12	1.2
	81-U	0.105	15	12	1.3
	81-X	0.126	15	13	1.2
	81-W	0.115	16	14	1.2
CH_3CCl_2-PL	101-C	0.044	10	7	1.3
	102-D	0.032	5	4	1.3

[a] Relative to polystyrene standards.

Table V
X-ray Diffraction Data for Selected Poly(CCl_3-PL) and Poly(CH_3CCl_2-PL)

		racemic[a]		optically active[a]	
monomer	ring no.	2θ	intensity[b]	2θ	intensity[b]
CCl_3-PL	1	4.6	m	5.0	m
	2			7.6	w
	3			17.6	w
CH_3CCl_2-PL	1	4.6	m	4.8	m
	2			7.5	w
	3			17.7	vw

[a] Analysis of the polymers prepared from racemic and optically active monomers. [b] m = medium; w = weak; vw = very weak.

are compatible with the columns of the GPC apparatus.

X-ray Diffraction Measurements. Table V summarizes the X-ray diffraction measurements which were performed. For poly(CCl_3-PL), a sample (81-X) prepared from a racemic monomer was compared with a sample (58-J) prepared from an optically active monomer. Both samples have a diffraction pattern that contains a halo at $2\theta \simeq 4.8°$, characteristic of the amorphous fraction of the sample. The former sample does not contain any crystalline peak whereas the latter does. The former sample is then completely amorphous and the latter semicrystalline.

Similarly, a poly(CH_3CCl_2-PL) sample (101-C) prepared from a racemic monomer only gives rise to an amorphous halo and is an amorphous polymer; a poly(CH_3CCl_2-PL) sample (100-B) prepared from an optically active monomer exhibits several X-ray diffraction peaks and is a semicrystalline polymer.

Calorimetric Measurements. Table VI gives the glass transition temperature (T_g), the melting temperature (T_m) measured at the end of the melting peak, and in some instances, the decomposition temperature (T_d) measured at the beginning of the decomposition peak of most polylactones prepared in this study. It also gives the enthalpy of fusion (Δ*H*) when applicable.

Poly(CCl_3-PL)'s prepared from an optically active monomer exhibit T_g's of the order of 170 °C whereas those prepared from a racemic monomer have a T_g of 130–140 °C. The higher T_g's of the former samples are partly due to the higher molecular weights and partly due to the stereoregularity of the chain. A softening temperature of 135–141 °C was also reported by Iida et al.[10] for an amorphous poly(CCl_3-PL) prepared by using a stereospecific catalyst.

Similarly, the poly(CH_3CCl_2-PL)'s prepared from an optically active monomer exhibit a T_g of about 112 °C whereas those prepared from a racemic monomer have a T_g of about 102 °C.

All these T_g's are much larger than that of PHB which is also included in Table VI for comparison purposes. This significant increase is due to an increase in polarity and bulkiness of the substituents of the poly(CCl_3-PL) and poly(CH_3CCl_2-PL) samples.

In agreement with X-ray diffraction data, Table VI shows no T_m for the polylactones prepared from racemic monomers. They, however, decompose at 200 °C. In contrast, the polylactones prepared from optically active monomers have T_m's of 217–237 °C (poly(CH_3CCl_2-PL)) and 256–275 °C (poly(CCl_3-PL)), and, therefore, they are more thermally stable.

It is finally noticed that the enthalpies of fusion of all semicrystalline polymers are low as compared with that of PHB which can be considered as a typical semicrystalline polymer. These low values indicate low degrees of crystallinity, in agreement with X-ray results which gave weak patterns after long exposure times.

Discussion and Conclusion

One of the main objectives of this work was to verify the polymerizability of high optical purity β-monosubstituted β-propiolactones into stereoregular polymers. In order to do so, it was required to synthesize high optical purity monomers. The method described by Wynberg and Staring[18] was found to be as successful for CH_3CCl_2-PL as it was for CCl_3-PL. It also provides the opportunity to prepare both enantiomers with high optical purities. If these enantiomers can be converted into the corresponding polymers without racemization, racemate complexes similar to those which have been recently described with poly(α-methyl-α-ethyl-β-propiolactone) could be prepared.[28]

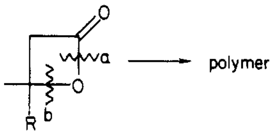
Table VI
Calorimetric Analysis of Poly(CCl_3-PL) and Poly(CH_3CCl_2-PL) Prepared from Racemic and Optically Active Monomers

monomer	expt	ee, %	T_g, °C	T_m, °C	T_d, °C	Δ*H*, J/g
CCl_3-PL	58-J	98	170	≃256	>256	7
	83-Z	98	175	≃275	>275	28
	59-N	0	139			
	66-P	0	132			
	68-Q	0	133			
	80-T	0	139			
	81-U	0	143			
	81-X	0	136		≃200	
	81-W	0	125		≃200	
	81-V	0	124		≃200	
CH_3CCl_2-PL	97-A	95	110	217	≃217	22
	100-B	95	115	237	≃237	29
	101-C	0	103		≃200	
	102-D	0	101		≃200	
CH_3-PL	PHB		4	180		88

The reaction of ketene with an aldehyde, however, requires an activation of the carbonyl group. This activation is usually done with electron-withdrawing groups such as halogens, esters, and ethers. In this work, we have used chlorine atoms for that purpose. It is doubtful that an alkyl substituent could give high optical purity lactones without activation of the carbonyl group even by using a chiral base catalyst.

The enantiomeric excess of the CH_3CCl_2-PL could be determined by NMR spectroscopy with the use of a europium chiral shift reagent. This method is simple and accurate. It led to an optical rotation value of 18.5° for the pure isomer.

The ring opening polymerization of β-substituted β-lactones can follow one of these two paths:



(5)

Path a is called an acyl cleavage and path b an alkyl cleavage. The polymerization initiator must be chosen to avoid racemization by using an optically active monomer.

For β-monosubstituted β-propiolactones, anionic, cationic, and organometallic initiators can be used; in fact, several of them have been reported in the literature with racemic monomers bearing alkyl and other substituents (including a trichloromethyl group).[6–11,13,17]

Anionic and cationic initiators could lead to an alkyl cleavage. This is welcomed for the polymerization of optically active α-substituted β-propiolactones[1–3] but unacceptable for the polymerization of optically active β-substituted β-propiolactones owing to racemization.

Organometallic initiators lead to an acyl cleavage of the β-lactones according to the mechanisms proposed by Shelton et al.[7] and Araki et al.[29] These mechanisms do not induce racemization and, therefore, triethylaluminum and its derivatives seemed to be appropriate initiators for the polymerization of CCl_3-PL and CH_3CCl_2-PL.

It is believed that the polylactones prepared from the optically active monomers exhibit a certain degree of stereoregularity. This statement could not be proved, as it was proved before for poly(α-methyl-α-ethyl-β-propiolactone) by using high-resolution NMR spectroscopy,[3] due to the insolubility of the polymers. Nevertheless, several experimental observations indicate that this statement cannot be entirely false: (a) the low solubility of these polymers, (b) their high values of T_g, (c) their X-ray diagrams, (d) their melting behavior, and (e) in fact that they have, in general, different properties from the corresponding polylactones prepared from racemic monomers. An atactic polymer bearing such large substituents would most likely be amorphous and highly soluble.

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