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Haloaldehyde Polymers. XXXVI. Optically Active Polychloral Initiated with Strong Chiral Anionic Initiators

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HALOALDEHYDE POLYMERS. XXXVI.* OPTICALLY ACTIVE POLYCHLORAL INITIATED WITH STRONG CHIRAL ANIONIC INITIATORS

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ABSTRACT

Polychloral was prepared in which the optical activity arose exclusively from macromolecular asymmetry (i.e., helical conformation). Strong chiral initiators used at 0.5 mol% concentration gave optically active polychloral. Maximum values of optical rotations for polychloral samples were obtained with the following initiators: lithium methyl (+)-hydroxidemandelate $[\alpha]_D^{25} = +3600°$, lithium methyl (-)-hydroxidemandelate $[\alpha]_D^{25} = -4670°$. A technique was developed to measure reliably the optical rotation of polychloral samples in film form.

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INTRODUCTION

Optically active synthetic polymers in which the optical activity arises principally from the secondary structure of the polymer (e.g., a helix) are a recent development [1-3]. One of the first syntheses that resulted in a "pure" helical structure was that of hexahelicene [4]. This could be resolved into a right- and a left-handed helix with opposite signs of rotation; it has a large specific rotation, $[\alpha]_D^{25} = +3700°$. This high optical rotation coming from a helix encouraged the synthesis of optically active polymers with only macromolecular asymmetry. In the past few years, three kinds of polymers have been prepared in which the optical activity arises solely from molecular asymmetry. They are polyisocyanides, poly(triphenylmethyl methacrylate), and polychloral.

Polyisocyanides [also called poly(iminomethylenes)] [5, 6] are prepared by the cationic polymerization of isocyanides by Lewis acids [7]. It was determined that polyisocyanides were in the form of a tightly-wound spiral with a 4/1 helical conformation. Each carbon atom in the polymer backbone was substituted, which caused a great deal of steric hindrance, especially with a bulky substituent like a *t*-butyl group. By means of a column packing of insoluble poly[(+)-*sec*-butyl isocyanide], which had only one screw-sense, poly(*t*-butyl isocyanide) was separated into (+) and (-) antipodes [8, 9].

Triphenylmethyl methacrylate (TrPMA) was also polymerized to an optically active polymer by anionic polymerization. Using the optically active initiator, lithium (*R*)-*N*-(1-phenylethyl)-anilide, poly(triphenylmethyl methacrylate) was prepared with a specific rotation of -104° at 589 nm. By using a lithium counterion complexed with (-)-sparteine to polymerize TrPMA, PTrPMA with a specific rotation of +363° at 589 nm was obtained [10, 11].

Polychloral having an optical activity originating from the secondary structure (i.e., the helix) was also prepared [1, 2]. Earlier attempts were made in 1963 and in 1973 to prepare optically active polychloral initiated with lithium cholesteroxide [12, 13]. Polychloral was recognized to be isotactic and helical, and could not undergo helix inversions because of the bulky trichloromethyl group. The optically active initiator tetramethylammonium (+)-ketopinate induced macromolecular asymmetry in polychloral, yielding a polymer with a specific rotation of +2400 ± 800° at 589 nm. In another case, the use of the optically active (+)-methyl-*n*-propylbenzylphenyl phosphonium counterion to induce molecular asymmetry resulted in optically active polychloral with a specific rotation of -2700 ± 200° at 589 nm [2].

In the anionic polymerization of chloral it has been found that the initiating ion adds to 1 mol of chloral monomer even slightly above the ceiling

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temperature (T_c) of polymerization if the initiating anion is a strong nucleophile. This was established during study of the initiation of chloral polymerization with the *t*-butoxide anion of lithium *t*-butoxide [14]. An essentially quantitative addition of the *t*-butoxide to 1 mol of chloral has been found by NMR spectroscopy to occur even above T_c to form a rather weak chloral-terminated alkoxide which does not continue to polymerize or even to propagate significantly above T_c [15]. Below T_c, this anion is capable of propagation to form high molecular weight isotactic polychloral [16-18]. Some aspects of this polymerization, especially preliminary studies of the initiation reactions, have recently been published [18-26].

The objective of the present work was to study the polymerization of chloral with optically active alkoxides in an attempt to establish to what degree polychloral is able to form exclusively isotactic product of only one handedness.

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EXPERIMENTAL PART

A. Materials

The following chemicals were obtained from the sources indicated: *n*-butyllithium, 2.1 *M* in *n*-hexane (Alfa-Ventron Co.); *t*-butyllithium, 1.5 *M* in *n*-pentane (Aldrich Chemical Co.); trichloroacetaldehyde (chloral) (Montrose Chemical Co.); cholesterol (Aldrich Chemical Co.); cyclohexane (Fisher Scientific Co.); Diazald (Aldrich Chemical Co.); diethyl ether, anhydrous (Matheson, Coleman, and Bell, Inc.); *d*(+)-mandelic acid (Aldrich Chemical Co.); *l*(-)-mandelic acid (Aldrich Chemical Co.); *d,l*-mandelic acid (Aldrich Chemical Co.); trichloroacetyl chloride (Aldrich Chemical Co.); diphenyl ether (Fisher Scientific Co.); Molecular Sieves, 3Å, from Fluka Chemical Co.

Chloral (4 L) was preliminarily distilled from phosphorus pentoxide (200 g) to convert any residual chloral hydrate to chloral. Prior to polymerization, it was further purified by fractional distillation through a 90-cm column packed with glass helices. Polymerization-grade chloral had a purity greater than 99.5% as judged by gas chromatography [28].

Cholesterol was recrystallized from hot 95% ethanol and dried overnight in an Abderhalden apparatus at 40°C and 0.2 torr.

n-Hexane was washed with concentrated sulfuric acid, neutralized with a 5% sodium bicarbonate aqueous solution, and washed with deionized water. It was predried over anhydrous magnesium sulfate and then refluxed over freshly cut sodium metal in a nitrogen atmosphere. The *n*-hexane was fractionally distilled at atmospheric pressure, with the middle fraction being collected and stored in a Schlenk tube containing activated 3Å Molecular Sieves.

Diethyl ether was heated to reflux overnight under nitrogen over freshly cut sodium metal and fractionally distilled at atmospheric pressure under nitrogen. The middle fraction was collected and stored in a Schlenk tube which contained activated 3Å Molecular Sieves.

Cyclohexane was washed with concentrated sulfuric acid, neutralized with 5% aqueous sodium bicarbonate, and washed with water. It was then washed with saturated aqueous sodium chloride and predried by storing over anhydrous magnesium sulfate. The cyclohexane was placed in a fractional distillation apparatus which had been flamed out under a nitrogen stream. It was refluxed under a nitrogen atmosphere over freshly cut sodium metal. A distillation forecut was discarded with the middle fraction being collected in a Schlenk tube which contained activated 3Å Molecular Sieves.

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B. Measurements

^{1}H-NMR spectra were obtained on a 60-MHz Varian T-60 NMR spectrometer. Spectra were taken at 25°C in $CDCl_3$ using tetramethylsilane (TMS) as an internal reference. Chemical shifts are reported in ppm, with TMS having $\delta = 0.00$ ppm.

^{13}C-NMR spectra were obtained on a Varian CFT-20 NMR spectrometer. Spectra were taken with complete proton decoupling at 25°C in $CDCl_3$ or D_2O using TMS or 1,4-dioxane, respectively, as internal references. All chemical shifts are reported in ppm relative to TMS. Typical instrument parameters for data acquisition were spectral width 4000 Hz, acquisition time 1.023 s, pulse width 19 μs, pulse delay 0-20 s, and sensitivity enhancement -0.800 s.

Melting points were measured on a Melt-Temp capillary melting point apparatus at a heating rate of 2°C/min. All melting points are uncorrected.

Gas chromatograms were obtained on a programmable Varian Aerograph Model 1400. Typically, a 900 X 3 mm column was used containing Porapak Q support. Helium was used as the transport medium.

Optical activity measurements were made in an electronic Perkin-Elmer 141MC polarimeter at room temperature and at wavelengths available from sodium or mercury lamps. All optical activities are reported as specific rotations. For polychloral films, specific rotations were obtained from measurements made on the solid state. A cell to hold the films consisted of two circular pieces of aluminum 27 mm in diameter with a 10-mm hole drilled in the middle with glass over the holes. The film cell was held together by screws and was bolted into the polarimeter. A film disk (thickness was determined by a friction stop micrometer) was placed in the film cell along with a drop of diphenyl ether. The optical rotation, α, was read off the polarimeter, and each disk of film was measured at three orientations of the film holder, 120° apart, to avoid any anisotropy. Six different disks of film were measured for each condition under which films were prepared. The specific rotations of the films were averaged, with the specific rotations determined from

$$[\alpha]_\lambda = \frac{(\bar{\alpha})}{(l)(\rho)},$$

where $\bar{\alpha}$ is the average rotation in degrees, l is the film thickness in dm, and ρ is the density of polychloral (1.9 g/cm^3). A typical film thickness was 0.15 mm.

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C. Preparation of Initiators

1. Lithium Cholesteroxide

Cholesterol (3.46 g, 8.95 mmol) was loaded and sealed via septum into a test tube in an inert environment. *n* Hexane (15.4 mL) and *n*-butyl lithium (2.1 *M* in *n*-hexane, 4.3 mL, 9.0 mmol) were injected into the vented test tube with butane escaping. Most of the insoluble cholesterol reacted, forming a solution.

2. Lithium Methyl *d*(+)-, *l*(-)-, or *d,l*-Hydroxidemandelate

a. Esterification of d,l-Mandelic Acid. *d,l*-Mandelic acid was esterified in methanol using *p*-toluenesulfonic acid as catalyst; mp 54-56°C (literature 57-58°C) [29].

b. Esterification of d(+)- or l(-)-Mandelic Acid. Diazomethane in diethyl ether (prepared from Diazald) was added slowly to a chilled solution of the appropriate mandelic acid (10.7 g, 70.4 mmol) dissolved in diethyl ether (75 mL). The rapid evolution of nitrogen gas was observed with the complete dissipation of the yellow diazomethane color. Unreacted mandelic acid was removed by washing with 5% aqueous sodium bicarbonate and water. The ether layer was dried by anhydrous sodium sulfate. The diethyl ether was removed on a rotary evaporator at 20 torr, leaving a light-yellow oil which subsequently crystallized. The crude product was sublimed overnight in a vacuum sublimator at 0.5 torr and 40°C. Yield of methyl *d*(+)- or *l*(-)-mandelate 6.1 g (59%); mp 55-56.5°C (literature 55.5°C [30]). Methyl *d*(+)-mandelate, $[\alpha]_D^{RT}$ + 142.2°, $[\alpha]_D^{RT}$ (literature +143° [30]) in methanol at 0.15 g/2 mL; optical purity = 99.4%. Methyl *l*(-)-mandelate, $[\alpha]_D^{RT}$ = -140.5° (literature -143° [29]) in methanol at 0.15 g/2 mL; optical purity = 98.3%.

c. *Reaction of Methyl d(+)-, l(-)-, or d,l-Mandelate with t-butyllithium.* The appropriate methyl mandelate was resublimed through phosphorus pentoxide at 0.2 torr and room temperature. Methyl mandelate (0.51 g, 3.07 mmol) was then placed in a dry 25 X 200 mm test tube in a nitrogen environment and sealed with a serum cap. Methyl mandelate was dissolved by a mixture of diethyl ether (4.5 mL) and cyclohexane (2.0 mL). The solution was cooled to -22°C with a Dry Ice/carbon tetrachloride bath. *t*-Butyllithium (1.95 mL, 2.93 mmol, 1.5 *M* in pentane) was slowly injected into the methyl mandelate solution, with gas evolving and a fine white suspension forming. The mixture was allowed to warm to room temperature for 5 min and was used immediately to polymerize trichloroacetaldehyde.

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D. Polymerization of Trichloroacetaldehyde

1. Lithium Cholesteroxide as Initiator

In a serum-capped 500-mL Erlenmeyer flask was injected trichloroacetaldehyde (150 mL, 1530 mmol) and *n*-hexane (190 mL) under nitrogen. The flask was placed in a 40°C oil bath for 10 min with lithium cholesteroxide (6.6 mL, 3.1 mmol, 0.2 mol%), injected into the trichloroacetaldehyde solution. The initiated monomer was placed in a -20°C freezer overnight so that polymerization could proceed. The polymer was milled and extracted with acidified methanol (10 vol% HCl) at room temperature for 1 day. The polymer was rinsed with methanol and dried at 0.1 torr prior to final stabilization by refluxing in a 0.64-*M* solution of PCl_5 in CCl_4 for 3 days. The polymer was collected by filtration, washed successively with CCl_4 and acetone, and extracted for 2 days with acetone in a Soxhlet extractor. The polymer was dried at 20 torr for 1 day. Yield of polychloral = 127 g (56%).

2. Lithium Methyl *d*(+)-, *l*(-)-, or *d,l*-Hydroxide Mandelate as Initiator

Glass plates (180 X 180 X 6 mm) were washed with a sodium dodecylsulfate solution, rinsed with deionized water, swabbed with acetone, and dried for 2 days in a 125°C oven. A film assembly was prepared by placing two 3500-denier polyurethane elastomer threads between two hot glass plates held together by Boston clamps. The film assemblies were placed in an oven at the temperature at which the monomer and initiator were mixed and held.

In a dry, serum-capped, 125-mL Erlenmeyer flask was placed trichloroacetaldehyde (60 mL, 620 mmol). The flask was immersed in an ethylene glycol thermostat bath set at either 65.0 or 75.0°C for 10 min. The heterogeneous suspension of lithium methyl *d*(+)-, *l*(-)-, or *d,l*-hydroxidemandelate (3.1 mmol, 0.5 mol%) in cyclohexane/diethyl ether was injected into the warm trichloroacetaldehyde, resulting in a clear, colorless solution. Ten minutes after initiator injection, an aliquot of the initiated monomer was removed with a warm syringe and injected into two warm film assemblies. The film assemblies were plunged into an ice water slurry overnight so that polymerization could occur. The film casting process was repeated at 20, 30, and 50 min intervals after the mixing of initiator and monomer. The film assemblies were separated and the films were floated off glass plates in the presence of acidified methanol (10 vol% HCl), which serves to stabilize the films. The films were washed with methanol and then soaked in methanol for 1 day. A 12-mm disk of film was cut from the bulk sample while it was still wet with methanol. The disk was soaked in diphenyl ether for at least 2 days prior to optical activity measurements.

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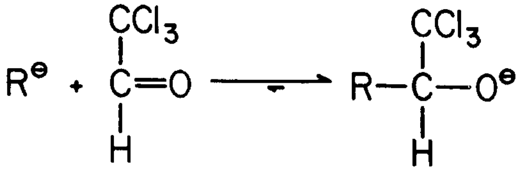
RESULTS AND DISCUSSION

The basic requirement for optical activity to arise exclusively from a polymer's helical conformation (herein referred to as macromolecular asymmetry) is that it polymerizes in an isotactic fashion. In addition, it is highly desirable that the polymer has high conformational energy barriers to prevent helix inversion, which results in a loss of optical activity. Polychloral meets these requirements since it is isotactic and has high conformational energy barriers due to the bulky trichloromethyl group alpha to the polymer backbone. But these specifications are not sufficient as evidenced by the absence of optical activity in polychloral polymerized by a typical alkoxide initiator, such as lithium *t*-butoxide. The absence of optical activity under such circumstances is due to the equally probable formation of dextrorotary and levorotary helices. This leads to a third requirement: an asymmetric center must be present in either the initiator, its counterion, or the monomer itself to give preference to a given handed helical form. This use of an asymmetric center to lead to macromolecular asymmetry is consistent with Flory's observation that an asymmetric center in a chain molecule introduces a distinction between right- and left-handed rotations and that the two states will not occur with equal frequency [31].



$$R^{\ominus} + \underset{H}{\overset{CCl_3}{C}}{=}O \longrightarrow R-\underset{H}{\overset{CCl_3}{C}}-O^{\ominus}$$

$R^{\ominus}$ = strong nucleophile

$R'-O^{\ominus}$

In this work, the asymmetric center is in the strong nucleophilic initiator, the alkoxide. The asymmetric center is placed alpha to the alkoxide moiety to enhance its interaction with the first chloral unit whose subsequent configuration and conformation impact the rest of the polymer chain.

Polychloral prepared by optically active alkoxides possesses a limited number of true asymmetric centers that can contribute to the total optical activity, but the contribution of the initiator at 0.5 mol% and the first few monomer units should be relatively small. To corroborate this, the compound's methyl *d*(+)- and *l*(–)-trichloroacetylmandelate were prepared to approximate the optical activity of the end groups that result when the antipodes of lithium methyl hydroxidemandelate are used as initiators.

The specific rotation of +97.7° for methyl *l*(-)-*O*-trichloroacetylmandelate was used to estimate the initiator end group's optical activity assuming that *all* the initiator was incorporated as a polymer end group. A 0.5 mol% concentration of methyl *O*-trichloroacetylmandelate in chloral monomer would correspond to a concentration of 0.016 g/mL. However, upon polymerization, a volume reduction occurred as evidenced by the monomer density, 1.5 g/mL, compared to the polymer density of 1.9 d/mL. This effectively increases the concentration to 0.021 g/mL. By using $\alpha = [\alpha] lc$, α for the model end group in the polymer was estimated, based on the average film path length (thickness) of 0.15 mm. The rotation, α, is 0.0031 for the model initiator end

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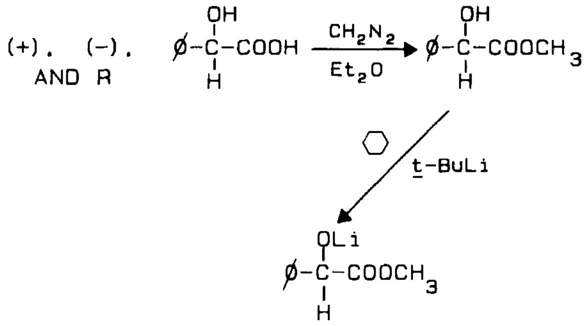
group. From the equation $[\alpha] = \bar{\alpha}/l_p$, the maximum specific rotation which the initiator end group should contribute to the polymer is 1, and even if the first few units in the polymer chain have a comparable optical activity contribution is still less than the standard deviation of the optical activity measurements on the films.

The first chiral alkoxide initiator to be evaluated in the polymerization of chloral was lithium cholesteroxide (0.5 mol%). Since this initiator, as prepared, is unstable above the ceiling temperature of chloral monomer, hexane diluent was added to depress the ceiling temperature, but the diluent prevented the formation of coherent films for the measurement of optical activity. To obtain indirect evidence of the optical activity, the polymer was ground (30-150 mesh) and stabilized by converting the hydroxyl end groups to chlorides by phosphorus pentachloride. This powder was used as a column substrate to partially resolve (approximately 18%) a 1/1 mixture of poly(*R*-(+)-α-methylbenzyl methacrylate) and poly(*S*-(-)-α-methylbenzyl methacrylate) [32]. The partial resolution implies that the polychloral initiated by cholesteroxide had optical activity.

LITHIUM METHYL (HYDROXIDE) MANDELATE
LiMM



To obtain direct measurement and proof of the optical activity of polychloral initiated by a chiral alkoxide, initiators based on mandelic acid were studied, specifically lithium methyl hydroxidemandelate, which was prepared by first esterifying the appropriate mandelic acid, resulting in methyl mandelate, methyl *d*(+)-mandelate, and methyl *l*(-)-mandelate, having specific rotations of 0°, + 142°, and -141°, respectively. The optical purity of methyl *d*(+)-mandelate was 99%, while that of methyl *l*(-)-mandelate was 98%. The specific rotation of the lithium methyl hydroxidemandelate initiators could not be determined due to its instability or insolubility in most solvents. In initial experiments, cyclohexane and ether diluents were removed from the alkoxide initiator, but substantial initiator racemization occurred, as evidenced by the resulting polychloral having a low optical activity and by acidification of the initiator to reisolate methyl *d*(+)-mandelate which had undergone 43% racemization during the reaction sequence. However, when the initiator was slurried in ether and cyclohexane, and injected into warm chloral, polychloral with much higher optical activity was obtained.

Chloral and lithium methyl hydroxidemandelate initiators at 0.5 mol% concentration were mixed together at either 65.0 or 75.0°C. From this initiated monomer maintained at 65.0 or 75.0°C, polychloral films were obtained by cryotachensic casting 10, 20, 30, and 50 min after mixing. Films prepared by the lithium methyl hydroxidemandelate initiators were translucent but became transparent after soaking in diphenyl ether. Each specific rotation for any polychloral film was averaged from 15 to 18 measurements. For polychloral initiated by the racemic initiator, the specific rotation was +5 ± 10. The specific rotations of polychloral initiated by the *d*(+) antipode for various temperatures and holding times are reported in Table 1. The specific rotations for polychloral initiated by the *l*(-) antipode are reported in Table 2.

One of the striking results for polychloral prepared from either of the initiator antipodes (Tables 1 and 2) is that the specific rotation increased severalfold with increasing holding time at 65 and 75°C prior to cryotachensic polymerization (T_c = 58°C for neat chloral). At a given holding time the optical activity increased as the temperature was increased from 65 to 75°C. This indicates the critical nature of the initiation step in a macromolecular asymmetric polymerization process.

The time-temperature dependence of the optical activity suggests differences in the kinetic and the thermodynamic considerations of the initiation step. Prior work [15] indicated that, above the ceiling temperature, a strong nucleophile (e.g., an alkoxide) forms a 1:1 adduct with chloral. This, in conjunction with our observation of increasing polymer optical activity, implies that the initiating 1:1 adduct probably exists as a mixture of racemic and meso placement (i.e., kinetically preferred), but one of these configurational/conformational sequences is thermodynamically favored, as evidenced by the optical activity increasing with both time and temperature. This implies that, in any macromolecular asymmetric polymerization system, the thermodynamic equilibrium of the initiation sequence should be evaluated by a set of time-temperature experiments.

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TABLE 1. Optically Active Polychloral Initiated by Lithium (+) Methyl Hydroxidemandelate

	$[\alpha]_D^{25}$, Film	
Holding time, min	65.0°C	75.0°C
10	+940 ± 60	+1420 ± 110
20	+990 ± 140	+3600 ± 110
30	+1100 ± 70	+2890 ± 200
50	+1690 ± 340	–

Since specific rotation measurements are wavelength dependent, rotations were determined at several wavelengths available from a sodium or a mercury lamp on a polychloral film with the highest observed specific rotation at the sodium-D line (589 nm) (the *l*(-) antipode-initiated polychloral with a holding time of 50 min and a bath temperature of 75.0°C). Specific rotations could not be determined at wavelengths shorter than 334 nm due to light absorption by the diphenyl ether. The optical rotary dispersion (ORD) data are found in Table 3.

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TABLE 2. Optically Active Polychloral Initiated by Lithium (-) Methyl Hydroxidemandelate

	$[\alpha]_D^{25}$, Film	
Holding time, min	65.0°C	75.0°C
10	-900 ± 60[a]	-1310 ± 100
20	-1190 ± 90	-2550 ± 60
30	-1630 ± 180	-4030 ± 480
50	-3580 ± 310	-4670 ± 240[b]

[a] When the film assembly was at ~75°C instead of 65°C, $[\alpha]_D^{25}$ = -1230 ± 150, i.e., 37% higher.

[b] Film prepared under this set of conditions was used for optical rotary dispersion measurements.

TABLE 3. Optical Rotary Dispersion Data for Polychloral Initiated by Lithium (–) Methyl Hydroxidemandelate Held at 75.0°C for 50 min

λ, nm	$[\alpha]_\lambda^{25}$	λ, nm	$[\alpha]_\lambda^{25}$
589	-4710 ± 110	407.78	-11 300 ± 150
579.07	-4790 ± 140	404.66	-11 100 ± 60
576.96	-4820 ± 150	366.33	-14 700 ± 40
546.07	-5460 ± 160	365.48	-14 700 ± 80
435.83	-9460 ± 210	365.02	-14 400 ± 70
434.75	-9580 ± 140	334.15	-18 400 ± 120

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The plot of specific rotation versus wavelength results in a monotonic curve (Fig. 1), which implies that the optical activity measurements are being made far from the optically active transition. ORD data can sometimes be fitted to a single-term Drude equation,

$$[\alpha]_\lambda \lambda^2 = [\alpha]_\lambda \lambda_c^2 + k,$$

where $[\alpha]$ is the specific rotation, λ is the wavelength, λ_c is the approximate wavelength of the optically active transition, and k is a characteristic constant. A Yang-Doty plot is shown in Fig. 2. The straight line has a correlation function of 0.99, and the intercept indicates that the optically active transition may occur at 183 nm, which cannot be currently confirmed by direct measurement.

SUMMARY

We have shown that optically active polychloral can be prepared in which the optical activity arises exclusively from the polymer's helical conformation. This was achieved by using a chiral alkoxide initiator to induce a predominance of one helical form over the other. It was also observed that the optical activity increases with the time and temperature at which initiated monomer is held prior to polymerization. This strongly suggests that thermodynamic equilibrium takes considerable time to be reached. The maximum specific rotation

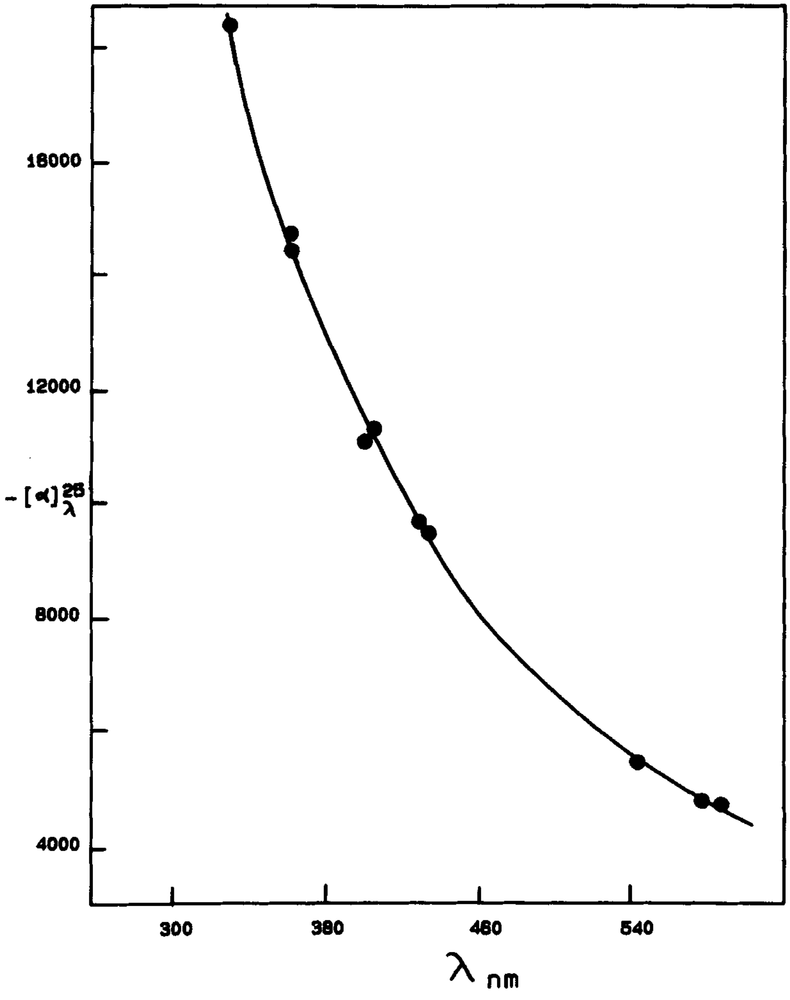

FIG. 1. Optical rotary dispersion curve of polychloral initiated by Li(−)MM at 75.0°C for 50 min.

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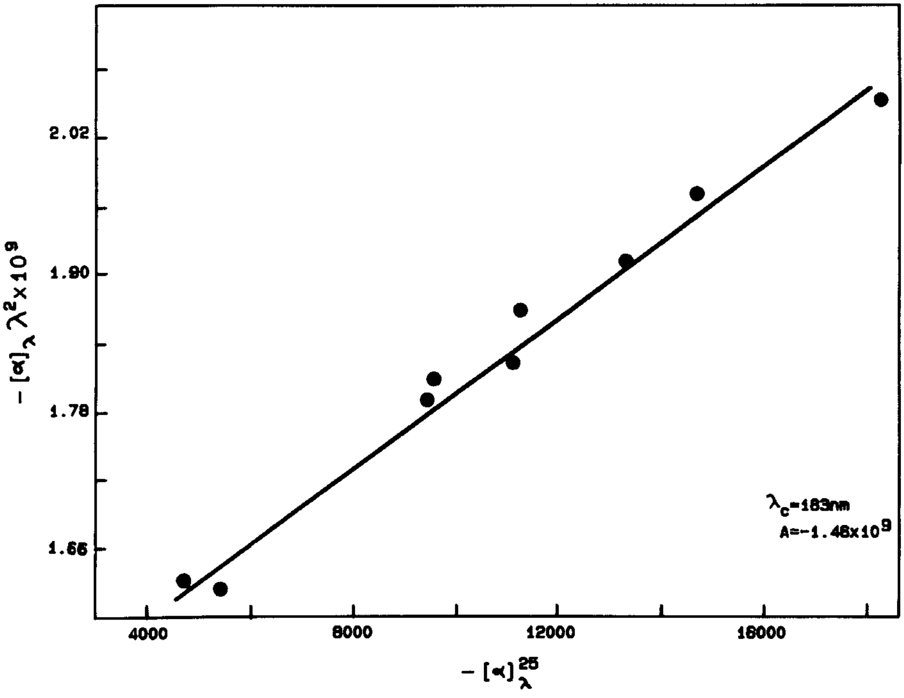

FIG. 2. Yang-Doty plot of ORD data for polychloral initiated by LI(-)MM at 75.0°C for 50 min.

of -4670° for polychloral made with these mandelate alkoxide initiators indicates at least a minimum optical activity for future polychloral work when evaluating the efficiency of chiral initiators in inducing macromolecular asymmetry.

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REFERENCES

[1] W. J. Harris and O. Vogl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 22,* 309 (1981).

[2] L. S. Corley, PhD Dissertation, University of Massachusetts, Amherst, 1979.

[3] L. S. Corley and O. Vogl, *Polym. Bull., 3,* 211 (1980).

[4] M. S. Newman and D. Lednicer, *J. Am. Chem. Soc., 78,* 4765 (1956).

[5] R. J. M. Nolte, A. J. M. vanBeijnen, and W. Drenth, *Ibid., 96,* 5932 (1974).

[6] F. Millich and G. Baker, *Macromolecules, 2,* 122 (1962).

[7] F. Millich, in *Advances in Polymer Science* (H. J. Cantow, ed.), Springer-Verlag, Heidelberg, 1975, pp. 117-141.

[8] R. J. M. Nolte, A. J. M. vanBeijnen, and W. Drenth, *J. Am. Chem. Soc., 96,* 5932 (1974).

[9] W. Drenth and R. J. M. Nolte, *Acc. Chem. Res., 12,* 30 (1979).

[10] Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, and H. Yuki, *J. Am. Chem. Soc., 101,* 4763 (1979).

[11] Y. Okamoto, K. Suzuki, and H. Yuki, *J. Polym. Sci.–Polym. Chem. Ed., 18,* 3043 (1980).

[12] O. Vogl, *Chemist, 62*(9), 16 (1985).

[13] O. Vogl and K. Hatada, Unpublished Results, 1973.

[14] K. Hatada, L. S. Corley, Sh. S. Vezirov, and O. Vogl, *Vysokomol. Soedin., Ser. A, 19*(9), 1987 (1977).

[15] P. Kubisa and O. Vogl, *Polymer, 21,* 525 (1980).

[16] P. Kubisa, K. Neeld, J. Starr, and O. Vogl, *Ibid., 21,* 1433 (1980).

[17] K. Neeld and O. Vogl, in *Macromolecular Reviews,* Vol. 16 (A. Peterlin, ed.), Wiley-Interscience, New York, 1981, pp. 1-40.

[18] P. Kubisa, L. S. Corley, T. Kondo, and O. Vogl, *Polym. Eng. Sci., 21,* 829 (1981).

[19] J. Zhang, G. D. Jaycox, and O. Vogl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 26*(1), 156 (1985).

[20] O. Vogl, L. S. Corley, W. J. Harris, G. D. Jaycox, and J. Zhang, *Makromol. Chem., Suppl., 13,* 1 (1985).

[21] O. Vogl, in cooperation with L. S. Corley, T. Doyle, W. J. Harris, G. D. Jaycox, and J. Zhang, *Prepr., Japan-U.S. Polym. Symp., Kyoto,* 1985, p. 7.

[22] O. Vogl, "Aldehyde Polymers," in *Encyclopedia of Polymer Science and Engineering,* Vol. 1 (H. F. Mark, N. Bikales, C. G. Overberger, and H. Menges, eds.), Wiley, New York, 1986, p. 623.

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[23] O. Vogl and J. Zhang, *Polym. Prepr., SPSJ Annu. Meet., Kyoto, 35*(1), 45 (1986).

[24] O. Vogl and G. D. Jaycox, *ChemTech, 11,* 698 (1986).

[25] A. Abe, K. Tasaki, K. Inimata, and O. Vogl, *Macromolecules, 19,* 2707 (1986).

[26] J. Zhang, G. D. Jaycox, and O. Vogl, *Polym. J., 19,* 603 (1987).

[27] J. Zhang, G. D. Jaycox, and O. Vogl, *Polymer, 29,* 707 (1988).

[28] P. Kubisa and O. Vogl, *Macromol. Synth., 6,* 49 (1977).

[29] *Beilstein Handbuch der Organischen Chemie,* Vol. X, 4th ed., Springer-Verlag, Berlin, 1927, p. 195.

[30] *CRC Handbook of Chemistry and Physics,* 53rd ed., Chemical Rubber Co., Cleveland, Ohio, 1972.

[31] P. J. Flory, *Statistical Mechanics of Chain Molecules,* Wiley-Interscience, New York, 1969.

[32] K. Hatada, S. Shimizu, H. Yuki, W. Harris, and O. Vogl, *Polym. Bull., 4,* 179 (1981).

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