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HALOALDEHYDE POLYMERS. XXXVII.* OPTICALLY ACTIVE POLYCHLORAL INITIATED WITH WEAK CHIRAL ANIONIC INITIATORS

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ABSTRACT

Chloral polymerizations initiated with weak chiral initiators, used at 0.5 mol% concentration, gave optically active polychloral. Maximum rotations of the various polychloral samples, measured in film gorm, depended on the initiator as follows: tetramethylammonium (+)-*O*-acetylmandelate $[\alpha]_D^{25} = -1860°$, tetramethylammonium (-)-*O*-acetylmandelate $[\alpha]_D^{25} = +1180°$, tetramethylammonium (+)-α-methoxymandelate $[\alpha]_D^{25} = -190°$, tetramethylammonium (-)-α-methoxymandelate $[\alpha]_D^{25} = +210°$.

INTRODUCTION

Chloral (trichloroacetaldehyde) can be polymerized to form an isotactic polymer whose structure is that of a 4/1 helix with a repeat distance of 5.2 Å [1-5]. "Strong" anionic initiators, such as lithium *t*-butoxide or other alkox-

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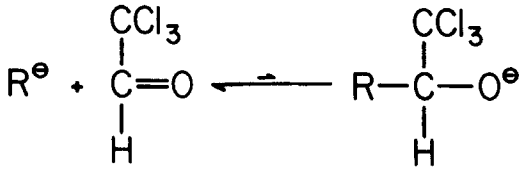
ides of aliphatic or alicyclic alcohols, when added to chloral above its ceiling temperature (T_c), form a 1:1 adduct that leads to an essentially quantitative initiation of chloral polymerization [6-8]. When the initiated monomer is cooled below the T_c, the resulting polymer is presumably of a reasonably narrow molecular weight distribution, as implied by its brittleness. The insolubility of polychloral does not allow the determination of the molecular weight and molecular weight distribution by the conventional solution methods of osmometry, viscometry, GPC, or light scattering. Determination of the molecular weight has been achieved in the solid state by using ^{14}C *t*-butoxide (i.e., "strong" initiator) as the initiating species and the ^{35}Cl halide of a phosphorus or ammonium salt (i.e., "weak" initiator) as the initiating species [9].

Unlike the fast and quantitative addition of alkoxides to chloral above T_c to form the polymer-propagating species [10], weak nucleophiles, such as carboxylates, chloride, and even chloral-terminated alkoxides, and chloral do not substantially form the propagating species above T_c; thus their equilibria (Eq. 1) are shifted to the left, favoring the starting products. Only significantly below T_c does the formation of the propagating species occur effectively, resulting in rapid and efficient polymerization. Traditionally, chloral polymerization is performed by placing the initiated chloral in an ice-water cooling bath in order to dissipate the heat of the polymerization [11, 12]. In such circumstances the actual temperature of the polymerizing mixture is only about 10 to 20°C below T_c [13]. Polymerizations carried out by weak nucleophiles always give tough samples of polychloral with apparently a broader molecular weight distribution [14] than obtained by strong alkoxide initiators.

When chiral alkoxides were used as initiators, the polychloral formed was optically active with specific rotations of up to several thousand degrees [15-17] when measured in film form.



(1)

$R^{\ominus}$ = weak nucleophile

$R'\text{-}COO^{\ominus}$, $Cl^{\ominus}$, $R'\text{-}O\text{-}CH(CCl_3)\text{-}O^{\ominus}$

It was the objective of this work to study the polymerization of chloral with weak chiral anionic initiators in which the asymmetric center in the carboxylate is as close as possible to the first monomer unit in the polymer chain in order to prepare polychloral samples of high optical activity, or at least to determine what influence the initiation equilibrium has on the degree of one-handedness of the polymer formed.

EXPERIMENTAL PART

A. Materials

The following chemicals were obtained from Aldrich Chemical Co. and used as received: boron trifluoride etherate, *t*-butyllithium (1.5 *M* in *n*-pentane), *d*(+)-ephedrine, *l*(-)-ephedrine, *d*(+)-mandelic acid, *l*(-)-mandelic acid, *d,l*-mandelic acid, deuterium oxide, deuterochloroform, Diazald, 2(2-ethoxyethoxy)-ethanol, trichloroacetyl chloride, tetramethylammonium hydroxide (20% in methanol).

Cyclohexane, diethyl ether, diphenyl ether, 1,4-dioxane, ethanol, *n*-hexane, and phosphorus pentoxide were from Fisher Scientific Co.; lithium aluminum hydride and *n*-butyllithium (2.1 *M* in *n*-hexane) from Alfa-Ventron Co.; Molecular Sieves, 3 Å, from Fluka Chemical Co.

Chloral (4 L) was placed in a dry, one-neck, 5 L round-bottom flask, and phosphorus pentoxide (200 g) was added to convert any residual chloral hydrate to anhydrous chloral. The heterogeneous mixture was refluxed overnight in a nitrogen atmosphere. Crude chloral was removed from the phosphorus residues by simple distillation and was further purified by fractional distillation through a 90-cm column packed with glass helices. This polymerization-grade chloral had a purity of over 99.5% as judged by gas chromatography. The monomer was kept under reflux in the distillation apparatus but was freshly distilled prior to any polymerization [11].

n-Hexane was heated to reflux over sodium and fractionally distilled; the middle fraction was collected in a flamed-out Schlenck tube containing activated 3 Å Molecular Sieves. Anhydrous diethyl ether was also distilled from sodium directly into a Schlenck tube containing activated 3 Å Molecular Sieves. Cyclohexane was treated similarly.

B. Measurements

^{1}H-NMR spectra were obtained on a 60-MHz Varian T-60 NMR spectrometer. Spectra were typically taken at 25°C in $CDCl_3$ with tetramethylsilane

(TNS) as an internal reference. Chemical shifts are reported in ppm using the δ scale 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 with TMS or 1,4-dioxane, respectively, as internal references.

Melting points were measured on a MEL-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 eluent.

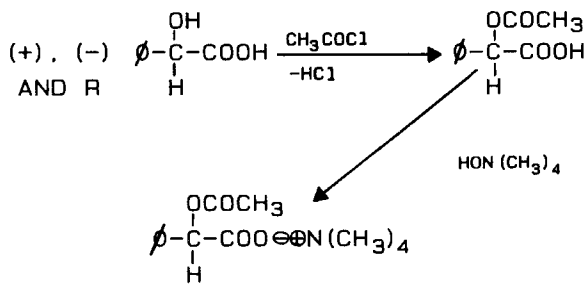
Optical activity measurements were made in an electronic Perkin-Elmer 141MC polarimeter. Measurements were made at room temperature and at wavelengths which were available from sodium or mercury lamps. Measurements were made on solutions in appropriate solvents in a 1-dm cell. All optical activities are reported as specific rotation. Specific rotations of polychloral were obtained from measurements made on film samples.

C. Syntheses of Chiral Initiators

1. Tetramethylammonium *d*(+)-, *l*(−)-, or *d,l-O*-Acetylmandelate

a. Acetylation of d(+)-, *l*(−)-, *or d,l-Mandelic Acid.* *d*(+), *l*(−)-, or *d,l*-mandelic acid (5.0 g, 33 mmol) was reacted with acetyl chloride (7.0 mL, 98 mmol) [18]. Yield 5.5 g (86%), mp 97.5-99°C (literature 96.5-98°C [19]). For *l*(−)-*O*-acetylmandelic acid, $[\alpha]_D^{25} = (-)153°$, $[\alpha]_D^{25}$ literature $= (-)154°$ [11] (methanol, $c = 0.1$ g/mL), optical purity 99%. For d(+)-*O*-

TETRAMETHYLAMMONIUM ACETYLMANDELATE
(TMAAC)



(2)

acetylmandelic acid, $[\alpha]_D^{25} = (+)151°$, $[\alpha]_D^{25}$ literature [20] = (+)154° (acetone, 2.5 g/100 mL), optical purity 98%.

b. Titration of d(+)-, l(-)-, or d,l-O-Acetylmandelic Acid with Tetramethylammonium Hydroxide. d(+)-, l(-)-, or d,l-O-Acetylmandelic acid (5.0 g, 26 mmol) was dissolved in methanol (50 mL). A drop of phenolphthalein in methanol was added, and the *O*-acetylmandelic acid solutions were titrated to a pink end point with 20% tetramethylammonium hydroxide in methanol. The solution was then back-titrated slightly with a solution of *O*-acetylmandelic acid. The volume of the solution was reduced to half by boiling off methanol, and 1,4-dioxane (60 mL) was added to the remainder. The solution was again reduced to one quarter of its volume and allowed to cool. White crystals deposited as platelets. They were collected and dried in an Abderhalden apparatus at 40°C and 0.05 torr, mp 184-187°C (dec.). ^{13}C NMR in D_2O: δ C–CO–O^- 176.1, O–CO–CH_3 174.2, aromatic 136.9, 129.8, 129.5, Ar–CH–CO 78.7, $N^+(CH_3)_4$ 56.2, 56.0, 55.8, and CO–CH_3 21.4 ppm. Tetramethylammonium d(+)-*O*-acetylmandelate, $[\alpha]_D^{25}$ = (+)88° (methanol, 0.3 g/100 mL). Tetramethylammonium l(-)-*O*-acetylmandelate, $[\alpha]_D^{25} = (-)86°$ (methanol, 1.3 g/100 mL).

2. Tetramethylammonium d(+)-, l(-)-, or d,l-α-Methoxymandelate

a. Esterification of d,l-Mandelic Acid. Into a dry 500-mL round-bottom flask was placed d,l-mandelic acid (112 g, 736 mmol), *p*-toluenesulfonic acid (14 g, 74 mmol, 10 mol%), and methanol (300 mL, a fivefold excess relative to mandelic acid). The reaction was blanketed with nitrogen and refluxed overnight. Methyl mandelate was isolated by extraction into diethyl ether (300 mL). Unreacted acid was removed by washing the product with 5% aqueous sodium bicarbonate solution. The ether layer was washed with deionized water, extracted with saturated aqueous sodium chloride, and stored over anhydrous magnesium sulfate. Diethyl ether was removed on a rotary evaporator at 20 torr. Crystalline methyl mandelate was dried at room temperature and 0.1 torr, mp 54-56°C (literature 57-58°C [21]). Yield 102 g (83%). ^{13}C NMR: δ CO 174.0, aromatic carbons 138.4, 128.6, 128.5, and 126.7, Ar–CH–CO 72.9, and $COOCH_3$ 52.8 ppm.

b. O-Methylation of Methyl Mandelate. In a 1-L, single-neck, round-bottom flask was placed methyl mandelate (70 g, 420 mmol), trimethyl orthoformate (700 mL, 6400 mmol), and BF_3•etherate (7.0 mL, 57 mmol). The transetherification [22] was blanketed with nitrogen and refluxed overnight.

Crude product was isolated after destroying BF_3·etherate and trimethyl orthoformate with acidified methanol. The product was extracted with diethyl ether, and the ether layer was washed with a 5% aqueous sodium bicarbonate solution and subsequently dried over anhydrous magnesium sulfate. Ether was removed on a rotary evaporator at 20 torr. The crude product was subjected to the methylation reaction described above two more times to ensure complete methylation. The product was fractionally distilled at 0.15 torr; the middle fraction, having bp 63-67°C, was isolated, yield 51.5 g (68%). ^{13}C NMR in $CDCl_3$: δ –CO– 171.1, aromatic carbons 136.3, 128.8, 128.7, 127.2, Ar–CH–CO– 82.6, –O–CH_3 57.3, and –CO–OCH_3 52.2 ppm.

c. Hydrolysis of Methyl α-Methoxymandelate. In a 500-mL round-bottom flask was placed methyl α-methoxymandelate (51.5 g, 285 mmol), methanol (50 mL), and sodium hydroxide (40 g, 1000 mmol) dissolved in water (250 mL). A white salt precipitated shortly, and the heterogeneous mixture was heated at a gentle reflux overnight. To isolate the product, concentrated hydrochloric acid was added slowly until the white salt dissolved. This solution was extracted with diethyl ether, washed with 5% aqueous sodium bicarbonate and water, and dried over anhydrous calcium sulfate. The ether was removed on a rotary evaporator at 20 torr, leaving a viscous oil which slowly crystallized. Yield 36 g (76%). ^{13}C NMR in $CDCl_3$: δ –CO– 174.3, aromatic carbons 135.9, 128.9, 128.7, and 127.3, Ar–CH–CO– 82.3, and –OCH_3 57.2 ppm.

d. Resolution of r-*α-Methoxymandelic Acid.* In a 50-mL Erlenmeyer flask was dissolved r-α-methoxymandelic acid (10 g, 60 mmol) and *l*(-)-ephedrine (10 g, 55 mmol) in methanol (27 mL) by gentle heating for 1 h. The flask was held at room temperature overnight, during which time white crystals formed. They were washed with methanol (6 mL), boiled in methanol (12 mL) for 5 min, and chilled to 0°C. The white crystals remaining were collected and were designated Batch A.

All methanol fractions were collected and used to dissolve an additional portion of α-methoxymandelic acid (9.0 g, 54 mmol) and *l*(-)-ephedrine (9.0 g, 49 mmol) with gentle heating for 1 h. The isolation and purification processes of the previous paragraph were repeated. The resulting crystals were designated Batch B.

Again, all methanol fractions were collected and an additional portion of α-methoxymandelic acid (11.4 g, 68.6 mmol) and *l*(-)-ephedrine (11.4 g, 62.2 mmol) were dissolved in the combined methanol fractions by gentle heating for 1 h. The above isolation and purification processes were repeated. The resulting crystals were designated Batch C.

All methanol fractions were collected with the methanol removed by rotary evaporation at 20 torr. A gold crystalline material remained, which was designated Batch D. Batch D was dispersed in water (120 mL) and concentrated hydrochloric acid (12 mL), giving an opaque white solution which was extracted with diethyl ether (150 mL). The ether layer was washed with water, dried over anhydrous magnesium sulfate, and the ether was removed on a rotary evaporator at 20 torr, leaving an oil. Crude yield of partially resolved *d*(+)-α-methoxymandelic acid = 17.9 g. $[\alpha]_D^{25}$ = (+)96.3°, $[\alpha]^{25}$ literature [20] = (+)150° (methanol, *c* = 6.7 g/100 mL), optical purity 64.2%. This *d*(+)-α-methoxymandelic acid was reresolved with *d*(+)-ephedrine as follows: In a 50-mL Erlenmeyer flask was placed *d*(+)-α-methoxymandelic acid (17.9 g, 108 mmol), *d*(+)-ephedrine (17.9 g, 108 mmol), and methanol (28 mL). Solution was achieved by gentle heating for 1 h. The solution was allowed to remain at room temperature overnight with white crystals forming. They were collected, washed with methanol (10 mL), and dispersed in water (75 mL) and concentrated hydrochloric acid (7.5 mL), giving an opaque white solution which was extracted with diethyl ether (100 mL). The ether layer was washed with water, predried by washing with saturated aqueous sodium chloride, and stored over anhydrous sodium sulfate. The ether was removed by rotary evaporation at 20 torr, leaving an oil which slowly crystallized. Yield of *d*(+)-α-methoxymandelic acid 11.3 g (74%). $[\alpha]_D^{25}$ = (+)135°, $[\alpha]_D^{25}$ literature [20] = (+)150° (methanol, *c* = 6.7 g/100 mL), optical purity 90%.

Crystalline Batches A, B, and C were combined so that *l*(-)-α-methoxymandelic acid could be isolated. Batches A, B, and C were dispersed in water (100 mL) and concentrated hydrochloric acid (10 mL), giving a white opaque solution. This was extracted with diethyl ether (150 mL). The ether layer was washed with water, predried by washing with saturated aqueous sodium chloride, and stored over anhydrous sodium sulfate. The ether was removed by rotary evaporation at 20 torr, which left a slowly crystallizing oil. Yield of *l*(-)-α-methoxymandelic acid 10.2 g (67%). $[\alpha]_D^{25}$ = (-)144°, $[\alpha]_D^{25}$ literature [20] = (-)150° (methanol, *c* = 6.7 g/100 mL), optical purity 96%.

e. Titration of d(+)-, l(-)-, or d,l-α-Methoxymandelic Acid. α-Methoxymandelic acid (6.0 g, 36 mmol) was dissolved in methanol (15 mL) in a 125-mL Erlenmeyer flask. (Approximately 0.5 mL of this solution was set aside for back-titration.) A drop of 1% phenolphthalein in methanol was added to the methoxymandelic acid and the solution was titrated with 10% tetramethylammonium hydroxide in methanol to a pink phenolphthalein end point. The solution was then back-titrated, 1,4-dioxane (50 mL) was added to the flask, and some methanol was removed by boiling the solution until slightly turbid. The mixture was chilled and white crystals collected (nitro-

gen atmosphere). Tetramethylammonium α-methoxymandelate was dried overnight at 40°C and 0.2 torr in an Abderhalden drying apparatus. ^{13}C NMR in D_2O: δ CO 178.8, aromatic carbons 139.1, 129.6, 129.4, 128.2, CH 85.7, $-OCH_3$ 57.4, and $\overset{+}{N}(CH_3)_4$ 56.2, 56.0, and 55.8 ppm. $[\alpha]_D^{RT} = (+)52.1°$ (methanol, $c = 0.1$ g/2 mL) for tetramethylammonium *d*(+)-α-methoxymandelate. $[\alpha]_D^{RT} = (-)56.4°$ (methanol, $c = 0.026$ g/2 mL) for tetramethylammonium *l*(-)-α-methoxymandelate.

D. Polymerization of Chloral

1. Tetramethylammonium *d*(+)-, *l*(-)-, or *d,l*-*O*-Acetylmandelate as Initiator

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

Tetramethylammonium *d*(+)-, *l*(-)-, or *d,l*-*O*-acetylmandelate (0.84 g, 3.2 mmol, 0.5 mol%) was placed in a dry 125-mL Erlenmeyer flask while in a nitrogen-filled glove bag. The flask was sealed with a rubber septum and removed from the glove bag. Into another dry, serum-capped, 125-mL Erlenmeyer flask was injected approximately 70 mL distilled chloral. The two flasks containing initiator and monomer were immersed in an ethylene glycol thermostat bath set at 70.0, 75.0, or 85.0°C. The flasks were allowed to come to the bath temperature for 10 min. With a warm syringe, chloral (60 mL, 620 mmoles) was injected into the flask containing the tetramethylammonium *O*-acetylmandelate initiator. A yellow opaque solution formed. Ten minutes after the monomer and initiator had been mixed, an aliquot of the mixture was removed with warm syringe and injected into two warm film assemblies. The film assemblies were plunged into an ice-water slurry overnight so that polymerization could proceed. This process of casting films from initiated monomer was repeated 20, 30, and 50 min after the initial mixing of monomer and initiator.

The next day the film assemblies were separated and the film was floated off the glass plate in acidified methanol (10% HCl). The films were kept in acidified methanol for 1 day to stabilize them [23]. The films were rinsed with methanol and soaked in methanol for 1 day. Typically, a 12-mm disk

of film was cut with a No. 6 cork borer from a "wet" film. The disk was soaked in diphenyl ether for at least 2 days prior to optical measurements.

2. Tetramethylammonium *d*(+)-, *l*(−)-, or *d,l*-α-Methoxy Mandelate as Initiator

The procedure was equivalent to that presented above with the following differences: Tetramethylammonium *d*(+)-, *l*(−)-, or *d,l*-α-methoxymandelate (0.64 g, 2.8 mmol, o.5 mol%) was used; approximately 60 mL of monomer-grade chloral was used; the temperatures were 65.0, 70.0, 80.0, or 85.0°C; the chloral injected was 50 mL (510 mmol).

E. Preparation of Compounds as Model Polymer End Groups

1. Methyl *l*(−)- Trichloroacetylmandelate

In a dry 10-mL round-bottom flask was placed a stirring bar and methyl *l*(−)-mandelate (1.0 g, 6.1 mmol). A condenser fitted with a rubber septum and a nitrogen inlet and outlet was attached to the flask. Trichloroacetyl chloride (3.0 mL, 20 mmol) was injected into the flask with the methyl *l*(−)-mandelate, dissolving to form a clear, colorless solution. The reaction was performed at room temperature, and the progress of the reaction was followed by ^{1}H-NMR spectroscopy. The reaction was judged to be complete (~3 days) when the α-proton signal of methyl mandelate could no longer be seen at δ 5.20 ppm. Excess trichloroacetyl chloride was removed by Kugelrohr distillation at 0.10 torr and 80°C. The product formed white crystals spontaneously. It was dried in an Abderhalden apparatus at 0.10 torr and 40°C overnight; mp 73.5-75.5°C. ^{1}H NMR in $CDCl_3$: δ Ar-H 7.50 (s), –CH– 6.08 (s), and $COOCH_3$ 3.83 ppm (s). ^{13}C NMR in $CDCl_3$: δ –CO–OCH_3 167.4, –CO–CCl_3 161.2, aromatic carbons 132.1, 129.8, 129.0, 127.5, –CH– 89.0, –CCl_3 77.8, and –$COOCH_3$ 52.9 ppm. $[\alpha]_D^{20}$ = (-)95.4° (methanol, c = 0.1 g/mL) for methyl *l*(−)-trichloroacetylmandelate.

2. Methyl *d*(+)-Trichloroacetylmandelate

In a dry 10-mL round-bottom flask was placed a stirring bar and methyl *d*(+)-mandelate (1.0 g, 6.1 mmol). A condenser fitted with a rubber septum and a nitrogen inlet and outlet was attached to the flask. Trichloroacetyl chloride (3.0 mL, 27 mmol) was injected into the flask with the methyl *d*(+)-mandelate, dissolving to form a clear, colorless solution. The reaction was done at room temperature. Reaction progress was monitored with ^{1}H-NMR spectroscopy

by following the disappearance of the α-proton in methyl mandelate. Reaction was complete after 3 days. Excess trichloroacetyl chloride was destroyed by adding water. The product was extracted into diethyl ether. The ether layer was washed with 2 X 50 mL of 5% aqueous sodium bicarbonate and 2 X 50 mL water and dried over anhydrous magnexium sulfate. After evaporation of the diethyl ether, a white crystalline product was obtained which was dried in an Abderhalden apparatus at 0.1 torr and 40°C overnight; mp 73.5-75.5°C. ^{1}H NMR in $CDCl_3$: δ Ar–H 7.50 (s), –CH– 6.08 (s), and $COOCH_3$ 3.83 ppm (s). ^{13}C NMR in $CDCl_3$: δ –CO–OCH_3 167.4, –CO–CCl_3 161.2, aromatic carbons 132.1, 129.8, 129.0, and 127.5, –CH– 89.0, –CCl_3 77.8, and –$COOCH_3$ 52.9 ppm. $[\alpha]_D^{20}$ = (+)97.7° (methanol, c = 0.1 g/mL) for methyl d(+)-trichloroacetylmandelate.

3. Attempted Preparation of Optically Active Polychloral Oligomer

Tetramethylammonium l(–)-O-acetylmandelate (0.84 g, 3.2 mmol) was placed in a 25-mL Erlenmeyer flask which was then covered with a serum cap. Chloroform (6.0 mL) was injected to dissolve the initiator. The initiator solution was warmed to 50°C, and warm chloral (1.5 mL, 15.4 mmol) was injected into the initiator solution. The initiated chloral was cooled to 0°C overnight with polymerization occurring. The "polymer" was soaked in acidified methanol (10% HCl), washed with methanol, and then dried. Yield 1.1 g (48%). The product was insoluble in water, methanol, diphenyl ether, dimethylsulfoxide, and hexafluoroacetone. Observed chlorine content 72.1%.

RESULTS AND DISCUSSION

Polychloral can be prepared in which the optical activity arises from its helical conformation (i.e., macromolecular asymmetry). This is possible because the monomer polymerizes in an isotactic fashion, the conformational energy barrier of the polymer is high (hindering helix inversion), and asymmetric initiators can lead to a predominance of one of the two helical forms.

Mandelic acid derivatives were selected as chiral initiators for the polymerization of chloral because they permit preparation of both strong (i.e., alkoxides) and weak (i.e., carboxylates) chiral initiators from a common material. This differentiation permits the effect of the distance of the initiator's asymmetric center from the first chloral unit in the polymer in inducing macromolecular asymmetry (i.e., the asymmetric center is β or γ to the chloral unit in the alkoxide and carboxylate initiators, respectively) to be evaluated. An-

other advantage of mandelic acid derivatives is the ready availability of *d*(+)- and *l*(-)-mandelic acids, which provides greater synthesis options in preparing the chiral initiators.

Two sets of tetramethylammonium mandelate initiators were prepared in which the α-hydroxy group of the mandelic acid was either acetylated or methylated. The tetramethylammonium *O*-acetylmandelate (TMAAc) initiators, TMArAc, TMA(-)Ac, and TMA(+)Ac, were prepared by acetylating the appropriate mandelic acid to the *O*-acetylmandelic acids, which were titrated with tetramethylammonium hydroxide to obtain the initiators (Eq. 3). The specific rotation for *l*(-)-*O*-acetylmandelic acid was (-)153°, and it was (+)151° for *d*(+)-*O*-acetylmandelic acid, with respective optical purities of 99 and 98%. The specific rotations of the initiators TMArAc, TMA(-)Ac, and TMA(+)Ac were, respectively, 0, (-)86, and (+)88°. To determine if gross initiator racemization occurred during preparation, TMA(-)Ac was acidified to reisolate the starting product of *l*(-)-*O*-acetylmandelic acid. The specific rotation of the reisolated *l*(-)-*O*-acetylmandelic acid was (-)144°, whereas it was (-)153° originally, indicating that a maximum of 6% racemization could have occurred during initiator preparation. It was also observed that by heating TMA(-)Ac initiator at 75°C for 50 min in chloroform resulted in a maximum loss of 2% of the specific rotation. It appears that initiator racemization is not a major consideration in the use of mandelate derivatives.

TETRAMETHYLAMMONIUM α-METHOXYMANDELATE (TMAαM)

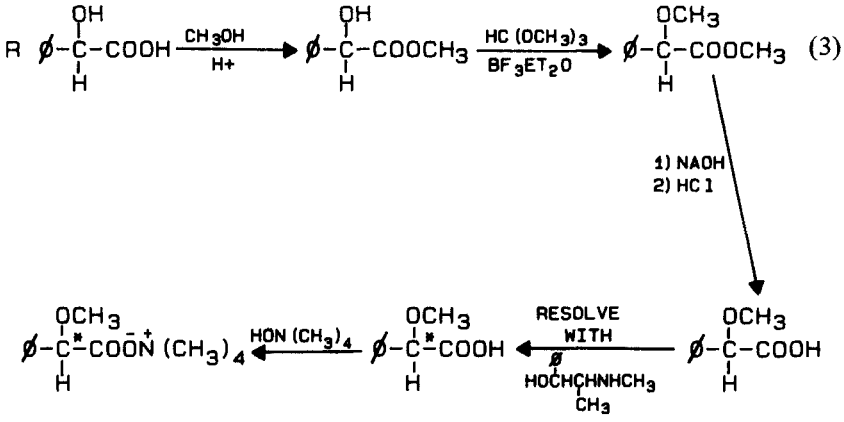


TABLE 1. Optically Active Polychloral Initiated by TMA(+)Ac

Time initiated chloral is held at temperature, min	$[\alpha]_D^{25}$, Film		
	70.0°C	75.0°C	85.0°C
10	-790 ± 70	-1420 ± 160	-1820 ± 220
20	-1130 ± 80	-1760 ± 70	-1860 ± 70
30	-1290 ± 40	-1650 ± 60	-1570 ± 50
50	-1330 ± 40	-1680 ± 50	-1280 ± 70

TMAAc initiators at 0.5 mol% concentration were added to chloral monomer at 70.0, 75.0, or 85.0°C. From this monomer/initiator mixture, polychloral films were cryotachensically cast 10, 20, 30, and 50 min after mixing. Translucent films of polychloral were obtained which became transparent upon soaking in diphenyl ether. The specific rotation reported for any polychloral film was averaged from 15-18 measurements. For polychloral initiated by optically inactive TMArAc, $[\alpha]_D^{25} = (+)5 \pm 10°$, showing no optical activity, as expected.

What is initially striking about the specific rotations for polychloral samples initiated by TMA(+)Ac and by TMA(-)Ac, reported in Tables 1 and 2, is the magnitude of the rotations. The other distinction is that specific rotation typically increases with either increasing monomer/initiator holding time above T_c or with increasing holding temperature.

To allay concerns that the increasing specific rotations might be associated

TABLE 2. Optically Active Polychloral Initiated by TMA(-)Ac

Time initiated chloral is held at temperature, min	$[\alpha]_D^{25}$, Film	
	75.0°C	85.0°C
10	+260 ± 70	+1170 ± 40
20	+500 ± 20	+1150 ± 40
30	+580 ± 30	+1020 ± 40
50	+660 ± 30	+1180 ± 90

with side reactions of the acetyl group, the α-methoxymandelate initiators were investigated. Initial efforts were made to prepare α-methoxymandelic acid directly from the optically active acid(s), but gross racemization occurred. The tetramethylammonium α-methoxymandelates were prepared by a five-step reaction sequence (Eq. 2) including a resolution step (see Experimental part). The specific rotations of *d*(+)- and *l*(-)-α-methoxymandelic acid were (+)135 and (-)144°, respectively, with optical purities of 90 and 96%. The corresponding tetramethylammonium α-methoxymandelate initiators, TMArαM, TMA(+)αM, and TMA(-)αM, had respective rotations of 0, (+)52, and (-)56°.

Polychloral films were prepared with TMAαM initiators as described above for TMAAc initiators. For polychloral initiated with TMArαM, $[\alpha]_D^{25}$ = +10 ± 10°, again showing the expected nominal value of zero.

The specific rotations for polychloral initiated with TMA(+)αM and TMA(-)αM in Tables 3 and 4 are approximately an order of magnitude less than those found when TMA(+)Ac and TMA(-Ac initiators were used

TABLE 3. Optically Active Polychloral Initiated by TMA(+)αM

Time initiated chloral is held at temperature, min	$[\alpha]_D^{25}$, Film			
	65.0°C	70.0°C	80.0°C	85.0°C
10	-105 ± 15	-120 ± 5	-175 ± 20	-160 ± 5
20	-135 ± 10	-160 ± 20	-150 ± 20	-160 ± 20
30	-130 ± 15	-190 ± 15	-160 ± 10	-140 ± 10
50	-140 ± 10	-160 ± 5	-160 ± 10	-160 ± 10

TABLE 4. Optically Active Polychloral Initiated by TMA(-)αM

Time initiated chloral is held at temperature, min	$[\alpha]_D^{25}$, Film	
	70.0°C	80.0°C
10	+210 ± 20	+190 ± 10
20	+180 ± 20	+190 ± 10
30	+190 ± 20	+180 ± 20
50	+180 ± 20	+170 ± 10

(Tables 1 and 2). In spite of the magnitude difference in the specific rotations, the polychlorals made with both sets of asymmetric initiators display an initial increase in specific rotation with increasing monomer/initiator holding time and increasing holding temperature. The same time-temperature dependence was also observed in our work with the alkoxide of methyl mandelate. It is believed to arise from the differences in the kinetic and thermodynamic preferences of the initiation step. Specifically, it is believed that a small fraction of carboxylate has added to chloral monomer above T_c with the resulting configuration of the asymmetric center in the reacted chloral gradually coming to the thermodynamically preferred equilibrium concentration of each enantiomer. As to the eventual decrease in specific rotation, it is believed that the chiral initiators slowly racemize above T_c with the two "chloral" enantiomers approaching equal concentration.

The order-of-magnitude difference in the specific rotations of polychloral initiated by TMAAc and TMAαM should be attributable to the combined steric and electronic differences between the acetate and the methoxy group on the asymmetric center. The acetate group is larger and more polar and should interact more strongly with the first chloral unit in the polymer chain, which should lead to a higher predominance of a given configurational/conformational state in a polymerizing chain and result in higher optical activity. Our work with optically active alkoxide initiators, which results in the asymmetric center being closer to the first chloral unit, resulted in specific rotations higher than reported here for the carboxylate initiators. This implies that steric effects are useful to enhance the induction of macromolecular asymmetric optical activity.

Efforts were made to prepare polychloral oligomers (i.e., $n = 5$) with TMAAc initiators so that it could be determined when the helical conformation makes significant contributions to the optical activity. Product obtained with 16.7 mol% initiator behaved as though it was of high molecular weight, which was confirmed by elemental analysis. A polychloral pentamer has a calculated chlorine content of 57.1%, while the reaction product had 72.1%, which corresponds to a degree of polymerization greater than 1000. This implies that only a fraction of the 0.5 mol% of carboxylate initiator is incorporated into the optically active polychloral and makes a negligible contribution to its optical activity, as was also suggested by model compound work presented elsewhere.

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