

## Haloaldehyde Polymers XXXIII.<sup>†</sup> Polymerization of Chloral with Chiral Anionic Initiators. Stereochemistry of Initiation

*Dedicated to the Memory of the late Professor Ichiro Sakurada*

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**ABSTRACT:** The addition of trichloroacetaldehyde (chloral) to an equimolar amount of the lithium alkoxide of (–)borneol gave, after acetylation with acetic anhydride, diastereomers which were separated by gas chromatography. The products resulted from meso and racemic addition of the (–)borneoxide on chloral. Di-addition products with two chloral residues were also isolated but the individual isomers were not identified. Similar studies with the alkoxides of racemic alcohols were also undertaken. An analysis of their addition products suggested that the individual (*R*) and (*S*) components of the chiral alkoxides added chloral in a stereochemically preferred manner. This preference was most pronounced for those alkoxides which possess a high degree of steric bulk around their chiral carbon atoms.

**KEY WORDS** Chloral Polymerization / Stereochemistry / Racemates as Initiators / Borneol / Isotactic / Helical /

The synthesis of polymers characterized by a preferred helical screw sense is a subject of considerable experimental interest. For helical macromolecules devoid of chirality at the atomic level, a preferred screw direction can be obtained in one of two ways: (1) through the complete or partial resolution of a racemic screw pair, or (2) through the use of chiral initiating species which preferentially induce the formation of one helical screw sense over the other. Using the second approach, we<sup>1–15</sup> have prepared optically active polychloral with specific rotations approaching 5,000 degrees at the sodium D-line. This high optical rotatory power is believed due to macromolecular asymmetry inherent in the polymer's back-bone. Similar studies have been reported for poly(triphenylmethyl meth-

acrylate)<sup>16,17</sup> and the polyisocyanides.<sup>18,19</sup>

The preparation of optically active polychloral based on macromolecular asymmetry, *i.e.*, preferred helicity, requires that the polymer chain form a tight helix with no conformational reversals. Crystallographic evidence indicates that polychloral is isotactic and that it is characterized by 4<sub>1</sub> helical order in the solid state.<sup>20–22</sup> Steric repulsion arising from the polymer's bulky trichloromethyl side groups tends to stabilize the persistence of one screw direction along the polymer chain.

Of critical importance, however, are the initiation and propagation steps at equilibrium which ultimately lead to the formation of the polychloral helix. Chiral initiating species can induce the formation of a single screw direction only if these steps proceed with a high

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degree of stereoselectivity. It has been postulated that the stereochemical outcome of the helix formation process is directly tied to the degree of steric interaction between the asymmetric initiator (or the propagating end of an oligomer) and the incoming monomer units undergoing addition.<sup>7,8,23</sup> Generally, the greater the degree of interaction, the greater the stereoselectivity (racemic or meso attack) associated with a particular addition step.

Earlier work in our laboratory with chiral anionic initiators demonstrated that the highest optical rotations in polychloral were obtained with strong nucleophilic initiating species, *e.g.*, alkoxides, possessing steric bulk around their anionic sites. Weak initiators, or those having little steric bulk, generally afforded far lower rotation values.<sup>5,7</sup>

For the purposes of this study, it was desired to: (1) trap (*via* acetylation) the mono-, di-, and possibly tri-addition products derived from the embryonic stages of the polymerization reaction with chiral alkoxide initiators, (2) determine as much as possible the number of diastereomers present at each addition step, and (3), for the mono-addition product, identify the individual diastereomers formed.

## EXPERIMENTAL

### Materials

Chloral (Montrose Chemical Co.) was heated to reflux for one day over phosphorous pentoxide (granules, 50 g per liters of chloral) and then distilled into a flask which had been flamed out and allowed to cool under a flow of dry nitrogen. The flask was connected to a fractional distillation apparatus which was equipped with a 1.2 m long column packed with glass helices. Under careful exclusion of air (less than 2 ppm oxygen) chloral was heated under total reflux for several days and then distillation was started. In the early stages, the distillation was kept at reflux ratios between 100:1 and 50:1. During this entire time, dry, oxygen-free nitrogen was used to protect the

system against atmospheric oxygen and moisture. Gas chromatography was used to monitor the purity of the distillate. When the purity reached levels of 99.9% or higher, the distillation was terminated and a constant reflux was begun. Monomer grade chloral (purity in excess of 99.9%) was distilled off as needed and was used immediately.

[(1*S*)-endo](−)-Borneol (99%),  $[\alpha]_D^{20}$ :  $-35.6^\circ$  ( $c = 5$ ,  $C_2H_5OH$ ), ( $\pm$ )-2-phenyl-2-butanol (99%), (*R*)-(+)-2-methyl-1-phenyl-1-propanol (98%), ( $\pm$ )-1-phenyl-1-propanol (99%), *s*-phenethyl alcohol (98%), ( $\pm$ )-1-cyclohexylethanol (97%), cyclohexyl methyl ketone (tech.), and phenylmagnesium bromide (3M solution in diethyl ether) were obtained from Aldrich Chemical Co. and were used without further purification.

*t*-Butyl methyl ketone (Aldrich Chemical Co.) was distilled under nitrogen before use. Analysis by Gas Chromatography showed a purity greater than 98%.

Diethyl ether (Mallinckrodt Inc, USP) was dried over sodium metal and distilled under dry nitrogen.

*n*-Butyllithium (1.6 M in hexane) and *t*-butyllithium (1.8 M in *n*-pentane) were obtained from Aldrich Chemical Co. Actual molarities were determined according to the procedure of Winkle *et al.*<sup>24</sup>

Methylcyclohexane (Aldrich Chemical Co., 99%) was dried with 4 Å molecular sieves for at least one week prior to use.

Acetic anhydride (Aldrich Chemical Co., A.C.S. reagent) was used as received.

### Measurements

<sup>1</sup>H NMR spectra were obtained on a JEOL FX-900 90 MHz spectrometer or a Varian EM-390 90 MHz NMR spectrometer. Optical rotation measurements were obtained on a Perkin-Elmer 241 Polarimeter in a microcell (volume: 1 ml, path length: 10.0 cm) at room temperature. Analysis of chloral purity was carried out on a Varian Aerograph 920 gas chromatograph (column: 2 m × 6.4 mm stain-

less steel, packed either with Anakrom AS which was coated with 20% silicone DC-200, or packed with Porapak Q). An Aerograph 1400 gas spectrometer (column: 2 m × 3.2 mm stainless steel, packed either with Chromasorb W which was coated with 3% OV-101 or packed with Chromasorb W-AW coated with 15% OV-275) was used for the analysis of the acetylated addition products formed from the initiating alkoxides and chloral. The column temperature was programmed from 130 to 250°C. The relative amounts of the components in the product mixtures were determined by measuring the peak areas. For preparative work, a Varian Aerograph 920 gas spectrograph was used (column: 1.5 m × 6.4 mm, aluminum) packed with Chromasorb W, 45/60 mesh, coated with 10% Carbowax 20 M).

#### Procedures

*Synthesis of 1-t-Butyl-1-phenyl Ethanol.* A 500 ml 3-neck flask equipped with a magnetic stirrer, a dropping funnel, and a condenser was connected to a vacuum line and was flamed out under dry nitrogen. After the flask had cooled to room temperature under dry nitrogen, phenylmagnesium bromide (60 g) was added and with stirring, *t*-butyl methyl ketone was added dropwise. A 25°C water bath was used to control the reaction temperature. After the addition of the ketone was completed, the reaction mixture was heated to reflux for 2 h, then cooled to room temperature. Crushed ice (40 g) was added followed by 150 ml of a 50% aqueous NH<sub>4</sub>Cl solution. The organic phase was separated and washed once with saturated aqueous sodium bisulfite solution, twice with a sodium bicarbonate solution, and then water. The organic phase was dried over anhydrous magnesium sulfate and then distilled. The main fraction was collected at 60°C at 0.4 mm. GC analysis indicated purity greater than 90%.

<sup>1</sup>H NMR spectrum: δ 7.18–7.60 ppm (–C<sub>6</sub>H<sub>5</sub>), 3.40 ppm (–OH), 1.56 ppm (–CH<sub>3</sub>),

and 0.90 ppm (–OC(CH<sub>3</sub>)<sub>3</sub>).

*Synthesis of 1-t-Butyl-1-cyclohexyl Ethanol.* To a 250 ml 3-neck flask equipped with a magnetic stirrer which had been dried as before was added methylcyclohexane (100 ml) and cyclohexyl methyl ketone (6.9 ml, 50 mmol). *t*-Butyllithium (3.4 ml, 54 mmol, 1.8 M solution in *n*-pentane) was slowly injected into the flask with a gas tight syringe. The reaction mixture was warmed until the reaction became exothermic. After the addition of the lithium reagent was completed, the mixture was heated to 70°C for 8 h. When the reaction was judged complete, 30 ml of water was added to quench the reaction. The organic phase was separated and dried over anhydrous magnesium sulfate. GC analysis of the crude mixture indicated the presence of a trace of unreacted ketone. The mixture was distilled and a single component was collected in the range of 65–66°C at 0.3 mm. Purity as judged by GC was 99%.

<sup>1</sup>H NMR spectrum: δ 2.50 ppm (–OH), 1.1–1.8 ppm (–C<sub>6</sub>H<sub>11</sub>), 1.01 ppm (–CH<sub>3</sub>), and 0.95 ppm (–C(CH<sub>3</sub>)<sub>3</sub>).

*Addition Reaction of Chloral to Lithium Borneoxide and Endcapping with Acetic Anhydride.* A 100 ml 3-neck flask had been oven dried at 110°C for 3 h, flamed out, and then allowed to cool to room temperature under dry nitrogen. (–) Borneol (1.60 g, 10.4 mmol) was placed into the flask and methyl cyclohexane was injected. Most of the borneol dissolved in the solvent but as the contents were cooled to –5°C, some of the borneol precipitated forming a fine suspension. *t*-Butyllithium (5.0 ml, 9.0 mmol) was added very slowly to the contents of the flask with a gas tight syringe and the mixture was gradually warmed to about 50°C. Chloral (1.0 ml, 10 mmol) which had been warmed to 50°C was added with a warmed syringe to the initiator suspension, forming a clear solution. After 30 min the reaction was quenched with acetic anhydride (1.0 ml, 10.5 mmol). The reaction vessel was allowed

to remain at the reaction temperature for about 30 min before being cooled to room temperature. The reaction mixture was poured into water, the organic phase was separated, washed with aqueous sodium carbonate solution and then dried with sodium sulfate. The solution was distilled under reduced pressure. A forerun of solvent and low boiling compounds was removed and the middle fraction was collected between 94 and 96°C at 0.15 mm. Yield, 1.32 g (38%).

Gas chromatography of the fraction showed two major peaks representing the two diastereomeric addition products and a trace of lower boiling impurities.

<sup>1</sup>H NMR spectrum:  $\delta$  6.23 ppm (—OCH<sub>2</sub>—(CCl<sub>3</sub>)—O—), 6.19 ppm (—OCH<sub>2</sub>(CCl<sub>3</sub>)—O—), 4.22—4.39 ppm (—CH<sub>2</sub>—O—CH(CCl<sub>3</sub>)—), 2.10—2.18 ppm (protons on bornyl ring), 2.18 ppm (—COCH<sub>3</sub>), 0.97 ppm (—CH<sub>3</sub>), 0.87 ppm (—CH<sub>3</sub>), and 0.86 ppm (—CH<sub>3</sub>).

*Elemental Analysis.* Calcd: C, 48.92%; H, 6.15%; Cl, 30.94%. Found: C, 48.79%; H, 6.39%; Cl, 30.94%.

*Separation and Collection of the Diastereomers of 1-Acetoxy-1-borneoxy-2,2,2-trichloroethane Formed above by Gas Chromatography.* The gas chromatographic analysis of the two diastereomers was performed on a Varian Aerograph 920 equipped with a 1.5 m × 6.4 mm aluminum column packed with Chromosorb W, 45/60 mesh, coated with 10% Carbowax 20M. Operation parameters were as follows: column temp: 170°C, detector temp: 200°C, injection temp: 210—220°C, carrier gas: He (50 ml min<sup>-1</sup>), sample amount for each injection: 10 microliter: 35 injections. A small U-tube glass was used to collect each isomer. No cold trap was used as air-cooling was sufficient to condense the individual components. 27 mg diastereomer #1 (first peak) (purity: 90%) and 24 mg diastereomer #2 (second peak) (purity: 82%) were collected and used for optical rotation measurements.

Optical rotation: Diastereomer #1  $[\alpha]_D^{25} = -29.3^\circ$  ( $c = 2.7$ , ethanol). After correcting

for 100% purity, diastereomer #1  $[\alpha]_D^{25} = -27.9^\circ$ . Diastereomer #2  $[\alpha]_D^{25} = -39.0^\circ$  ( $c = 2.4$ , ethanol). After correcting for 100% purity, diastereomer #2  $[\alpha]_D^{25} = 41.4^\circ$ .

*Preparation of the Di-Addition Product between Chloral and Lithium Borneoxide.* The procedure was similar to that employed for the synthesis of the mono-addition product described above except that the molar ratio of chloral to the alkoxide was changed from 1:1 to 2:1 (or even higher) and the acetate end-capping step was carried out at temperatures below 20°C to promote the addition of the second chloral molecule to the chloral terminated alkoxide. A typical gas chromatogram of the product mixture showed two large peaks after the two diastereomer peaks for the mono-addition product and a set of smaller peaks at longer retention times corresponding to the linear trimer fraction.

*Addition Reaction of Chloral with Various Racemic Lithium Alkoxide Species.* The general procedure for the addition of chloral to the alkoxide initiators, followed by acetate end-capping, was similar to that used for the synthesis of the mono-addition product between (—)-borneoxide and chloral except that *n*-butyllithium was used to generate the alkoxide species from the racemic alcohols and the addition temperature was kept between 40—43°C. These mono-addition products were purified by vacuum distillation and were characterized by both GC and <sup>1</sup>H NMR spectroscopy. The stereoselectivity of the addition step was estimated from the GC peak ratios and <sup>1</sup>H NMR data. The following compounds were synthesized:

*1,1,1-Trichloro-4-*t*-butyl-4-phenyl-3-oxa-2-pentyl Acetate.* C<sub>6</sub>H<sub>5</sub>—C(*t*-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)—O—CH(CCl<sub>3</sub>)—OCOCH<sub>3</sub>, purity: greater than 90%, GC: two peaks (peak ratio, 52:48), <sup>1</sup>H NMR spectrum:  $\delta$  7.25—7.65 ppm (aromatic, C<sub>6</sub>H<sub>5</sub>), 6.31 ppm (—O—CH(CCl<sub>3</sub>)), 6.47 ppm (—O—CH<sub>2</sub>(CCl<sub>3</sub>)), 2.09 ppm (—OCOCH<sub>3</sub>), 1.86 ppm (—OCOCH<sub>3</sub>), 1.71 ppm (—CH<sub>3</sub>), 1.49 ppm (—CH<sub>3</sub>), and 0.95 ppm (—C(CH<sub>3</sub>)<sub>3</sub>).

*1,1,1-Trichloro-4-methyl-4-phenyl-3-oxa-2-hexyl Acetate.*  $C_6H_5-C(CH_3)(C_2H_5)-O-CH(CCl_3)-OCOCH_3$ , purity: 95%, GC: two peaks (peak ratio, 70 : 30),  $^1H$  NMR spectrum:  $\delta$  7.30–7.60 ppm ( $C_6H_5$ ), 6.38 ppm ( $-O-CH(CCl_3)-O-$ ), 2.06 ppm ( $-OCOCH_3$ ), 1.80 ppm ( $-OCOCH_3$ ), 1.54 ppm ( $-CH_3$ ), 2.10–1.70 ppm ( $-CH_2-$ ), and 0.83 ppm ( $-CH_3$ ).

*1,1,1-Trichloro-4-phenyl-4-isopropyl-3-oxa-2-butyl Acetate.*  $C_6H_5-CH(i-C_3H_7)-O-CH(CCl_3)-OCOCH_3$ , because only small amount of the product was obtained, special purification was not carried out. GC: two peaks (peak ratio, 45 : 55).

*1,1,1-Trichloro-4-phenyl-3-oxa-2-hexyl Acetate.*  $C_6H_5-CH(C_2H_5)-O-CH(CCl_3)-OCOCH_3$ , GC: two peaks (peak ratio, 45 : 55),  $^1H$  NMR spectrum:  $\delta$  7.35–7.41 ppm ( $-C_6H_5$ ), 6.33 ppm ( $-O-CH(CCl_3)-O-$ ), 6.01 ppm ( $-O-CH(CCl_3)-O-$ ), 4.37 ppm ( $C_6H_5-CH(C_2H_5)-O-$ ), 2.18 ppm ( $-O-COCH_3$ ), 1.54 ppm ( $-O-COCH_3$ ), 1.64–2.10 ppm ( $-CH_2-$ ), 0.95 ppm ( $-CH_3$ ), and 0.90 ppm ( $-CH_3$ ).

*1,1,1-Trichloro-4-phenyl-3-oxa-2-pentyl Acetate.*  $C_6H_5-CH(CH_3)-O-CH(CCl_3)-OCOCH_3$ , purity 95%, GC: two peaks (peak ratio, 55 : 45),  $^1H$  NMR spectrum:  $\delta$  7.30–7.60 ppm ( $-C_6H_5$ ), 6.30 ppm ( $-O-CH(CCl_3)-O-$ ), 5.59 ppm ( $-O-CH(CCl_3)-O-$ ), 5.00 ppm ( $C_6H_5-CH(CH_3)-O-$ ), 2.15 ppm ( $-O-COCH_3$ ), 1.70 ppm ( $-O-COCH_3$ ), 1.56 ppm ( $-CH_3$ ), and 1.52 ppm ( $-CH_3$ ).

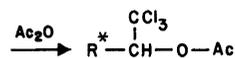
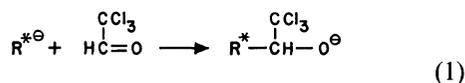
*1,1,1-Trichloro-4-cyclohexyl-4-*t*-butyl-3-oxa-2-pentyl Acetate.*  $C_6H_{11}C(CH_3)(t-C_4H_9)-O-CH(CCl_3)-OCOCH_3$ , purity: greater than 80%, GC: one peak,  $^1H$  NMR spectrum:  $\delta$  6.49 ppm ( $-O-CH(CCl_3)-OH$ ), 6.46 ppm ( $-O-CH(CCl_3)-O-$ ), 3.13 ppm ( $-O-COCH_3$ ), 2.16 ppm ( $-O-COCH_3$ ), 1.39 ppm ( $-CH_3$ ), 1.27 ppm ( $-CH_3$ ), 1.09 ppm ( $-C(CH_3)_3$ ), and 1.05 ppm ( $-C(CH_3)_3$ ).

*1,1,1-Trichloro-4-cyclohexyl-3-oxa-2-pentyl Acetate.*  $C_6H_{11}-CH(CH_3)-O-CH(CCl_3)-OCOCH_3$ , purity: greater than 85%, GC: two peaks (peak ratio, 20 : 80),  $^1H$  NMR spectrum:  $\delta$  6.29 ppm ( $-O-CH(CCl_3)-O-$ ), 6.27 ppm

( $-O-CH(CCl_3)-O-$ ), 3.60–3.94 ppm ( $C_6H_{11}-CH(CH_3)-$ ), 2.17 ppm ( $-O-COCH_3$ ), 1.30–1.90 ppm ( $-C_6H_{11}$ ), 1.19 ppm ( $-CH_3$ ), and 1.13 ppm ( $-CH_3$ ).

## RESULTS AND DISCUSSION

Chiral initiating alkoxides were allowed to react with chloral and the addition products were quenched with acetic anhydride (eq 1).



Normally, the addition products contained one chloral unit, but under certain reaction conditions, molecules with two chloral residues could be isolated. The products were identified by gas chromatography (GC) and proton nuclear magnetic resonance ( $^1H$  NMR) spectroscopy.

Treatment of (–)borneol with 0.90 equiv. of *t*-butyllithium afforded the borneoxide. A slight excess of the alcohol was used to avoid the production of any achiral initiating species. The addition of 1.0 equiv. of chloral to the (–)borneoxide suspension resulted in a clear solution. After 30 min the reaction was terminated with acetic anhydride. After work up and removal of solvent and lower boiling compounds by distillation, a middle

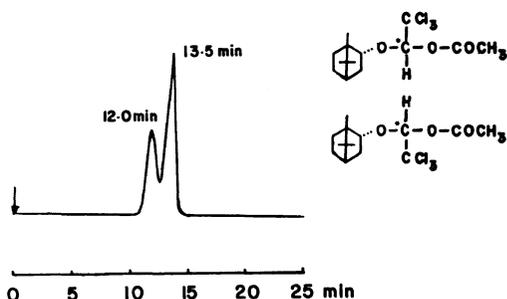
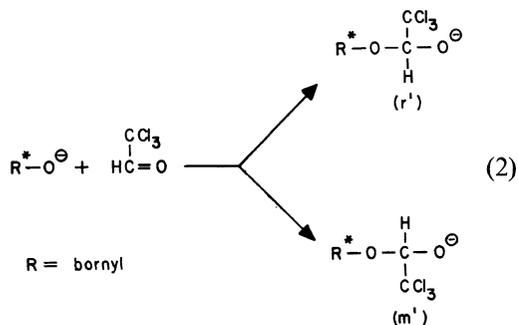


Figure 1. Gas chromatogram of mixture obtained from reaction of chloral with lithium (–)borneoxide (1:1).

fraction was collected between 94–96°C (0.15 mm) in 38% yield. GC analysis (Figure 1) showed this fraction to consist of two components with retention times of 12.0 and 13.5 min representing the two isomers, *i.e.*, diastereomers, resulting from *meso/racemic* attack of the (–)borneoxide on chloral. This assignment was consistent with <sup>1</sup>H NMR data (Figure 2) (eq 2).



We have investigated further the stereochemistry associated with this addition process and have found it to be highly temperature sensitive. As Figure 3 shows, the (–)borneoxide is most stereoselective at reaction temperatures near 40°C, affording one diastereomer in far greater amounts than the other. At progressively higher temperatures, this selectivity drops steadily until, near 90°C, either mode of attack becomes equally probable.

At the present time, we are unable to account for the apparent decrease in the (–)borneoxide's selectivity at lower temperatures. Related studies with the achiral initiator lithium *t*-butoxide have shown that a preference for the formation of di-, tri-, and ultimately higher-addition products exists as the reaction temperature is lowered in this system. This observation is consistent with the thermodynamic concept of ceiling temperature. It is conceivable that precipitation of higher oligomers from the reaction mixture (at temperatures below 40°C) could shift the equilibrium between the diastereomeric products present in the liquid phase. However, this

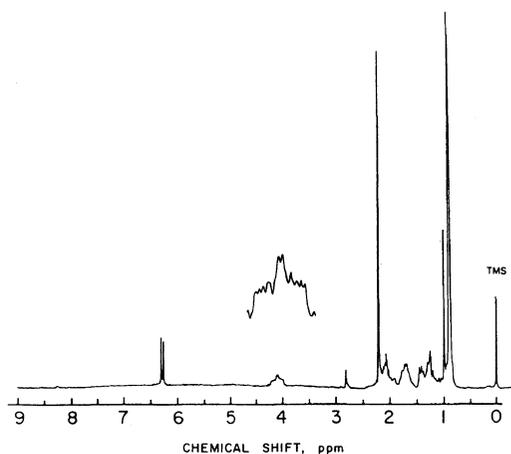


Figure 2. <sup>1</sup>H NMR spectrum of chloral-(–)borneoxide mono addition product.

hypothesis has not been verified.

The stereochemistry of the addition process is also sensitive to the molar ratio of chloral to borneoxide at constant temperature. As Figure 4 shows, below a 2:1 ratio of monomer to initiator, the stereoselectivity associated with the first addition step falls off sharply. As the ratio is raised, the selectivity of the (–)borneoxide ultimately levels off, remaining constant for a wide range of the monomer to initiator ratios, including those encountered for the polymerization reaction, *e.g.*, 500:1.

When a relatively large excess of chloral was added to the borneoxide initiator, and the end-capping and the work up steps were repeated as before, a number of components could be identified by GC analysis (Figure 5). These correspond to the mono-, di-, and tri-addition products formed between the initiating alkoxide and one, two, or three molecules of chloral, respectively. For the dimer fraction, four diastereomers can be expected depending on whether the first and second chloral addition steps proceeded in *meso* or *racemic* fashion. For the linear trimer fraction (GC retention time of 55–57 min), eight isomeric products are theoretically possible. As the GC data indicate however, only one major and one minor component are observed, suggesting

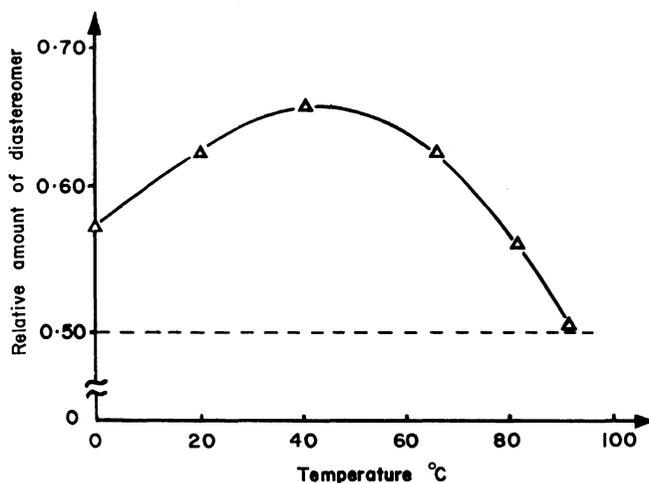


Figure 3. Relative amount of one diastereomer formed over the other in the reaction of chloral with lithium (-)-borneoxide (1:1).

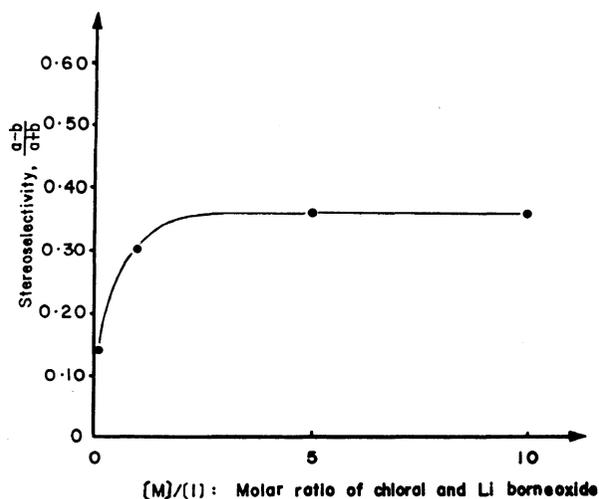


Figure 4. Stereoselectivity of addition step as a function of molar ratio of chloral:(-)-borneoxide.

that at this stage in the oligomerization of chloral, the formation of several isomeric products are highly favored relative to all others. We believe that these products result from *meso* and *racemic* addition of the (-)-borneoxide on chloral (albeit with unequal frequency) followed, in both cases, by additional *meso* placements of chloral to give two linear trimer species. These expectations are consistent with theoretical calculations carried

out by Professor Abe in Tokyo for the lithium *t*-butoxide case.<sup>23</sup>

The stereochemistry of the addition of monomer units and its implication to the helix formation process is outlined schematically in Figure 6. Focusing initially on the first addition step (ONE), chiral initiator can add chloral in either *meso* ( $m'$ ) or *racemic* ( $r'$ ) fashion. Because of the asymmetric nature of the initiator species, one mode of at-

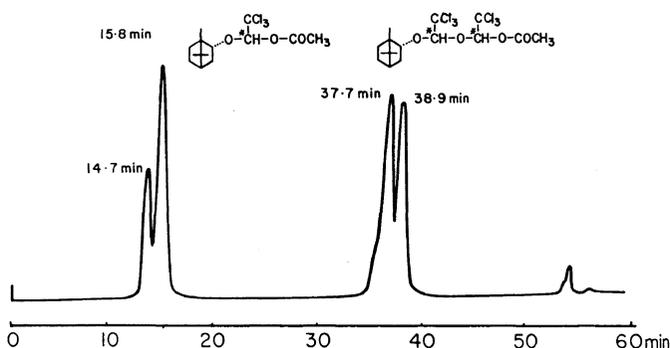


Figure 5. Gas chromatogram of mixture obtained from reaction of chloral with lithium (–)borneoxide (2:1).

ONE	m' MD	r' ML
TWO	m' m MD	r' m ML
	m' r ML	r' r MD
THREE	m' m m MD	r' m m ML
	m' m r ML	r' m r MD
	m' r m ML	r' r m MD
	m' r r MD	r' r r ML

L: Handedness of Helix  
 m: Meso      r: Racemic Placements of Monomer Units.  
 m': Meso      r': Racemic Placements of First Monomer Unit To Initiator.  
 M: Continued meso Placements of Monomer Units

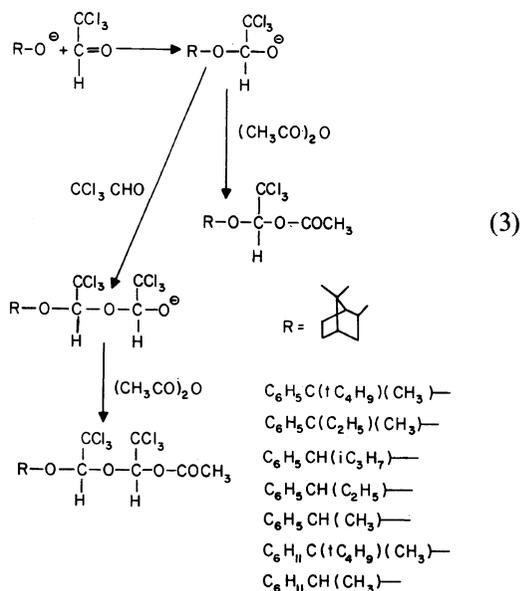
Figure 6. Stereochemistry of addition of monomer units and implications to the helix formation process.

tack will be more probable than the other. Because polychloral is isotactic, subsequent addition steps will generally proceed by *meso* (*m*) placement, yielding two helical coils (D and L) where one is predominant over the other. The greater the initiator's stereoselectivity for this addition step, the greater the predominance of one screw direction.

The embryonic stages of helix development can be more closely followed if the addition of the second chloral unit (TWO) and the third chloral unit (THREE) are also considered. As

Figure 6 shows, incorporation of an odd number of *racemic* (*r*) placements into the oligomer will act to invert the direction of the helical screw ultimately formed. An even number of *r* addition steps will have the same effect as total *m* addition. As this analysis indicates, the stereochemistry associated with the initiation and early propagation steps is of critical importance. Only if each step occurs with a high degree of stereoselectivity can a preferred helical screw direction be incorporated into isotactic polychloral.

The lithium alkoxides of racemic alcohols



Polymerization of Chloral with Chiral Initiators

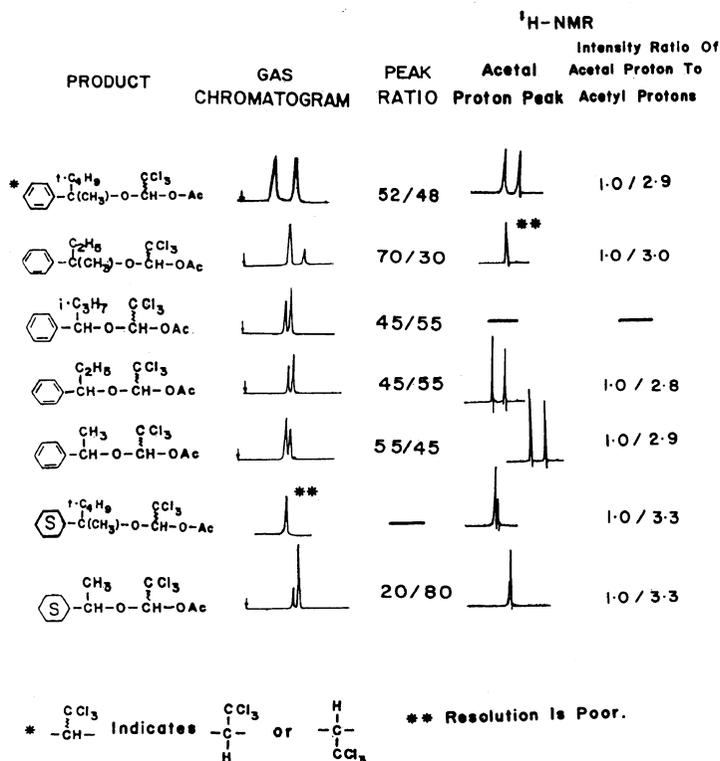


Figure 7. Stereochemistry of the addition of racemic lithium alkoxides to chloral (1 : 1).

were also used to probe the initiation step. Acetylated mono-addition products were prepared as before, and identifications were made by GC and <sup>1</sup>H NMR analyses. The (*R*) and (*S*) antipodes of each alkoxide can attack chloral in *meso* (*m'*) or *racemic* (*r'*) fashion, resulting in the formation of four stereoisomeric products. Hypothetically, if the (*R*) component of the alkoxide favors *m'* addition of chloral, then its mirror (*S*) isomer must favor *r'* addition with the same frequency, resulting in the production of enantiomeric (*R*)*m'* and (*S*)*r'* products. Unless the (*R*) and (*S*) alkoxide antipodes are completely stereoselective for their respective initiation steps (stereospecific process), a smaller quantity of the less probable (*R*)*r'* and (*S*)*m'* isomers will also result. When GC analyses are carried out on achiral supports, (*R*)*m'* and (*S*)*r'* will give rise to one peak, and their di-

astereomeric (*R*)*r'* and (*S*)*m'* isomers will give a second peak in the chromatogram. The stereochemistry of the addition step can be determined from analysis of the peak ratios. A racemic alkoxide that is not stereospecific will afford two peaks of equal size.

Figure 7 lists the results of this study for a variety of racemic alkoxide initiators. This is quite similar to the addition of the second chloral unit of lithium *t*-butoxide investigated earlier. As the data suggest, bulky alkoxides, e.g., cyclohexyl methyl methoxide, generally afforded peak ratios deviating greatest from unity. In fact, *t*-butyl cyclohexyl methyl methoxide gave an addition product with a poorly resolved single peak, suggesting, perhaps, some high degree of stereoselectivity in the initiation step. Interestingly, the achiral tricyclohexyl methoxide failed to afford any chloral addition products, apparently the

result of excessive steric hindrance of the alkoxide group.

We are presently continuing this study with a range of alkoxide species in an attempt to optimize the stereoselectivity of the initiation process. Ultimately, we hope to better determine what role the second and third addition steps play in the establishment of complete helicity in isotactic polychloral.

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#### REFERENCES

1. L. S. Corley, Ph.D. Dissertation, University of Massachusetts, Amherst (1979).
2. L. S. Corley and O. Vogl, *Polym. Bull.*, **3**, 211 (1980).
3. W. J. Harris and O. Vogl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **22**, 309 (1981).
4. K. Hatada, S. Shimizu, H. Yuki, W. J. Harris, and O. Vogl, *Polym. Bull.*, **4**, 179 (1981); *Corrections*, **4**, 683 (1979).
5. W. J. Harris, Ph.D. Dissertation, University of Massachusetts, Amherst (1982).
6. K. Hatada, T. Kitayama, S. Shimizu, H. Yuki, W. J. Harris, and O. Vogl, *J. Chromatogr.*, **248**, 63 (1982).
7. G. D. Jaycox, M.S. Thesis, University of Massachusetts, Amherst (1984).
8. J. Zhang, G. D. Jaycox, and O. Vogl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **26**, 156 (1985).
9. O. Vogl, L. S. Corley, W. J. Harris, G. D. Jaycox, and J. Zhang, *Makromol. Chemie, Suppl.*, **13**, 1 (1985).
10. O. Vogl, *The Chemist*, **62(9)**, 16 (1985).
11. O. Vogl, Preprints, Japan-U.S. Polymer Symposium, Kyoto, Japan, 1985, p 7.
12. T. R. Doyle and O. Vogl, *Polym. Bull.*, **14**, 6 (1985).
13. O. Vogl and J. Zhang, *Polym. Prepr., SPSJ Annual Meeting, Kyoto, Japan*, **35(1)**, 45 (1986).
14. T. R. Doyle and O. Vogl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **27(1)**, 375 (1986).
15. O. Vogl and G. D. Jaycox, *Chem. Tech.*, **16**, 698 (1986).
16. Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, and H. Yuki, *J. Am. Chem. Soc.*, **101**, 4763 (1979).
17. Y. Okamoto, K. Suzuki, and H. Yuki, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3043 (1980).
18. R. J. M. Nolte, A. J. M. van Beijnen, and W. Drenth, *J. Am. Chem. Soc.*, **96**, 5932 (1974).
19. W. Drenth and R. J. M. Nolte, *Acc. Chem. Res.*, **12**, 30 (1979).
20. P. Kubisa, L. S. Corley, T. Kondo, M. Jacovic, and O. Vogl, *Polym. Eng. Sci.*, **21**, 829 (1981).
21. E. G. Brame, A. M. Raevsky, G. K. Semin, G. D. Jaycox, and O. Vogl, *Polym. Bull.*, **10**, 521 (1983).
22. G. Wasai, T. Iwata, K. Hirano, M. Kuragano, T. Saegusa, and J. Furukawa, *Kogyo Kagaku Zasshi*, **67**, 1920 (1964).
23. A. Abe, K. Tasaki, K. Inomata, and O. Vogl, *Macromolecules* **19**, 2707 (1986).
24. M. Winkle, J. M. Lansinger, and R. C. Ronald, *Chem. Commun.*, 88 (1980).