# Haloaldehyde polymers: 32. Polymerization of chloral with lithium t-butoxide—stereochemistry of initiation and early propagation steps*

**Jingyun Zhang, Gary D. Jaycox† and Otto Vogl‡**
*Polytechnic University, 333 Jay Street, Brooklyn, NY 11201, USA*
*(Received 8 June 1987; revised 18 September 1987; accepted 30 September 1987)*

Oligomeric addition products formed between lithium t-butoxide and one, two, three or more equivalents of trichloroacetaldehyde were trapped by acetylation and then identified by gas chromatography and proton nuclear magnetic resonance spectroscopy. Individual diastereomers were recognized. Product formation was found to be sensitive to both the addition and endcapping temperatures employed.

**(Keywords: trichloroacetaldehyde; chloral; lithium t-butoxide; oligomers; stereoisomers; diastereomers; acetate endcapping; gas chromatographic analysis; proton nuclear magnetic resonance analysis)**

## INTRODUCTION

The polymerization of trichloroacetaldehyde (chloral) can be readily effected by a variety of anionic initiators using a cryotachensic polymerization technique[1,2]. In this two-step process, initiator is first homogeneously dispersed in chloral monomer at elevated temperatures. Polymerization is then induced by rapidly cooling the initiated monomer solution (holding solution) below its threshold polymerization temperature. For pure chloral monomer, this temperature lies near 58°C. Polychloral obtained in this way is completely isotactic and semicrystalline with a $4_1$ helical conformation in the solid state[3,4].

Although the cryotachensic process has been widely used to prepare polymers of chloral[5-7], the nature of the anionic species in the holding solution prior to the onset of polymerization has remained largely unexplored. In our laboratory, 90 MHz nuclear magnetic resonance ($^1$H n.m.r.) studies[8] have demonstrated that the composition of the holding solution is dependent upon the nucleophilicity of the initiating anion used to polymerize chloral. When weak nucleophiles, e.g. carboxylates, were employed in these studies, only monomer and unreacted initiator were detected in the holding solutions at elevated temperatures. In contrast, stronger nucleophiles like lithium t-butoxide were found to give chloral addition products under similar conditions. Here, adduct formation is highly favoured by the generation of an inductively stabilized propagating anion, which arises from attack of the initiator on one molecule of chloral. Because of the limited sensitivity inherent in the n.m.r. technique, the detection of smaller quantities of higher oligomeric addition products was difficult. The presence of these anions at or slightly above 58°C has been postulated in several studies and is fully consistent with the thermodynamic concept of a threshold polymerization temperature[7,9].

The stereochemistry associated with the early chain growth steps in the holding solutions has been of special concern. Although achiral initiators like lithium t-butoxide can add chloral in a stereo-random fashion, subsequent propagating steps must become more stereoselective towards *meso* addition if the polymer's $4_1$ helical coil is to form. Theoretical calculations[10] have suggested that this selectivity reaches its maximum very early in the oligomerization process. Thus, for strong nucleophilic initiators, the embryonic stages of helix development may be intimately tied to processes occurring in the holding solutions prior to the formal polymerization step.

In an attempt to verify these predictions, a new generation of studies aimed at better probing the stereochemistry associated with the early stages of chain growth was undertaken in our laboratory. Initiated monomer solutions were prepared with lithium t-butoxide at elevated temperatures. These were then treated with acetic anhydride in an attempt to trap the anionic species present in equilibrium. The acetylated products were analysed by gas chromatography (g.c.) and $^1$H n.m.r. spectroscopy. A number of oligomeric addition products were isolated depending upon the reaction conditions employed. Their individual diastereomeric components were identified. The results of this work are detailed below. A similar study with chiral (−)borneoxide as the initiating species is reported elsewhere[11].

## EXPERIMENTAL

### *Materials*

Chloral (Montrose Chemical Co.) was heated to reflux for one day over phosphorus pentoxide (50 g granules per litre of chloral) and then distilled into a flask that had been flamed out and allowed to cool under a flow of dry

* This paper is dedicated to Professor Takeo Saegusa, Kyoto University, Kyoto, Japan, on the occasion of his 60th birthday with our warmest personal wishes

† Present address: Department of Chemistry, Dartmouth College, Hanover, NH 03755, USA

‡ To whom correspondence should be addressed

0032-3861/88/040707-06$03.00

nitrogen. The flask was transferred to a fractional distillation apparatus equipped with a 1.2 m column packed with glass helices. Under careful exclusion of air (less than 2 ppm oxygen), chloral was heated under total reflux for several days. The chloral was then slowly distilled at a reflux ratio between 100:1 and 50:1. During this time, dry, oxygen-free nitrogen was used to protect the system from atmospheric oxygen and moisture. Gas chromatography was used to monitor the purity of the distillate. When purity levels reached 99.9% or higher, the distillation step was terminated. The remaining chloral was maintained in the still under a gentle reflux. Polymerization-grade chloral (>99.9%) was freshly distilled from the system prior to use.

Lithium t-butoxide (Alfa-Ventron, 99%) was sublimed and stored under dry nitrogen.

Methylcyclohexane (Aldrich, 99%) was distilled from sodium metal under nitrogen and stored over sodium wire.

Acetic anhydride (Aldrich, >99%) and cyclohexane (Aldrich, $H_2O < 0.005\%$) were used as received.

*Measurements*

$^1H$ n.m.r. spectra were obtained at room temperature on a JEOL FX-90Q 90 MHz spectrometer in acetone-$d_6$. Tetramethylsilane (TMS) was used as a reference. G.c. analysis of chloral purity was carried out with a Varian Aerograph 920 equipped with a 2 m × 6 mm stainless-steel column. Anakrom coated with 20% silicone DC-200 (1000 cP) or Poropak Q served as a column packing. G.c. analysis of the acetylated addition products formed between lithium t-butoxide and chloral was carried out with a Varian Aerograph 1400 equipped with a 2 m × 3 mm stainless-steel column. The column was packed with Chromasorb W, which had been coated with 3% OV-101. The column temperature was programmed from 110 to 250°C. The relative amounts of components in the product mixtures were determined by integrating peak areas.

*Procedures*

*Synthesis of 1,1,1-trichloro-4,4-dimethyl-3-oxa-2-pentyl acetate (mono-chloral addition product).* A solution of lithium t-butoxide (4.26 g, $5.32 \times 10^{-2}$ mol in 18 ml cyclohexane) was placed in a dry serum capped test tube and brought to 40°C in an oil bath. To this was syringed freshly distilled, pre-warmed (40°C) chloral (3.0 ml, $3.1 \times 10^{-2}$ mol). The addition afforded an immediate reaction and the contents of the test tube were noted to warm slightly. The reaction mixture was agitated and allowed to re-equilibrate to 40°C over a period of 15 min. Acetic anhydride (5.0 ml, $5.3 \times 10^{-2}$ mol) was then syringed into the test tube affording a small quantity of solid precipitate. After 1 h, the mixture was cooled from 40°C to room temperature and treated with deionized water (10 ml). The organic phase was isolated, washed first with aqueous sodium carbonate, then water until neutral, and dried over anhydrous sodium sulphate. The solution was distilled at atmospheric pressure and the main fraction collected between 197 and 200°C to give 4.41 g (91%) of a yellow liquid. Purity as judged by g.c.: 95%. $^1H$ n.m.r.: $\delta$ 6.35 (–O–CH($CCl_3$)–O–), 2.14 (–O–CO–$CH_3$), 1.32 (($CH_3$)$_3$C–O–). Analysis: calculated for $C_8H_{13}O_3Cl_3$, C 36.46%, H 4.97%, Cl 40.36%; found, C 35.90%, H 4.94%, Cl 40.15%.

*Synthesis of chloral diacetate.* To a mixture of acetic anhydride (16 ml, $1.7 \times 10^{-1}$ mol) and concentrated sulphuric acid (10 drops) at 80°C was slowly added freshly distilled chloral (8.3 ml, $8.6 \times 10^{-2}$ mol) with a dry syringe. The reaction mixture was brought to reflux for 5 h and then cooled, followed by aqueous extraction. The reaction product was distilled under reduced pressure and the main fraction collected at 89°C (2.5 mmHg) to afford about 12.5 g (58%) of product. Purity as judged by g.c.: 99%. $^1H$ n.m.r.: $\delta$ 7.15 (–O–CH($CCl_3$)–O–), 2.17 ($CH_3$–CO–O–). Analysis: calculated for $C_6H_7O_4Cl_3$, C 28.88%, H 2.83%, Cl 42.63%; found, C 28.90%, H 2.84%, Cl 42.59%.

*Synthesis of 1,1,1-trichloro-4-trichloromethyl-6,6-dimethyl-3,5-dioxa-2-heptyl acetate (di-chloral addition product).* A solution of lithium t-butoxide (0.92 g, $1.15 \times 10^{-2}$ mol in 35 ml methylcyclohexane) was placed in a dry flask and brought to 50°C in an oil bath. To this was syringed freshly distilled, pre-warmed (50°C) chloral (2.25 ml, $2.33 \times 10^{-2}$ mol). The addition afforded a yellow solution, which was cooled to 15°C. Acetic anhydride (1.1 ml, $1.17 \times 10^{-2}$ mol) was then slowly added with vigorous stirring. The reaction mixture was treated with deionized water (30 ml). The organic phase was separated, washed first with aqueous sodium carbonate, then water, and dried over anhydrous sodium sulphate. The solution was distilled at atmospheric pressure to remove solvent and lower-boiling compounds. G.c. and $^1H$ n.m.r. analyses of the crude residue showed the presence of several acetylated products, as follows.

*Mono-chloral product.* This had the shortest retention time, and was identical in all respects to the 1,1,1-trichloro-4,4-dimethyl-3-oxa-2-pentyl acetate prepared above.

*1,1,1-Trichloro-5-trichloromethyl-3-oxa-2-pentyl acetate.* This was a side product formed from a Tishchenko reaction on chloral, and was identical to the product synthesized independently from 2,2,2-trichloroethoxide and chloral, followed by acetate endcapping[12].

*Di-chloral product.* The product was isolated in pure form by distillation under reduced pressure. G.c. showed two diastereomers, with isomer ratio 29:71. $^1H$ n.m.r.: $\delta$ 6.97 (–O–C$\underline{H}$($CCl_3$)–O–CO–$CH_3$), 5.48 (($CH_3$)$_3$C–O–C$\underline{H}$($CCl_3$)–O–), 2.30 (–O–CO–$CH_3$), 1.41 (($CH_3$)$_3$C–O–); and $\delta$ 6.58 (–O–CH($CCl_3$)–O–CO–$CH_3$), 5.54 (($CH_3$)$_3$C–O–C$\underline{H}$($CCl_3$)–O–), 2.26 (–O–CO–C$\underline{H}_3$), 1.48 (($CH_3$)$_3$C–O–).

Trace quantities of higher oligomeric products were also observed by g.c. at longer retention times.

*Synthesis of linear tri- and tetra-chloral addition products.* The procedure for the preparation of higher chloral addition products was similar to that employed for the synthesis of the dimer (1,1,1-trichloro-4-trichloromethyl-6,6-dimethyl-3,5-dioxa-2-heptyl acetate) except that the acetic anhydride quenching step was carried out below 15°C and the molar ratio of chloral to alkoxide was greater than 2.0. Lower-boiling products were removed by distillation. G.c. and $^1H$ n.m.r. analyses of the residue indicated that a number of acetylated products were present, including residual amounts of the di-chloral adduct, as follows.

*Tri-chloral product* (54%). G.c. showed three diastereomers, with isomer ratio 79:14:7. $^1H$ n.m.r. (major isomer): $\delta$ 6.85 (–O–C$\underline{H}$($CCl_3$)–O–$COCH_3$), 6.02

(–O–CH(CCl$_3$)–O–), 5.63 ((CH$_3$)$_3$C–O–CH(CCl$_3$)–O–), 2.39 (–O–CO–CH$_3$), 1.47 ((CH$_3$)$_3$C–O–).

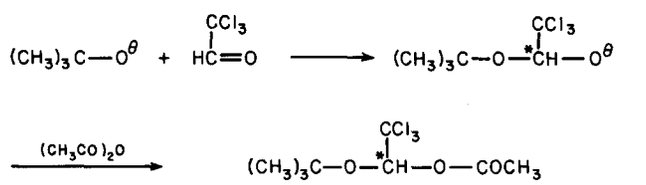
*Tetra-chloral product* (33%). G.c. showed two diastereomers, with isomer ratio 77:23. $^1$H n.m.r. (major isomer): $\delta$ 6.96 (O–CH(CCl$_3$)–O–COCH$_3$), 6.14 (–O–CH(CCl$_3$)–O–CH(CCl$_3$)–O–COCH$_3$), 5.95 ((CH$_3$)$_3$C–O–CH(CCl$_3$)–O–CH(CCl$_3$)–O–), 5.80 ((CH$_3$)$_3$C–O–CH–(CCl$_3$)–O–), 2.34 (–O–CO–CH$_3$), 1.45 ((CH$_3$)$_3$–O–).

The tri- and tetra-chloral addition products were isolated by distillation under reduced pressure. Their diastereomer ratios were not altered during this step.

## RESULTS AND DISCUSSION

The stereochemistry associated with the early stages of chloral polymerization was investigated in this study. Oligomeric addition products formed between lithium t-butoxide and one, two, three or more equivalents of chloral were trapped by quenching the reactions with acetic anhydride. The products were then identified by gas chromatography and $^1$H n.m.r. spectroscopy.

The formation of an acetylated mono-chloral addition product is outlined below:



(1)

Two enantiomeric species are expected, depending upon the mode of attack by the initiating anion. To limit the generation of higher oligomers, chloral was treated with a slight excess of lithium t-butoxide (cyclohexane, 40°C). The resulting anion was then endcapped with acetic anhydride (40°C). After workup and removal of lower-boiling compounds by distillation, the desired product was isolated as a single component by g.c. in 91% yield. The $^1$H n.m.r. spectrum of the product (*Figure 1*) was consistent with its proposed structure. The n.m.r. analysis of chloral diacetate (prepared for comparison) showed similar resonance patterns for the acetal and acetyl methyl protons.

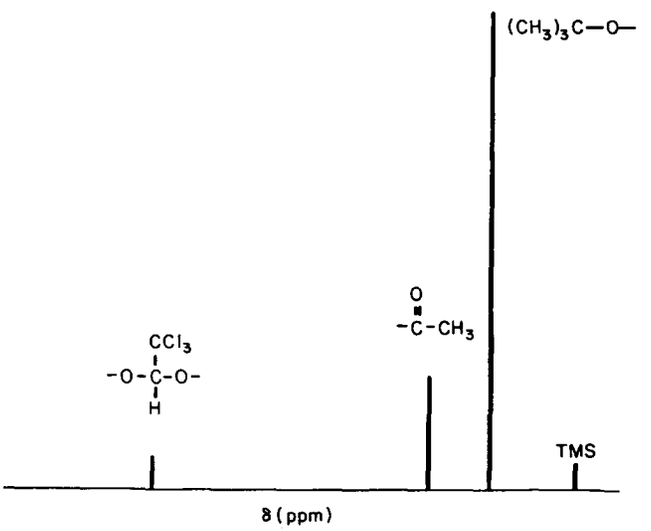



**Figure 1** $^1$H n.m.r. spectrum of 1,1,1-trichloro-4,4-dimethyl-3-oxa-2-pentyl acetate

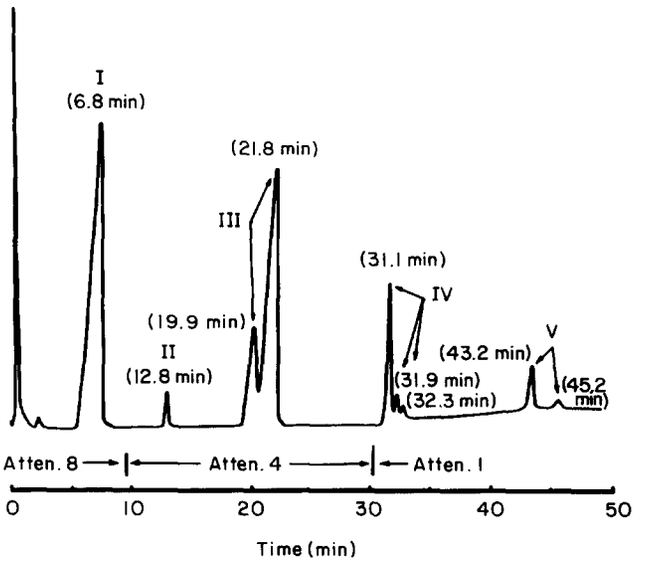



**Figure 2** Gas chromatogram of mixture obtained from the reaction of chloral with lithium t-butoxide (≥2:1), followed by acetate endcapping. Column temperature 110–250°C at 4°C min$^{-1}$

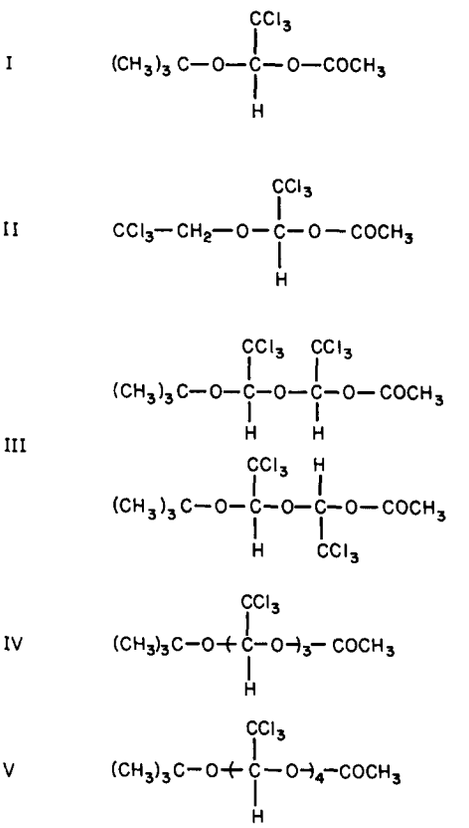



**Figure 3** Products obtained from the reaction of chloral with lithium t-butoxide (≥2:1), followed by acetate endcapping. See *Figure 2*

When two or more equivalents of chloral were added to the butoxide, and the endcapping step was carried out at 15°C or below, a number of acetylated components were identified by g.c. after workup (*Figure 2*). These were found to correspond to the mono-, di-, tri- and tetra-chloral addition products that had formed during the reaction (*Figure 3*). Included also was a small peak at 12.8 min. This was later identified as a side product presumably generated from a Tishchenko reaction on chloral. Peak assignments in the gas chromatogram were confirmed by $^1$H n.m.r. spectroscopy. A proton spectrum of the mixture is provided in *Figure 4*. Resonance

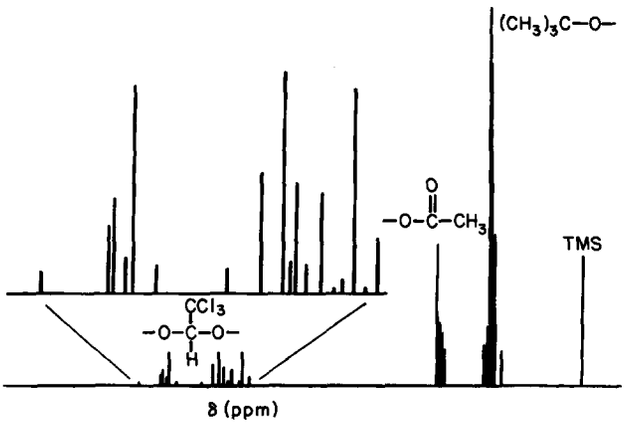
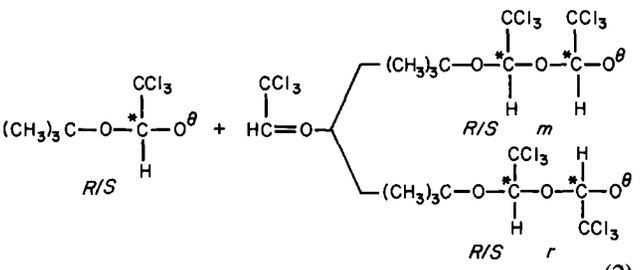



**Figure 4** $^1$H n.m.r. spectrum of mixture of acetylated chloral addition products

assignments for individual chloral addition products are given in the experimental section.

A closer inspection of the chromatogram in *Figure 2* indicated that the higher addition products *each* consisted of several resolvable components. The formation of a di-chloral adduct is illustrated below (endcapping step not shown):




(2)

Four stereoisomers are expected depending on the stereochemistry associated with each addition step. When a g.c. analysis of the mixture is carried out on an achiral support, the *Rm* and *Sr* enantiomers should give rise to one peak, and their diastereomeric *Rr* and *Sm* isomers should afford a second peak in the chromatogram. This is consistent with the g.c. data in *Figure 2*, which clearly show the presence of two resolvable components in the dimer fraction at 19.9 and 21.8 min. The large disparity in their peak areas suggests that the formation of one set of enantiomeric products is more highly favoured during the reaction. $^1$H n.m.r. analysis of the pure di-chloral adduct lends additional support to the g.c. data, as two distinct sets of resonances are observed in the proton spectrum (*Figure 5*).

A closer inspection of the linear trimer and tetramer fractions was gained by first removing most of the lower-boiling products under reduced pressure. Careful attention was given to ensuring that the trimer and tetramer adducts were not removed during this step. A gas chromatogram of the resulting mixture is included in *Figure 6*. For the tri-chloral product, four separate diastereomeric components are expected, again depending on whether each addition step proceeds by meso (*m*) or racemic (*r*) placement. For the linear tetra-chloral adduct, a total of eight such components are theoretically possible. As the g.c. data indicate, however, three resolvable components (IVa–c) comprise the trimer fraction, and only two distinct components (Va,b) are observed for the tetramer adduct. Moreover, for both the trimer and tetramer fractions, a *single* component is clearly dominant in each case.

These data suggest that, as chain growth proceeds past the dimer stage, subsequent chloral addition steps become more stereoselective, limiting the number of isomeric components formed prior to the endcapping step. An analogous series of studies with (−)borneoxide as the initiating anion afforded similar results[11]. There, g.c. analysis of the acetylated tri-chloral adduct showed the presence of only one major resolvable isomer.

These observations are consistent with molecular mechanics calculations for polychloral and several of its oligomeric model compounds. Using the MM2 force field program[13], Abe has suggested that the growth of an oligomeric chain becomes highly stereoselective towards *m* addition once the trimer stage is reached[10]. Additional *m* placements then generate the first turn in the polymer's $4_1$ helix. At this point in the growth process, random *r* placements are suppressed along the propagating chain.

The results of the present study, taken in conjunction with Abe's findings, shed considerable light on the origins of helicity in polychloral. If it can be assumed that the acetate endcapping step used here efficiently traps all anionic species present in the initiated monomer solution (and does not alter their equilibrium ratios), then it would appear that the helix-building process begins very early during the growth of the polychloral chain. If the monomer is cryotachensically polymerized with strong,

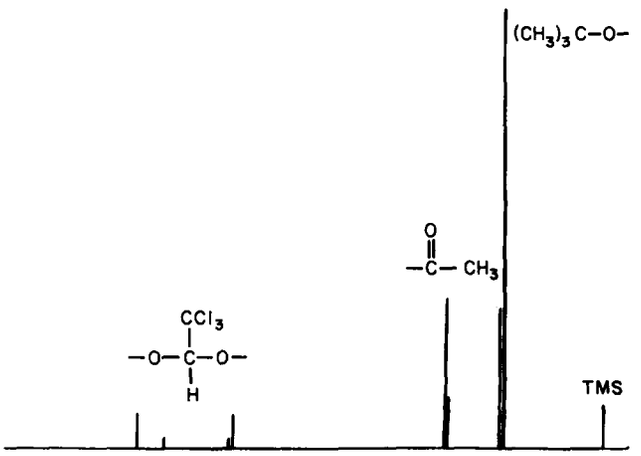



**Figure 5** $^1$H n.m.r. spectrum of 1,1,1-trichloro-4-trichloromethyl-6,6-dimethyl-3,5-dioxa-2-heptyl acetate (diastereomers)

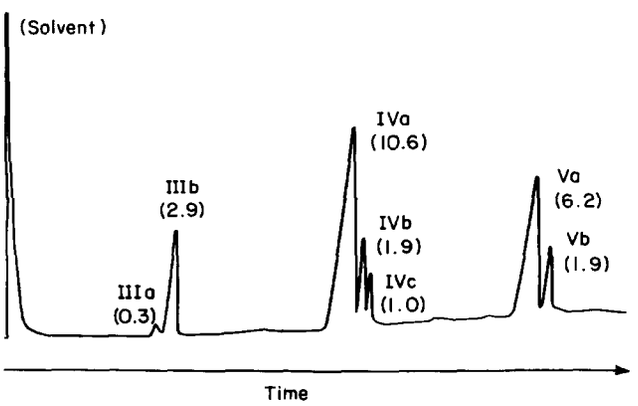



**Figure 6** Gas chromatogram of higher-boiling products obtained from the reaction of chloral with lithium t-butoxide, followed by acetate endcapping. Column temperature 130–250°C at 2°C min$^{-1}$

nucleophilic initiators, the embryonic stages of helix development might well be under way in the holding solutions at elevated temperatures prior to the formal polymerization step. A proper understanding of the origins of helicity in polychloral is essential for the synthesis of a polymer possessing a single screw direction[6,7].

Acetylated oligomer formation was further investigated as a function of the endcapping temperature employed during the reaction sequence. These data are summarized in *Tables 1–4*. As is evident, the formation of higher oligomeric products is favoured at lower endcapping temperatures—consistent with the thermodynamic concept of a threshold polymerization temperature. Interestingly, the diastereomer ratio (determined by integrating appropriate g.c. peaks) for *each* of the higher oligomeric products was found to be invariant to these temperature changes. The influence of endcapping temperature on the formation of the acetylated di-chloral addition product is presented in *Figure 7*.

Also studied was the generation of 1,1,1-trichloro-5-trichloromethyl-3-oxa-2-pentyl acetate, a side product presumed to arise from a Tishchenko reaction on chloral. The compound was synthesized independently from 2,2,2-trichloroethoxide and chloral, followed by acetylation with acetic anhydride[12]. The formation of the side product as a function of both 'initiation' and endcapping temperatures is outlined in *Figure 8*. As expected, increases in either temperature were found to afford greater quantities of this product. When the initiation and endcapping steps were both carried out near 65°C, the relative amount of the compound obtained in the product mixture approached 60%.

**Table 1** Acetylated product formation as a function of endcapping temperature[a]

| Endcapping temp. (°C) | Acetylated product ratio[b] mono:di |
|---|---|
| 40 | 7.7 |
| 18 | 3.6 |
| 0 | 2.5 |

[a] Initiation temperature 40°C
[b] Determined by integration of g.c. peak areas

**Table 2** Acetylated oligomer formation as a function of endcapping temperature[a]

| Endcapping temp. (°C) | Acetylated product (%)[b] | | | |
|---|---|---|---|---|
| | mono | di | tri | tetra |
| 20 | 70.0 | 28.0 | 1.6 | 0.4 |
| 8 | 67.6 | 29.7 | 2.0 | 0.6 |

[a] Initiation temperature 40°C
[b] Determined by integration of g.c. peak areas

**Table 3** Diastereomer ratio of di-chloral addition product as a function of endcapping temperature[a]

| Endcapping temp. (°C) | Diastereomer ratio[b] |
|---|---|
| 65[c] | 24:76 |
| 40 | 25:75 |
| 22 | 24:76 |
| 15 | 29:71 |
| 5 | 26:74 |
| 0 | 27:73 |

[a] Initiation temperature 40°C. Molar ratio chloral to lithium t-butoxide 2:1
[b] Determined by integration of g.c. peak areas
[c] Initiation temperature 65°C

**Table 4** Diastereomer ratio for resolved tri- and tetra-addition products as a function of endcapping temperature[a]

| Endcapping temp. (°C) | Resolved diastereomer ratio[b] | |
|---|---|---|
| | Trimer fraction | Tetramer fraction |
| 20 | 79:14:7 | 86:14[c] |
| 8 | 80:13:7 | 86:14[c] |

[a] Initiation temperature 40°C
[b] Determined by integration of g.c. peak areas
[c] Accurate measurement difficult because of small quantities of product formation

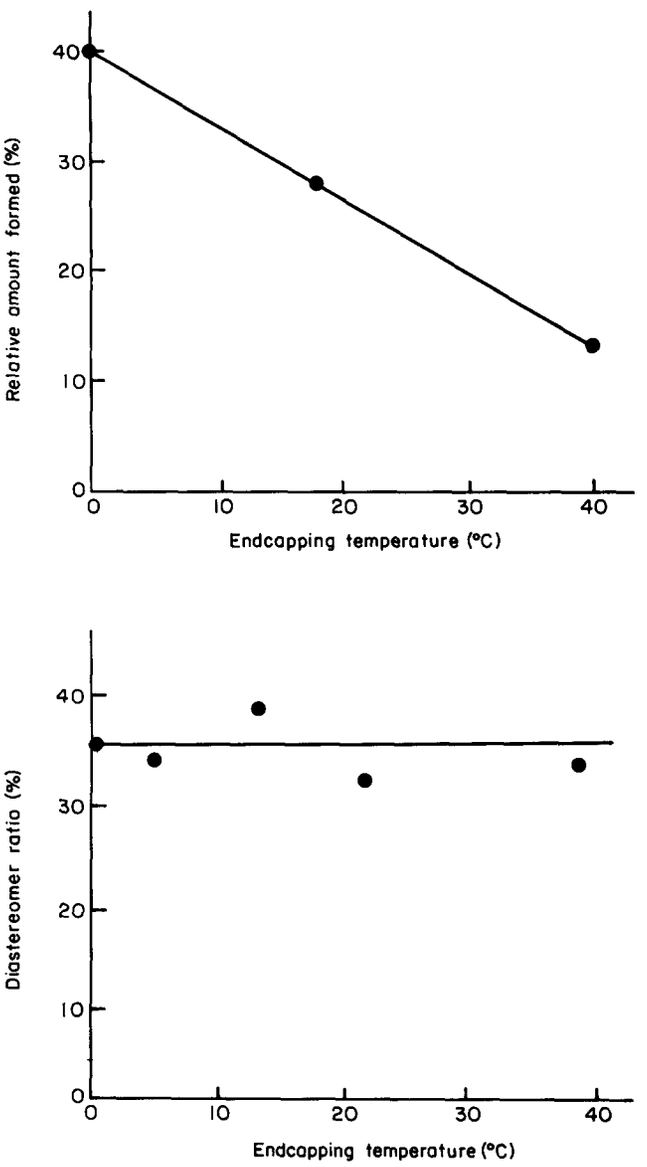



**Figure 7** Relative amount (%) of di-chloral addition product formed and resulting diastereomer ratio as a function of endcapping temperature (chloral to t-butoxide about 2:1; initiation temperature 40°C)

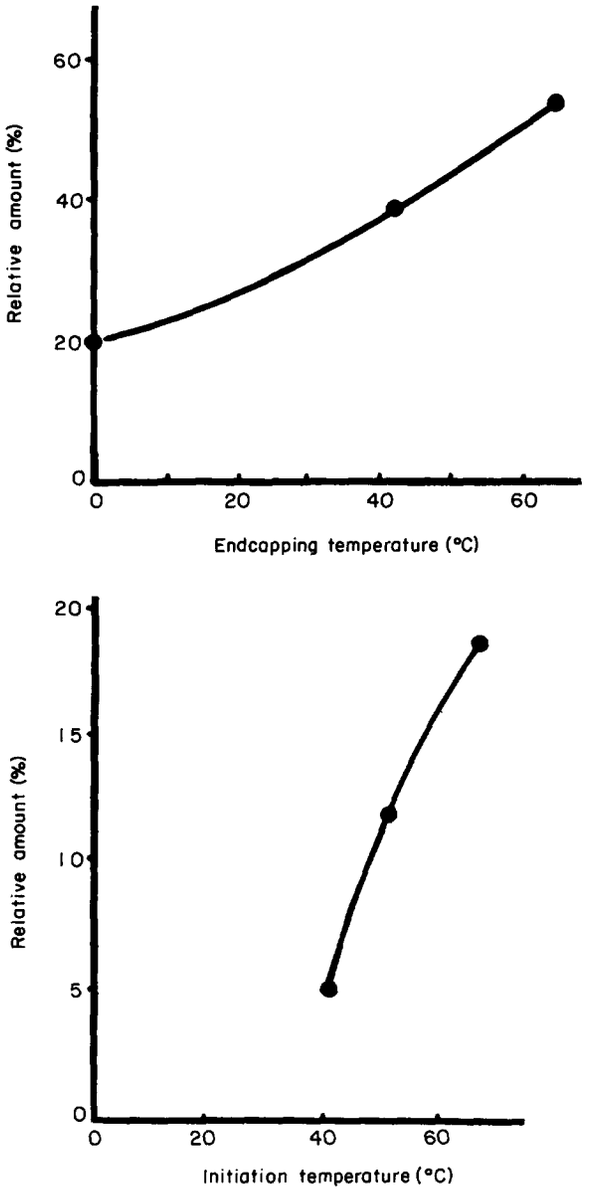



**Figure 8** Relative amount (%) of side product formed as a function of endcapping temperature (for initiation temperature of 65°C) and as a function of initiation temperature (for endcapping temperature of 0°C)

## CONCLUSIONS

The stereochemistry associated with the early stages of chloral polymerization was investigated in this study. Chloral monomer was treated with lithium t-butoxide (at varying molar ratios) under conditions that mimicked the cryotachensic polymerization process. The oligomeric species that resulted were trapped with acetic anhydride and analysed by g.c. and $^1$H n.m.r. spectroscopy. The analytical data suggest that early chain growth steps become stereoselective once the trimer stage is reached. This observation is consistent with theoretical calculations which show *m* propagation steps are highly favoured at this point. Oligomeric product formation was further shown to be dependent upon the temperature at which the acetate endcapping step was carried out. Finally, the formation of an undesired side product was minimized by carrying out the initiation and endcapping steps at reduced temperatures.

## ACKNOWLEDGEMENTS

This investigation was supported in part by the National Science Foundation (Grant Number DMR 8302134-01), the PPG Company, and the Herman F. Mark Chair of the Polytechnic University. J. Zhang would like to thank the Shanghai Institute of Organic Chemistry, Shanghai, PRC, for granting him a leave of absence. G. D. Jaycox is presently a Ph.D. candidate in the Department of Chemistry at Dartmouth.

## REFERENCES

1 Vogl, O., Miller, H. C. and Sharkey, W. H. *Macromolecules* 1972, **5**, 658
2 Kubisa, P., Corley, L. S., Kondo, T., Jacovic, M. and Vogl, O. *Polym. Eng. Sci.* 1981, **21**, 829
3 Wasai, G., Iwata, T., Hirono, K., Kuragano, M., Saegusa, T. and Furukawa, J. *Kogyo Kagaku Zasshi* 1964, **67**, 1920
4 Brame, E. G., Raevsky, A. M., Semin, G. K., Jaycox, G. D. and Vogl, O. *Polym. Bull.* 1983, **10**, 521
5 Corley, L. S., Ph.D. Dissertation, University of Massachusetts, Amherst, 1979
6 Harris, W. J., Ph.D. Dissertation, University of Massachusetts, Amherst, 1982
7 Jaycox, G. D., M.S. Thesis, University of Massachusetts, Amherst, 1984
8 Corley, L. S. and Vogl, O. *J. Macromol. Sci.* (*A*) 1980, **14** (7), 1105
9 Zhang, J., Jaycox, G. D. and Vogl, O. *Polym. Prepr., ACS Div. Polym. Chem.* 1985, **26** (1), 156
10 Abe, A., Tasaki, K., Inomata, K. and Vogl, O. *Macromolecules* 1986, **19**, 2707
11 Zhang, J., Jaycox, G. D. and Vogl, O. *Polym. J.* 1987, **19**, 603
12 Unpublished results from our laboratory
13 Allinger, N. L. and Yuh, Y. H. *Quantum Chem. Program Exch.* 1980, **12**, 395