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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Rational Design of Macromolecular Structures: Focusing on the Embryonic Stages of Polymerization

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**To cite this Article** Vogl, Otto , Jaycox, Gary D. , Simonsick Jr., William J. and Hatada, Koichi(1991) 'Rational Design of Macromolecular Structures: Focusing on the Embryonic Stages of Polymerization', Journal of Macromolecular Science, Part A, 28: 11, 1267 – 1284

**To link to this Article:** DOI: 10.1080/00222339108054099

**URL:** <http://dx.doi.org/10.1080/00222339108054099>

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## **RATIONAL DESIGN OF MACROMOLECULAR STRUCTURES: FOCUSING ON THE EMBRYONIC STAGES OF POLYMERIZATION**

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### **ABSTRACT**

Acetate-terminated oligomers of fluoral, chloral and bromal, prepared with the lithium alkoxides of *tert*-butanol and (–)-borneol, were analyzed by gas chromatography, polarimetry, NMR and mass spectroscopies, and by single crystal x-ray diffraction methods. The configurational and conformational properties of the “embryonic” adducts were found to depend strongly on the relative size of the trihalomethyl side group in these systems. The results of our efforts, summarized here, help to shed new light on the origins of helical geometry and crystalline order in polymers of the perhaloacetaldehydes.

## INTRODUCTION

Polymers can be viewed from both a macromolecular and a supramolecular perspective. Locally, the configurational and conformational properties of a polymer chain are capable of impacting directly on the supramolecular ordering found in a bulk polymer sample. The consequences of how "local" macromolecular structure influences polymer morphology is of special concern for the rational design of macromolecules having well-defined or tailor-made solid-state properties.

The chains of simple, regular polymers like linear polyethylene [1] tend to crystallize readily when cooled below their crystalline melting points. Generally, these polymers share a high degree of conformational flexibility at temperatures above their glass transitions. Consequently, regular morphological structures can develop upon crystallization. A wide variety of morphologies have been observed, including lamellar arrangements [2-4] and, on a larger scale, spherulites [5, 6], with the latter often connected by interpenetrating "tie molecules." The crystallization process can be facilitated by allowing the polymer chains to remain as mobile as possible or by subsequently annealing a partially crystallized sample at temperatures slightly under the melting point. In some instances, particularly for ultrahigh molecular weight polyethylene, extended chain conformations have been obtained by carrying out the crystallization process under high pressures [7], by "gel spinning" [8], or, to some extent, by employing solid-state extrusion techniques [9]. When manipulated in this manner, polyethylene samples have been fabricated with tensile moduli that approach the theoretical upper limit for a carbon-carbon chain. Similar results have been reported for polytetrafluoroethylene [10, 11].

Many polyolefins and polyaldehydes are capable of crystallizing in the solid state [12]. Generally, the more regular their "local" structures, the more readily crystallization takes place. Supramolecular ordering of polymer chains in a bulk sample is dictated in part by the configuration of the main chain, by the size and polarity of pendant side groups, and by the presence of "impurities," e.g., unusual linkages, branches, or a large number of endgroups, in the macromolecule. Of particular relevance here, isotactic polymers generally assume helical geometries in the crystalline state with alternate chain bonds occupying *trans* and *gauche* conformations. Because extended helical structures are readily incorporated into a regular crystalline lattice, the helical arrangement of the polymer backbone is highly favored under these circumstances [13].

Crystallographic studies have shown that polyoxymethylene crystallizes under equilibrium conditions to give a  $2_1$  helical structure [14] while isotactic polypropylene forms a  $3_1$  helical array [12, 15]. For the higher isotactic polyolefins and polyaldehydes, helical geometry in the crystalline state is governed by the size, polarity, and chirality of the side group, with left- and right-handed  $3_1$ ,  $7_2$ , and  $4_1$  helical symmetries being particularly common [12, 16]. As a rule, polymers that lack a high degree of stereoregularity, or those with a large number of "local" irregularities, usually take on more random chain conformations and are often devoid of extensive crystalline order in the solid state.

The preparation of semicrystalline macromolecules having well-defined or tailor-made solid-state properties clearly demands that close attention be paid to the polymerization reaction. In recent years, a new generation of studies has probed initiation and early chain growth steps as a way of gaining a better overall picture of the various chemical processes responsible for ordered structure in polymers. Notable efforts include the oligomerization of chloral [17–23], vinyl phenyl sulfoxide [24], triphenylmethyl methacrylate [25, 26], and, more recently, methyl methacrylate [27–30] by anionic polymerization methods and the synthesis of styrene-acrylonitrile oligomers by free radical methodology [31]. Oligomers have been synthesized as model compounds for polypropylene and polydiacetylene [32–34]. Of related interest are studies of various helicene oligomers which have been found to exhibit interesting chiroptical properties in solution [35].

Some of the earliest efforts in this area were performed in our laboratory and involved the synthesis of stable, acetate-terminated chloral oligomers, prepared with lithium *tert*-butoxide as an initiating species [17–20]. By following the growth of the embryonic polychloral chain "from the ground up," we were able to examine the stereochemistry associated with early chain growth steps and to demonstrate clearly that the polymer's isotactic  $4_1$  helical structure forms very early in the polymerization reaction [21, 22]. More recently, we have expanded the scope of our studies to include oligomers of fluoral and bromal and have employed the chiral initiator lithium (1*S*,2*R*,4*S*)-(–)-bornyl oxide to further aid our investigation [23, 36]. In most cases the oligomeric adducts prepared have been separated by chromatography and analyzed by NMR and mass spectroscopies, and when possible, by single crystal x-ray diffraction and chiroptical methods. The full experimental details of these efforts are communicated elsewhere [21–23, 36–46]. What follows is a concise summary of some of our more recent progress in this area.

## RESULTS AND DISCUSSION

### Oligomers of Fluoral

The treatment of lithium *tert*-butoxide with a stoichiometric excess of fluoral monomer, followed by acetate endcapping with acetic anhydride, leads to a number of acetylated products which can be resolved and separated by gas chromatography (GC) after work up. These correspond to the linear uni- (ca. 25%), di- (42%), tri- (19%), tetra- (8%), penta- (2.5%), hexa- (1.3%), hepta- (0.5%), octa- (0.3%), nona- (0.2%), and higher-chloral (trace) addition products that form during the reaction. An additional peak due to the by-product, fluoral diacetate, has also been experimentally observed. Peak assignments in the chromatogram have been confirmed by potassium ionization of desorbed species ( $K^+$ IDS) mass spectroscopy and by NMR methods. The  $K^+$ IDS ionization technique [47, 48] was employed in an attempt to minimize fragmentation of the oligomers during mass spectral analysis. Relevant mass spectral data for each oligomer fraction are compiled in Table 1. A representative  $^{19}\text{F}$ -NMR spectrum for the acetate-terminated trimer fraction is provided in Fig. 1.

Closer inspection of the GC and NMR data gleaned from our studies has revealed that individual fluoral trimer, tetramer, pentamer, and higher ordered fractions are each comprised of a number of diastereomeric components, strongly suggesting that in its embryonic stages of development, the growth of the polyfluoral chain occurs in a stereorandom fashion, leading to a significant amount of atactic, i.e., nonhelical, structure. These observations are fully consistent with earlier reports which have shown that the anionic polymerization of fluoral often leads to amorphous, atactic (or partially isotactic) polymer samples [49, 50].

The use of the chiral initiator lithium (–)-bornyl oxide for our oligomerization reactions has furnished a second “family” of linear, acetate-capped fluoral oligomers which have also been subjected to NMR and mass spectral analyses (see Table 1). As for the *tert*-butoxide initiator case, the analytical data obtained in our laboratory strongly support the notion that early fluoral chain growth steps proceed in a nonstereospecific manner.

### Oligomers of Chloral

As reported in several earlier studies [21–23], the addition of excess chloral monomer to lithium *tert*-butoxide or lithium (–)-bornyl oxide, followed by acetate endcapping, gives rise to a number of stable oligo-

TABLE 1.  $K^+$  IDS Mass Spectroscopic Data for *tert*-Butoxide-Initiated (TBI) and Bornyl Oxide-Initiated (BI), Acetate-Terminated Perhaloaldehyde Oligomers

Oligomer	Pseudomolecular ion <sup>a</sup> ( $[M]K^+$ , in Daltons)					
	Fluoral		Chloral		Bromal	
	TBI	BI	TBI	BI	TBI	BI
Diacetate	239		289		423	
Unimer	253	333	302	381	437	517
Dimer	351	431	449	529	717	797
Trimer	449	529	597	677	999	1077
Tetramer	547	627	745	825	1279	1357
Pentamer	645	725	893	973	1560	1641
Hexamer	743	823	1041	1119		
Heptamer	841	921	1189			
Octamer	939	1019				
Nonamer	1037	1117				
Decamer	1135	1215				
Undecamer	1233					

<sup>a</sup>Experimentally observed values. Typically  $\pm 1$  of calculated values.

meric products which are readily amenable to GC analysis. Linear species up to the heptamer (*tert*-butoxide initiated) and hexamer (bornyl oxide initiated) have now been synthesized in our laboratory. These derivatives have been identified by  $^1H$ - and  $^{13}C$ -NMR methods (Figs. 2 and 3) and by  $K^+$  IDS mass spectroscopy (see Table 1). Mass spectral data for the (–)-bornyl oxide-initiated unimer and hexamer adducts are provided in Figs. 4 and 5 along with chlorine isotope distribution calculations for these samples. Figure 6 shows similar isotope calculations for the experimentally elusive (–)-bornyl oxide-initiated nonamer analogue.

Detailed inspection of GC data for chloral oligomers prepared with lithium *tert*-butoxide reveals the existence of a dominant diastereomeric component in the trimer and tetramer fractions, and the presence of only one isomeric species in the higher oligomer fractions. Similar observations have been made for the (–)-bornyl oxide-initiated chloral oligomer family. For the *tert*-butoxide-initiated oligomer series, the *dominant*

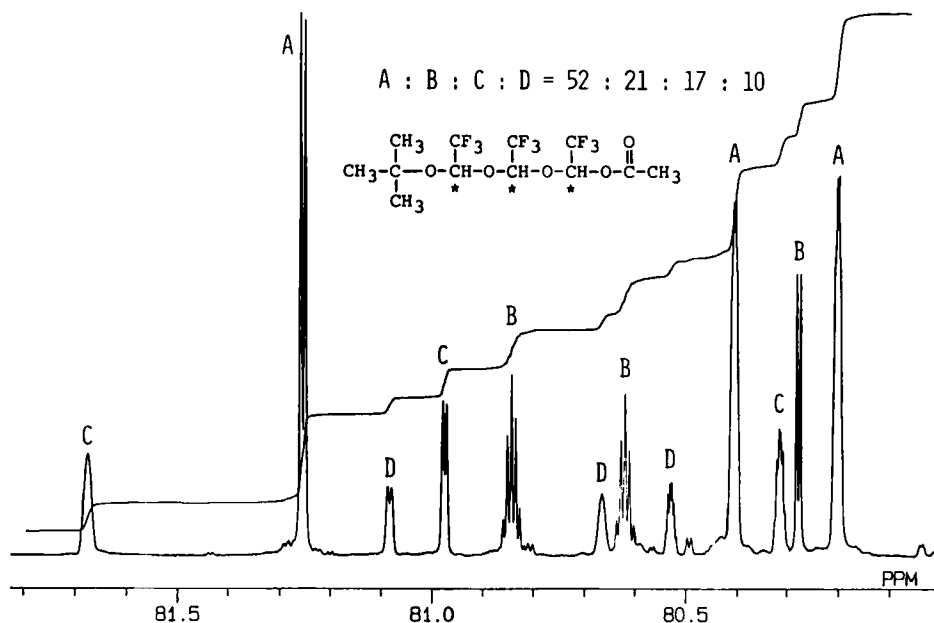


FIG. 1.  $^{19}\text{F}$ -NMR spectrum of the lithium *tert*-butoxide-initiated, acetate-terminated fluoral trimer ( $\text{CDCl}_3$ , 470 MHz).

linear dimer, trimer, and tetramer adducts, along with the pentamer and hexamer, have been chromatographically separated and isolated. Single crystals of each, grown slowly from dilute solutions of methanol, possess sharp, well-defined melting points. X-ray crystallographic analyses have confirmed that these species exist structurally as low molecular weight homologues of isotactic helical polychloral, with individual chloral residues linked together in meso (*m*) fashion. Structures for the helical *mm*-trimer and *mmmmm*-hexamer species are provided in Figs. 7 and 8, respectively. Relevant crystallographic and melting point data are tabulated in Table 2 for this series. Similar studies have been performed on chloral oligomers prepared with the chiral (–)-bornyl oxide initiator. Data are summarized in Tables 3 and 4. An x-ray structure for the (–)-bornyl oxide-initiated (*R,S*)-dimer is furnished in Fig. 9.

The results of our efforts described here provide strong evidence that the early stages of polychloral chain growth are remarkably stereospecific and that only the *one* dominant species—an isotactic “helical em-

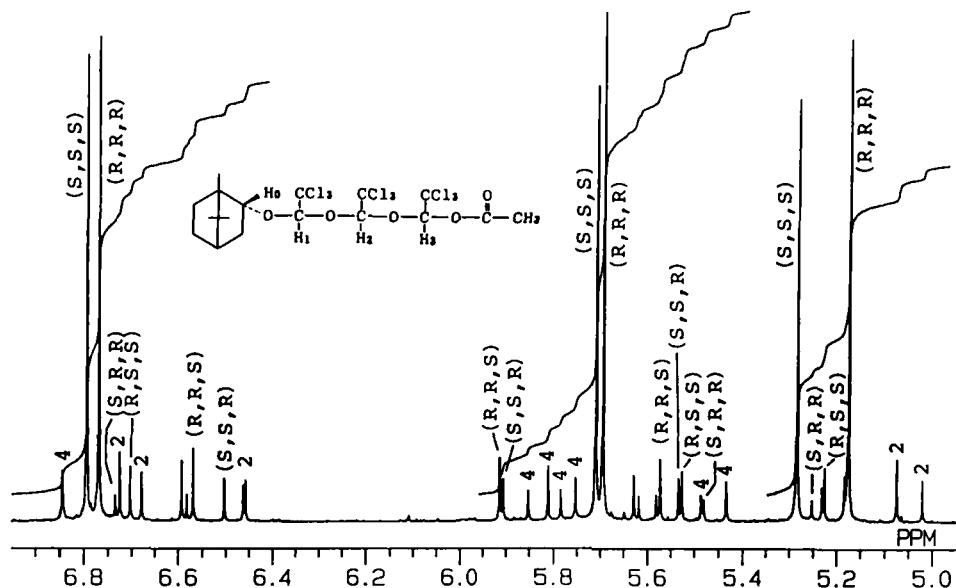


FIG. 2. <sup>1</sup>H-NMR spectrum of the lithium (-)-bornyl oxide-initiated, acetate-terminated chloral trimer (CDCl<sub>3</sub>, 500 MHz).

bryo" – continues to grow past the tetramer-pentamer stage. This behavior is in stark contrast to the fluoral case where a number of diastereomeric species are clearly propagating at this point. Indeed, our observations are consistent with the fact that only isotactic, semicrystalline polymers of chloral have been reported in the literature [51, 52]. Atactic, and presumably amorphous, polychloral has not been experimentally observed.

### Oligomers of Bromal

Acetate endcapped oligomers of bromal have been prepared via the agency of both the *tert*-butoxide and the (-)-bornyl oxide-initiating systems. However, the synthesis of higher ordered derivatives has been hampered by the relatively low ceiling temperature associated with the oligomerization reactions. Moreover, substantial quantities of bromal diacetate by-product are formed from the unreacted monomer in the acetic anhydride quenching step.



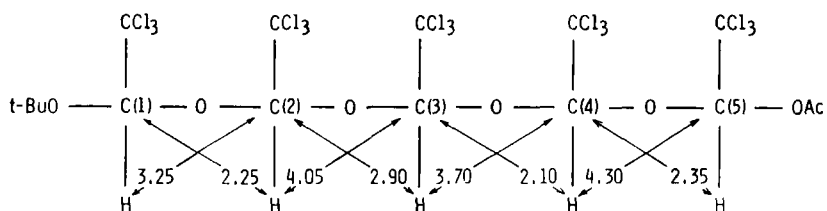
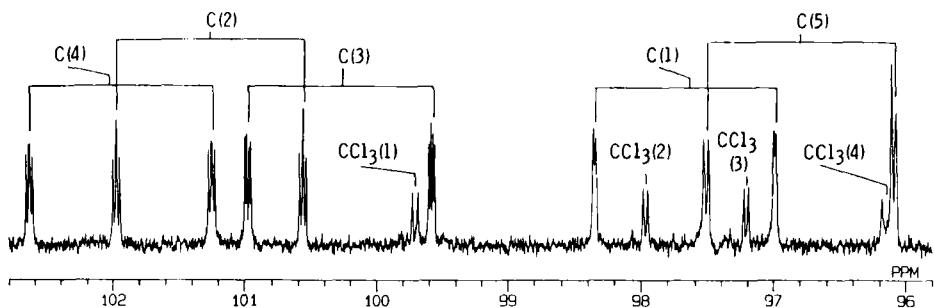


FIG. 3. Proton coupled  $^{13}\text{C}$ -NMR spectrum of the chloral pentamer and relevant  $^3J_{\text{CH}}$  coupling constants.

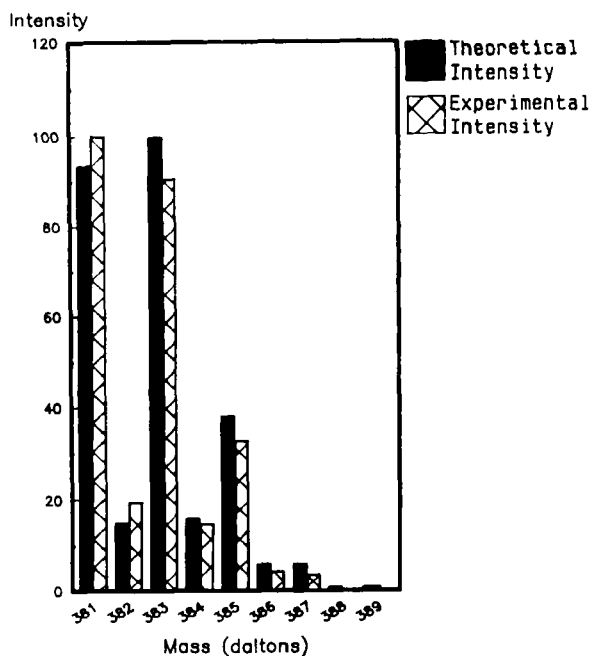


FIG. 4.  $\text{K}^+$ IDS mass spectral data for the lithium (-)-bornyl oxide-initiated, acetate-terminated chloral unimer with calculated chlorine isotope distribution.

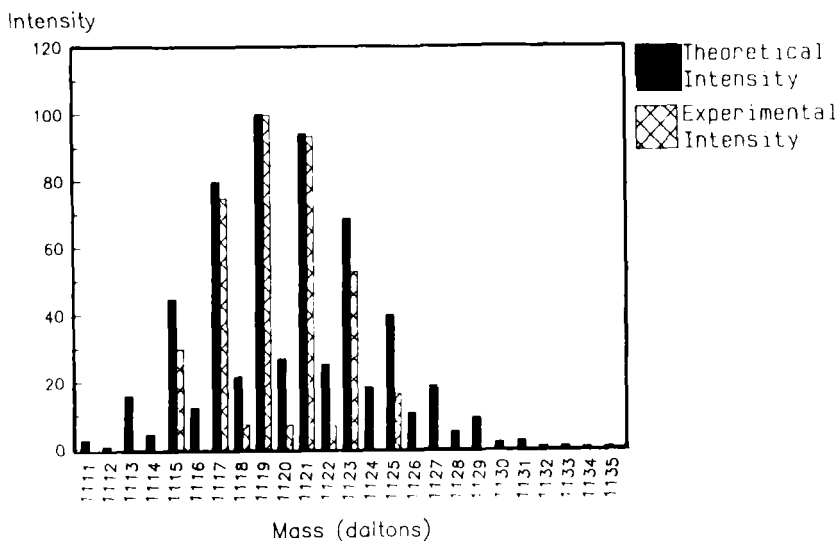


FIG. 5.  $K^+$ IDS mass spectral data for the lithium (–)-bornyl oxide-initiated, acetate-terminated chloral hexamer with calculated chlorine isotope distribution.

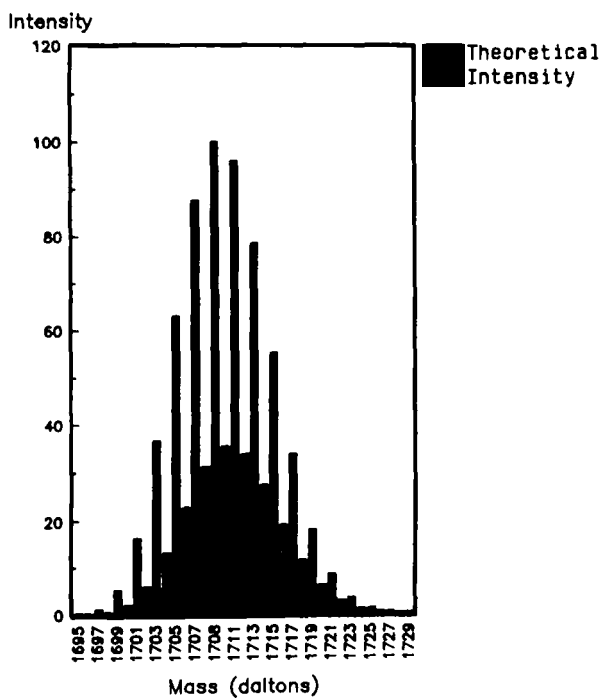


FIG. 6. Calculated chlorine isotope distribution for the lithium (–)-bornyl oxide-initiated, acetate-terminated nonamer.

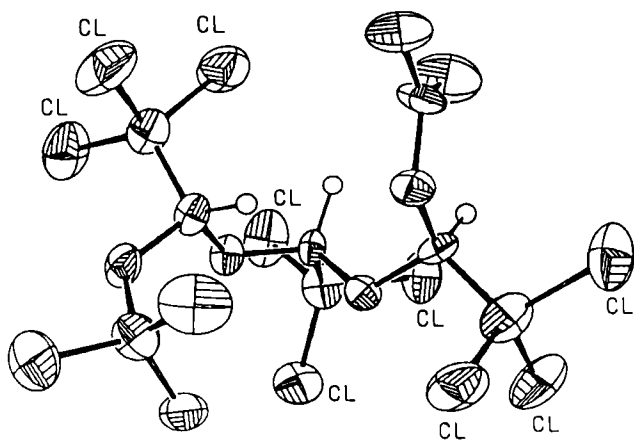


FIG. 7. Single crystal x-ray structure of the lithium *tert*-butoxide-initiated, acetate-terminated chloral  $3mm$ -(*S,S,S*) trimer.

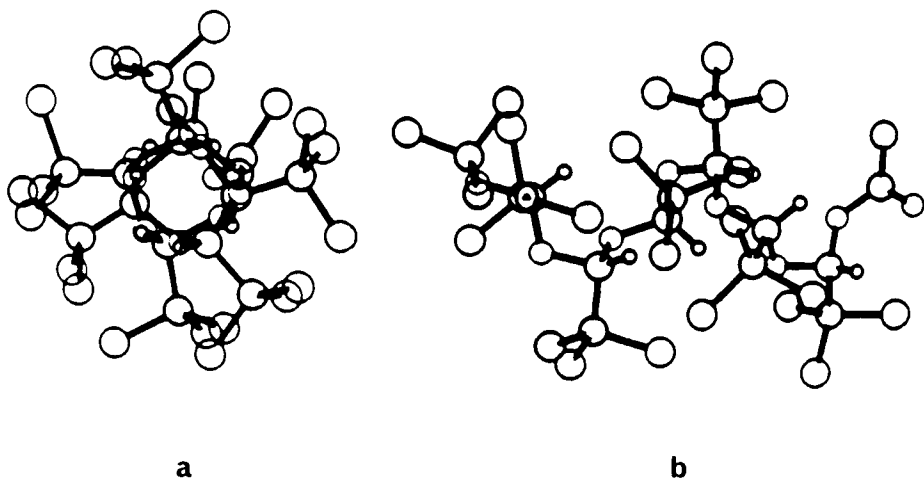


FIG. 8. Structure of the lithium *tert*-butoxide-initiated, acetate-terminated chloral hexamer: (a) view down *c*-axis; (b) side view.

TABLE 2. Relevant Crystallographic Properties of Major *tert*-Butoxide-Initiated, Acetate-Terminated Chloral Oligomers

Oligomer	Configuration <sup>a</sup>	mp °C	Crystal system	Space group
Dimer	<i>2m</i>	73	Triclinic	P1
Trimer	<i>3mm</i>	116	Monoclinic	P2 <sub>1</sub> /n
Tetramer	<i>4mmm</i>	255	Monoclinic	P2 <sub>1</sub> /a
Pentamer	<i>5mmmm</i>	225	Orthorhombic	Pca2 <sub>1</sub>
(- )Pentamer	<i>5mmmm</i>	212	Orthorhombic	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Hexamer	<i>6mmmm</i>	210	Monoclinic	C2/c

<sup>a</sup>*m* denotes meso configuration.

A GC chromatogram for the more widely studied *tert*-butoxide-initiated oligomer series, furnished in Fig. 10, clearly shows the presence of several lower oligomeric components in the reaction mixture after work-up. Unimer, dimer, trimer, tetramer, and pentamer species have now been identified by K<sup>+</sup>IDS mass spectroscopy (Table 1). In some cases, fragmentation ions also appear in the spectra. A K<sup>+</sup>IDS mass spectrum for the *tert*-butoxide-initiated bromal unimer, depicted in Fig. 11, contains an expected parent peak at *M/z* 437 and two secondary degradation peaks at *M/z* 357 and 277 due to sequential loss of hydrogen bromide. This behavior was not observed for the apparently more robust

TABLE 3. Relevant Crystallographic and Chiroptical Properties of Bornyl Oxide-Initiated, Acetate-Terminated Chloral Oligomers

Oligomer	Configuration <sup>a</sup>	[α] <sub>D</sub> <sup>b</sup>	mp °C	Crystal system	Space group
Unimer	( <i>R</i> )	(- )23.0	56	Monoclinic	P2 <sub>1</sub>
Dimer	<i>2r</i> -( <i>R,S</i> )	(- )21.6	116	Monoclinic	P2 <sub>1</sub>
Dimer	<i>2r</i> -( <i>S,R</i> )	-	76	Orthorhombic	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Dimer	<i>2m</i> -( <i>R,R</i> )	-	57	Orthorhombic	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Dimer	<i>2m</i> -( <i>S,S</i> )	(- )17.2	81	Orthorhombic	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>

<sup>a</sup>*m* and *r* denote meso and racemo configurations, respectively.

<sup>b</sup>Measured in CHCl<sub>3</sub> at 25°C.

TABLE 4. Isomer Composition of Bornyl Oxide-Initiated, Acetate-Terminated Chloral Oligomers

Oligomer	Configuration <sup>a</sup>	Relative amount, %
Unimer	( <i>R</i> )	57
	( <i>S</i> )	43
Dimer	<i>m</i> -( <i>R,R</i> )	23
	<i>m</i> -( <i>S,S</i> )	18
	<i>r</i> -( <i>R,S</i> )	34
	<i>r</i> -( <i>S,R</i> )	25
Trimer	<i>mm</i> -( <i>R,R,R</i> )	42
	<i>mm</i> -( <i>S,S,S</i> )	40
	<i>mr</i> -( <i>R,R,S</i> )	6
	<i>mr</i> -( <i>S,S,R</i> )	4
	<i>rm</i> -( <i>R,S,S</i> )	5
	<i>rm</i> -( <i>S,R,R</i> )	3

<sup>a</sup>*m* and *r* denote meso and racemo configurations, respectively.

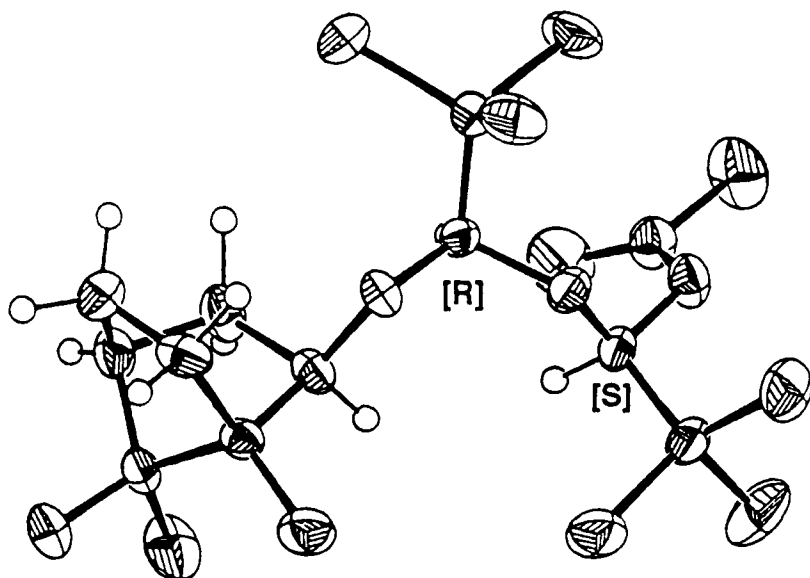


FIG. 9. Single crystal x-ray structure of the lithium (-)-bornyl oxide-initiated, acetate-terminated chloral (*R,S*) dimer.

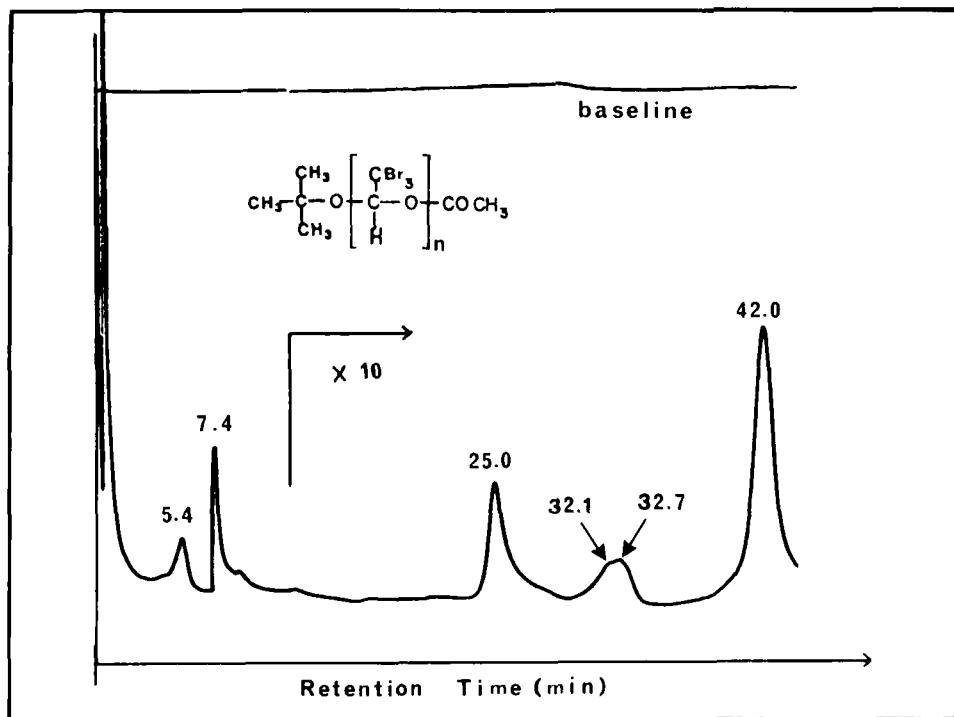


FIG. 10. GC spectrum of lithium *tert*-butoxide-initiated, acetate-terminated bromal oligomer series.

fluoral and chloral congeners. Attempts to isolate and fully characterize higher bromal oligomers are currently underway.

### Chiroptical Studies

As part of our continuing investigation, we have begun to examine the chiroptical properties of our acetate-terminated oligomeric species in some detail. Using high pressure liquid chromatography with chiral stationary phases, the *tert*-butoxide-initiated chloral *m*-dimer and *mmmm*-pentamer adducts have now been resolved into their (+) and (-) antipodes. In chloroform, the (+)*m*-dimer and (-)*m*-dimer exhibit specific rotations (sodium D-line) of (+)22.9° and (-)21.7°, respectively. Interestingly, the rotations observed for the "helical" (+)*mmmm*-

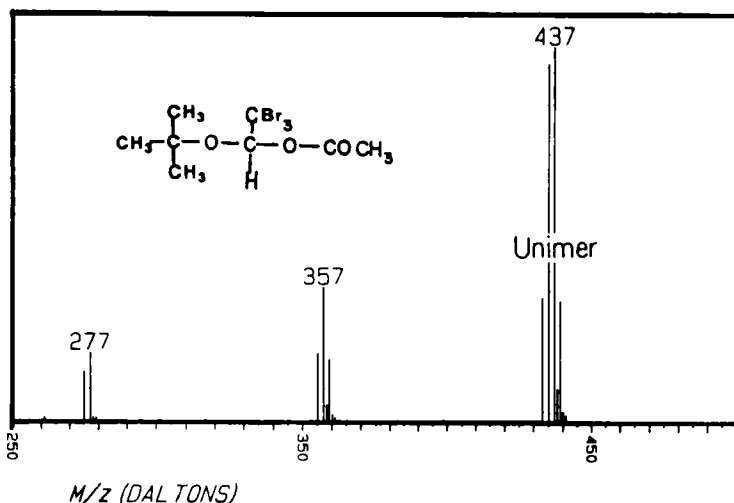


FIG. 11.  $\text{K}^+$ IDS mass spectrum of the lithium *tert*-butoxide-initiated, acetate-terminated bromal unimer ( $M/z$ : 437 daltons) and fragmentation peaks centered near  $M/z$ : 357 and 277 daltons.

and (–)*mmmm*-pentamer species appear to be little changed, with values of (+)22.6° and (–)23.3°, respectively.

Studies involving the (–)-bornyl oxide-initiated oligomer families are in their initial phases (see Table 3). Specific rotations (sodium D-line) for the unimeric (*R*) and (*S*) diastereomers of chloral and bromal have now been obtained, as has the rotation for the (–)-bornyl oxide-initiated unimer of formaldehyde. Preliminary analysis of these data suggest that the magnitude of the rotation values can be correlated to the relative steric bulk or volume of the trihalomethyl “side-group” present in these adducts, as illustrated in Fig. 12. Additional studies are currently underway in an attempt to further test the validity of this relationship.

## CONCLUSIONS

The results gleaned from our present study, when taken in conjunction with earlier theoretical [53] and experimental efforts [54, 55], are beginning to offer a unique perspective on how helical geometry and crystalline order ultimately develop in polymers of the perhaloacetalde-

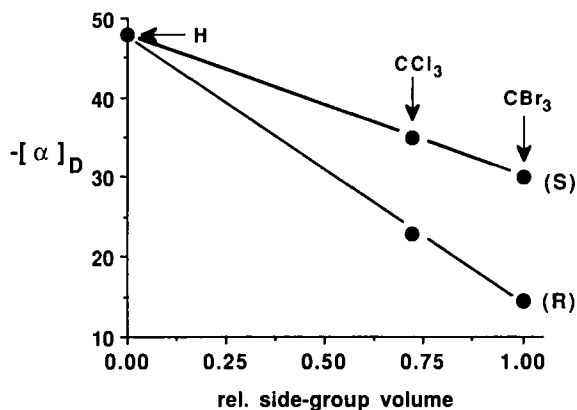


FIG. 12. Specific rotation (589 nm) of (–)-bornyl oxide-initiated (R)- and (S)-unimers as a function of relative side group volume. Volume of  $-\text{CBr}_3 = 1.0$ .

hydes. By focusing on the embryonic stages of the anionic polymerization reaction, it has become clear that the configurational and conformational geometries imparted to the perhaloacetaldehyde chain are both strongly dependent on the steric bulk of the pendent trihalomethyl side group residing in these systems. The relatively small trifluoromethyl moieties in polyfluoral are apparently unable to endow the propagating chain end with a high degree of stereospecificity for subsequent monomer addition steps. Consequently, a significant amount of atactic, non-helical structure will be incorporated into the bulk polymer sample. In sharp contrast, polychloral, with its more sterically demanding trichloromethyl side groups, appears to propagate almost entirely in an isotactic fashion, giving compact  $4_1$  helical coils capable of crystallizing in the solid state. Presumably, the polymerization of bromal also proceeds with a high degree of stereospecificity, leading to some kind of helical structure. Here, however, the tribromomethyl side group is so large that chain growth is hindered when compared to the other two cases.

A proper understanding of the origins of helical geometry in the polyperhaloacetaldehydes is essential for the rational design and synthesis of polymers having optical activity that is based exclusively on helical asymmetry in the crystalline state [56–58]. Of the three perhaloacetaldehyde monomers evaluated, chloral appears to be best suited for studies of this type.



### ACKNOWLEDGMENTS

This work was supported in part by the Herman F. Mark Chair of the Polytechnic University and by a grant from the National Science Foundation (DMR 8617788). We would like to thank F. W. H. Kruger for his assistance during the preparation of this manuscript.

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