

the preceding Account; they have let me use freely their work, and let me enjoy the illusion that what they do on their own is still partly mine, an illusion I also enjoy with my children and grandchildren; to Yoichi Nakatani, who has made it possible to

engage in the biophysical developments only superficially mentioned here but essential; and to Marie-Claire Dillenseger, who has often been more ambitious than myself for what we were doing and who has constantly challenged me to do better.

Mapping the Genesis of Helical Structure in Polymers of the Trihaloacetaldehydes

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Macromolecules are capable of occupying a host of different conformational forms. These range from randomly coiled wormlike chains to more spatially ordered structures. Helical geometries are encountered when internal rotational angles along the polymer backbone can repeat in a regular, sequential fashion. Widely recognized native helical structures include the

right-handed α -helix¹ found in many proteins and poly(α -amino acids) and single-, double-, and even triple-stranded helical arrangements common to the nucleic acid family of biopolymers.² Synthetically derived macromolecules can also adopt helical architectures. In contrast to their naturally occurring cousins, however, many of these polymers lack secondary bonding interactions which help to stabilize helical order in solution. Here, helicity is often confined to the solid state where crystalline packing forces encourage the formation of compact helical coils. Over the past five decades, a variety of helical motifs have been identified through X-ray diffraction studies.³ For the stereoregular polyolefins and polyaldehydes, these include both right- and left-handed helices with 3_1 , 4_1 , and nonintegral 7_2 arrangements⁴ of the polymer backbone.

The loss or absence of helical structure can have a profound impact on the behavior associated with a macromolecule. The physicochemical and biological consequences of helix to random coil transitions in nucleic acids and proteins have been a subject of intense scrutiny.⁵ For synthetic polymers, including many of

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(1) (a) Pauling, L.; Corey, R. B. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 235. (b) Walton, A. G. *Polypeptides and Protein Structure*; Elsevier: New York, 1981.

(2) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.

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(4) Helix symmetry is designated by N_m , where N monomer residues reside in m turns of the helical screw.

commercial interest, desirable materials properties such as mechanical strength and solvent resistance are intimately tied to crystalline morphologies that arise in response to helical architecture along the polymer chain. Not surprisingly, considerable effort has been directed toward gaining a better overall picture of the various chemical and physical processes that are ultimately responsible for helical order in man-made polymer systems.

For a number of years now, we have been interested in the synthesis and study of helical macromolecules, especially those belonging to the polytrihaloacetaldehyde family.⁶ Polytrichloroacetaldehyde, or polychloral, is known to possess 4_1 helical structure in its crystalline state.⁷ Using chiral initiators and helix-sense-selective polymerization techniques developed in our laboratory,⁸ we succeeded earlier in preparing semi-crystalline, isotactic polymers that exhibit exceptionally high optical rotatory power. Specific rotations in polychloral have ranged from $(+)$ 4000° to $(-)$ 4000° (sodium D line), depending upon how we "tune" or manipulate our anionic polymerization reactions.⁹ Because polychloral is devoid of chirality at the atomic level, this optical rotatory power is believed to stem from a predominance of one, i.e., right or left, helical screw sense that has been incorporated into the polymer sample.

Throughout the course of our polymerization studies, a number of fundamental questions have remained largely unanswered. For example, when does the first turn in the polymer's 4_1 helical coil emerge along the growing polyaldehyde chain? During the nascent stages of helix development, are helix inversion steps common? And, finally, how important is the monomer's sterically demanding trichloromethyl side group in promoting the formation of isotactic, helical structure in the polymer? To address some of these concerns, we initiated a new series of studies designed to track the growth of a polymer chain "from the ground up". By purposely intercepting chain growth at an oligomer stage and then subjecting the resulting low molecular species to a battery of analytical techniques, we have been able to effectively map the genesis of helical structure along a growing polychloral chain. In this Account, we highlight some of our more recent results and, in the process, attempt to provide answers to the three questions posed above.

Oligomerization of Chloral with Lithium *tert*-Butoxide

In the presence of trace amounts of lithium *tert*-butoxide or other suitable anionic initiating species, chloral

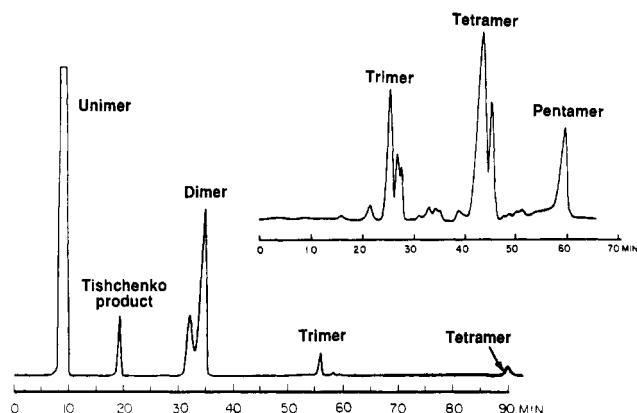


Figure 1. Gas chromatogram of linear *tert*-butoxide-initiated, acetate-terminated chloral oligomers. Inset: chromatogram of higher boiling trimer, tetramer, and pentamer adducts.

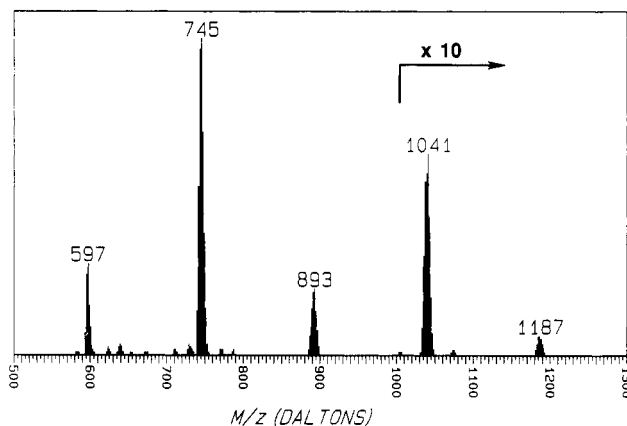
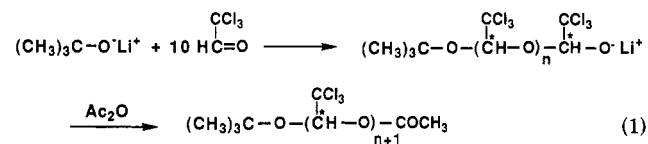


Figure 2. K^+ IDS mass spectrum of linear *tert*-butoxide-initiated, acetate-terminated chloral oligomers. Unimer and dimer species present below 500 Da are not shown. Peak intensities above 1000 Da have been enhanced by a factor of 10.

rapidly undergoes polymerization to give an isotactic, helical polymer.⁶ However, if the reaction is carried out under conditions where the system is "starved" for monomer, as in eq 1, chain growth is retarded and chloral oligomers are predominantly formed. As we demonstrated earlier, these "living" embryonic products can be trapped and rendered thermally stable by an acetic anhydride capping step.¹⁰



The subsequent analysis of our product mixtures by gas chromatography (GC) provided evidence for the existence of a number of acetylated species (Figure 1). As we expected, these were found to correspond to the linear unimer, dimer, trimer, tetramer, pentamer, and trace amounts of higher order chloral addition products which had formed during the oligomerization process.¹¹ Also present was an additional component at 19 min, which we later identified as a side product originating from a Tishchenko-like reaction on chloral.

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(11) (a) Zhang, J.; Jaycox, G. D.; Vogl, O. *Polymer* 1988, 29, 707. (b) Jaycox, G. D.; Xi, F.; Vogl, O.; Hatada, K.; Ute, K.; Nishimura, T. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1989, 30, 167.

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(8) (a) Corley, L. S.; Jaycox, G. D.; Vogl, O. *J. Macromol. Sci., Chem.* 1988, A25, 519. (b) Corley, L. S.; Vogl, O. *Polym. Bull.* 1980, 3, 211. (c) Harris, W. J.; Vogl, O. *J. Macromol. Sci., Chem.* 1989, A26, 1067.

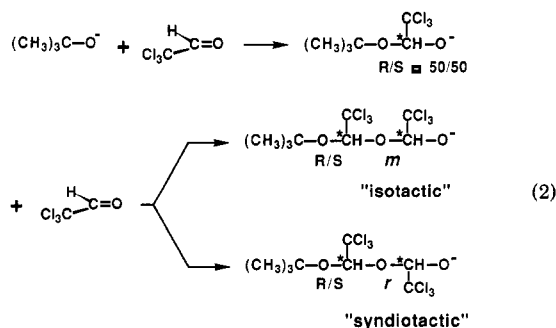
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Table I
K⁺IDS Mass Spectroscopic Data for
tert-Butoxide-Initiated (TBI) and Bornyl Oxide-Initiated
(BI), Acetate-Terminated Perhaloaldehyde Oligomers

oligomer	pseudomolecular ion ([M]K ⁺ , Da)					
	fluoral		chloral		bromal	
	TBI	BI	TBI	BI	TBI	BI
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	1187			
octamer	939	1019				
nonamer	1037	1117				
decamer	1135	1215				
undecamer	1233					

As detailed more extensively elsewhere,^{11,12} peak assignments in our chromatograms were initially established via a series of NMR and mass spectroscopic procedures. To minimize the degradation of our oligomers during mass spectral analyses, we utilized a relatively novel, soft ionization technique which is based on the thermionic emission of potassium from an aluminosilicate matrix. This procedure, termed potassium ionization of desorbed species,¹³ or K⁺IDS, gently furnished pseudomolecular ions for our oligomers in the form of [M]K⁺. For the *tert*-butoxide-initiated product mixture described here, oligomeric species as large as the heptamer ([M]K⁺ = 1187 Da) have been successfully detected without fragmentation. A K⁺IDS mass spectrum for our mixture of chloral oligomers is provided in Figure 2. Relevant mass data are compiled in the fourth column of Table I for this oligomer family.

Consistent with our expectations, the GC data presented in Figure 1 revealed that the dichloral addition product arising from the oligomerization reaction was actually comprised of two individual components, affording peaks at 32 and 34 min in the chromatogram. The fact that only a limited number of resolvable components were observed for the larger oligomeric adducts was somewhat surprising, however. To understand this, we can consider the formation of a *tert*-butoxide-initiated chloral dimer outlined in eq 2. Here, the final acetic anhydride capping step has been omitted for clarity.



In the first step, attack by the initiating alkoxide on the prochiral monomer will afford a "unimer" product having either an *R* or *S* configuration centered about

(12) Simonsick, W. J., Jr.; Hatada, K.; Xi, F.; Vogl, O. *Macromolecules* 1991, 24, 1720.

(13) (a) Rollgen, F. W.; Schultgen, H. R. *Org. Mass Spectrom.* 1975, 10, 660. (b) Bombick, D.; Pinkston, J. D.; Allison, J. *Anal. Chem.* 1984, 56, 396.

Table II
Properties of Major *tert*-Butoxide-Initiated Chloral
Oligomers

oligomer	con-figuration ^a	rel % ^b formed	mp (°C)	crystal system	space group
dimer	2 <i>m</i>	76	73	triclinic	<i>P</i> 1
trimer	3 <i>mm</i>	68	116	monoclinic	<i>P</i> 2 ₁ / <i>n</i>
tetramer	4 <i>mmm</i>	80	255	monoclinic	<i>P</i> 2 ₁ / <i>a</i>
pentamer	5 <i>mmmm</i>	>95	225	orthorhombic	<i>Pca</i> 2 ₁
hexamer	6 <i>mmmmm</i>	>95	210	monoclinic	<i>C</i> 2/ <i>c</i>

^a *m* denotes meso configuration. ^b Values ±3%.

its chiral carbon atom. The addition of the second chloral unit can also proceed in one of two stereochemically distinct ways, furnishing the dimer adduct as a pair of diastereomers. For our purposes, we define the second chloral addition step as being meso (*m*) if the resulting dimer possesses "isotactic" structure and racemic (*r*) if the product possesses "syndiotactic" structure.¹⁴ Of course, we can extend our analysis beyond the dimer stage. Since each subsequent chloral growth step can also occur in either a meso or a racemic fashion, a stereorandom growth process will afford a trimer adduct that is comprised of four separate diastereomeric components, a tetramer adduct having eight such components, and so on. When a GC analysis of the oligomer mixture is carried out on an achiral stationary phase that is capable of resolving individual diastereomers, an extremely complex chromatogram should be obtained. That the number of observable peaks for the trimer, tetramer, and pentamer fractions in Figure 1 diminished with increasing chain length, and that a single peak was clearly dominant in each case, suggested that the growth steps which afforded the larger oligomeric adducts were highly stereoselective, effectively limiting the number of diastereomeric components formed. In other words, our GC data supported the notion that some kind of embryonic structure was emerging as the oligomerization reaction propagated beyond the dimer stage.

To better determine the stereochemical nature of the embryonic adducts present in our oligomer product mixtures, the dimer-hexamer fractions were individually isolated through a series of distillation and chromatographic steps.^{11b,15,16} The individual fractions were then dissolved into methanol and allowed to stand at room temperature for periods which approached a full year. During this time, the major diastereomeric component present in each fraction slowly crystallized from solution. For example, the crystalline solid grown from the "dimer peak centered at 34 min in Figure 1. All of our solids possessed sharp melting points, ranging from 73 to 255 °C.¹⁶ Relevant melting point data for this crystalline dimer-hexamer series are tabulated in the fourth column of Table II.

Efforts to elucidate the stereostructure of the newly formed crystalline adducts were initially made through

(14) By definition, a series of meso growth steps will give rise to an isotactic polymer structure. Here, pseudochiral centers along the polymer backbone retain the same configuration, e.g., ...*R,R,R,R*... In contrast, a series of racemic placements will afford a syndiotactic polymer structure where pseudochiral centers along the backbone alternate in configuration, e.g., ...*R,S,R,S*...

(15) Hatada, K.; Ute, K.; Nakano, T.; Vass, F.; Vogl, O. *Makromol. Chem.* 1989, 190, 2217.

(16) (a) Ute, K.; Nishimura, T.; Hatada, K.; Xi, F.; Vass, F.; Vogl, O. *Makromol. Chem.* 1990, 191, 557. (b) Vogl, O.; Xi, F.; Vass, F.; Ute, K.; Nishimura, T.; Hatada, K. *Macromolecules* 1989, 22, 4658.

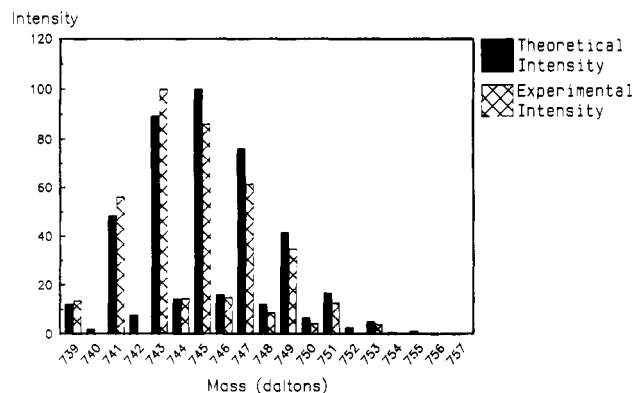


Figure 3. K^+ IDS mass spectral data for linear *tert*-butoxide-initiated chloral tetramer with calculated chlorine isotope distribution.

the use of NMR spectroscopy. As we detailed extensively in several reports,^{15,16} analysis of the major chloral dimer, trimer, and tetramer species by ^{13}C NMR and 2D NOE-correlated 1H NMR spectroscopy strongly hinted that individual monomer residues which comprised the crystalline oligomers were linked together in *meso*¹⁴ fashion. A more definitive assignment of structure was later provided by a series of single-crystal X-ray studies. We were extremely fortunate that the solids isolated from our oligomer solutions were readily amenable to crystallographic analyses of this kind. Our efforts,¹⁶ summarized in Table II, confirmed that the major dimer, trimer, tetramer, pentamer, and hexamer products generated during the *tert*-butoxide-initiated oligomerization reaction were *all* formed via a series of stereoselective *meso* placements, in excellent agreement with our NMR and GC investigations described above. Stated in another way, the major oligomeric products isolated from our studies were all found to be *low molecular weight homologues of isotactic, helical polychloral*.

Although space limitations preclude an extensive survey of our findings for this unimer-hexamer series, it will be instructive at this point to focus on the geometrically unique chloral tetramer in somewhat greater detail. As indicated in Table II, the major diastereomeric component isolated from our methanolic "tetramer solution" exhibited a sharp melting point at 255 °C. A K^+ IDS mass spectrum for this crystalline adduct is provided in Figure 3. Here, a cluster of ions ($[M]K^+$) is clearly centered at 743 Da. The cluster in the spectrum is due to the isotopic distribution of chlorine atoms in the molecule and agrees quite closely to the theoretical distribution predicted for the acetate-capped tetramer.^{12,17} X-ray crystallographic analysis of the tetrachloral product furnished a wealth of structural information.¹⁶ A projection of the unit cell along the *ca*-plane is shown in Figure 4. Four embryonic helices comprise the cell, each with a calculated repeat distance of 4.81 Å running along the *c*-axis of the crystal. This distance compares favorably to the 5.20 Å repeat length observed for isotactic polychloral in its crystalline state.^{7a} The *S,S,S,S* tetramer's helical architecture is better viewed in Figure 5. Here, four chloral residues provide the first left-handed turn in what is clearly an *embryonic* 4_1 helical screw. A num-

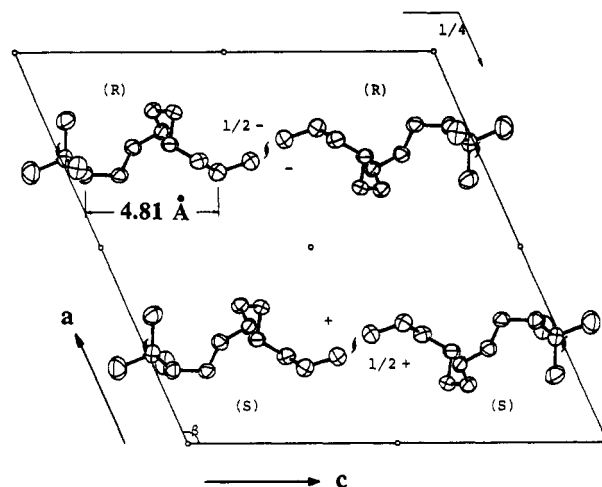


Figure 4. A (010) projection (*ca*-plane) of a unit cell for the *tert*-butoxide-initiated chloral tetramer. For clarity, only the acetal backbone and end groups are shown. Note the measured repeat distance of 4.81 Å.

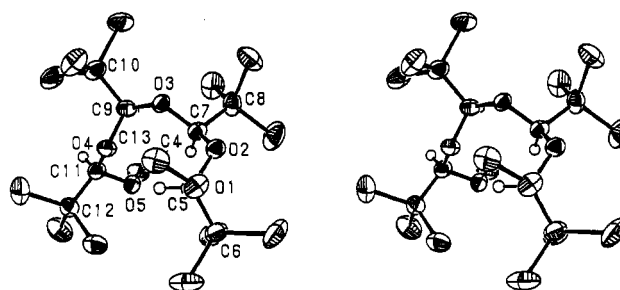
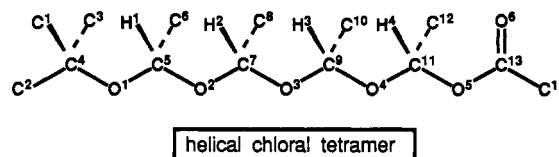


Figure 5. Single-crystal X-ray structure (stereoview) of *tert*-butoxide-initiated chloral *S,S,S,S* tetramer as viewed along the *c*-axis. Methyl carbons on *tert*-butoxy and acetyl end groups have been omitted for clarity. The numbering scheme for this figure is provided in the text.

bering scheme for the crystal structure displayed in the stereodrawing is provided:



Oligomerization of Chloral with Lithium (-)Bornyl Oxide

Although our data provided good evidence that isotactic, helical structure was developing very early in the growth of a polychloral chain, we elected to carry out a second generation of oligomerization reactions, this time using the secondary alkoxide derived from (1*S*,2*R*,4*S*)-(-)-borneol as an initiating species.¹⁸ Efforts



of this kind were deemed necessary to rule out the possibility that our results were being skewed or distorted by the sterically bulky *tert*-butoxide end group residing in our oligomer structures. Analysis of the (-)-bornyl oxide-initiated product mixtures by GC

(17) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980.

(18) (a) Zhang, J.; Jaycox, G. D.; Vogl, O. *Polym. J.* 1987, 19, 603. (b) Jaycox, G. D.; Hatada, K.; Xi, F.; Vogl, O. *Pac. Polym. Prepr.* 1989, 1, 267.

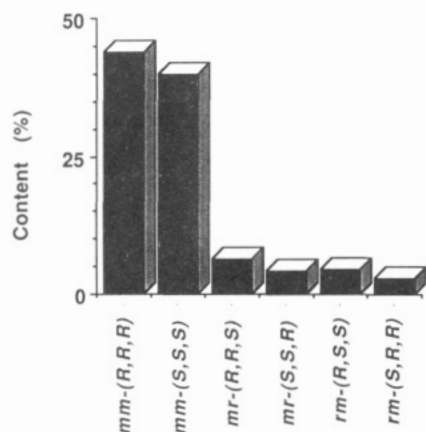


Figure 6. Relative isomer composition of (-)-bornyl oxide-initiated chloral trimer fraction as determined by 2D NOE-correlated ^1H NMR spectroscopy.

confirmed the formation of a number of low molecular weight oligomeric adducts. The existence of an acetate-terminated chloral unimer-hexamer family was clearly established via the agency of tandem NMR¹⁹ and mass spectroscopic procedures²⁰ described earlier. K^+IDS mass spectroscopic data for this oligomer series are tabulated in the fifth column of Table I.

A detailed inspection of the GC data for this new chloral oligomer family revealed a now familiar pattern. As for the *tert*-butoxide case shown in Figure 1, a limited number of diastereomeric components were observed in the chromatogram for the higher oligomeric products. A detailed study¹⁹ of the bornyl oxide-initiated trimer fraction by 2D NOE-correlated ^1H NMR spectroscopy confirmed that only six of the eight possible isomers were present in this mixture, and of the six, only the "isotactic" *mm*-(*R,R,R*) and *mm*-(*S,S,S*) species were formed to any significant extent (Figure 6). Indeed, trimers derived from two consecutive racemic growth steps, e.g., *rr*-(*R,S,R*) and *rr*-(*S,R,S*), were almost totally absent from the product mixture. That the growth of the *mm*-(*R,R,R*) trimer was slightly favored over its *mm*-(*S,S,S*) cousin is consistent with the use of the chiral (-)-bornyl oxide initiating species. As in our earlier work, X-ray crystallographic studies on single crystals isolated from our product mixtures lent additional support to our NMR findings.¹⁹

The Genesis of Helical Structure in Polychloral

The data gleaned from our (-)-bornyl oxide-initiated oligomer study, when taken in conjunction with the *tert*-butoxide work described earlier, clearly demonstrate the stereoselective nature of the chloral chain growth reaction. With this information in hand, we can now map the origins of helical structure in isotactic polychloral and, in the process, provide answers to the first two questions initially put forth in the introductory section above. As detailed in Figure 7, attack of an initiating *tert*-butoxide I^- on prochiral chloral monomer M_1 (designated $\text{I} + \text{M}_1$), followed by a rapid series of highly favored meso (*m*) addition steps ($+\text{M}_2$, $+\text{M}_3$, $+\text{M}\dots$), will give rise to an isotactic, helical "embryo"

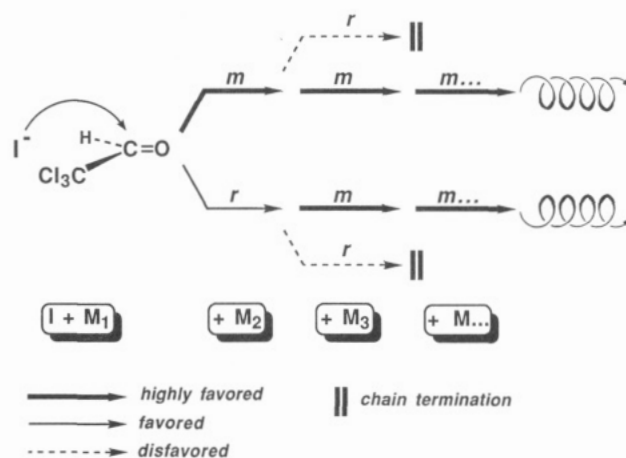


Figure 7. Schematic "map" detailing the origins of helical structure in polychloral.

like that pictured in Figure 5. Additional meso placements will then quickly generate the first several turns in the polymer's emerging 4_1 helical coil. As our map shows, an occasional racemic (*r*) growth step early in the oligomerization reaction will act to flip or invert the direction of this nascent helical screw. Because racemic growth steps become increasingly disfavored as chain growth proceeds past the dimer stage (consider the data in the third column of Table II), the population of oligomers having additional racemic placements will diminish rapidly and eventually die off. Attack by the achiral *tert*-butoxide on the opposite face of chloral monomer is, of course, equally likely. This event will trigger an identical cascade of steps and give rise to a racemic mixture of helical coils in the polymer sample. The situation for the chiral (-)-bornyl oxide initiator is little changed except, now, one mode of attack on the prochiral monomer is more highly favored and helix-sense selection will occur. From the data presented in Figure 6, it follows that polychloral prepared with the (-)-bornyl oxide should possess a slight excess of helices having the *R,R,R,R*,... absolute configuration. In other words, polychloral prepared with this initiator would be expected to display optical rotatory power that is based on helical asymmetry.⁹

It is interesting to note that the scenario painted above is fully consistent with a series of theoretical studies carried out almost eight years ago in collaboration with Abe and his co-workers.²¹ Molecular mechanics (MM2) calculations for polychloral and several of its oligomeric adducts predicted that, following attack of the initiating *tert*-butoxide, oligomeric chain growth should become highly stereoselective for meso addition as the trimer stage is reached. Indeed, on a relative scale, the "isotactic" *mm* trimer was found to be nearly 5 kcal mol⁻¹ more stable than its *mr* and *rm* isomers and almost 7 kcal mol⁻¹ more favorable than the experimentally elusive *rr* trimer species. Moreover, it was determined that a minimum of 5.6–6.0 kcal mol⁻¹ of energy would have to be expended to effect a helix inversion process along a short strand of the polymer chain. The investigators concluded that the stability of isotactic, helical structure in polychloral is greatly enhanced by the presence of sterically bulky trichloromethyl side groups unique to this system.

(19) Ute, K.; Oka, K.; Kashiyama, M.; Hatada, K.; Xi, F.; Vogl, O. *Makromol. Chem.* 1991, 192, 35.

(20) Simonsick, W. J., Jr.; Xi, F.; Hatada, K.; Vogl, O. *Monatsh. Chem.* 1991, 122, 967.

(21) Abe, A.; Tasaki, K.; Inomata, K.; Vogl, O. *Macromolecules* 1986, 19, 2707.

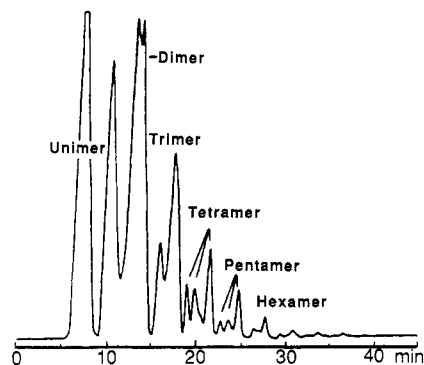


Figure 8. Gas chromatogram of linear *tert*-butoxide-initiated, acetate-terminated fluoral oligomers.

Oligomers Derived from Other Trihaloacetaldehyde Monomers

Having witnessed how readily helical geometry was incorporated into oligomers of chloral, we next expanded the scope of our investigation to include oligomers derived from fluoral (trifluoroacetaldehyde) and bromal (tribromoacetaldehyde). Would the embryonic stages of chain growth be altered by changing the size of the pendent trihalomethyl side group, as theory predicted? With the aid of the lithium *tert*-butoxide and (-)-bornyl oxide initiating species, four new oligomer families were prepared.^{22,23} As before, the respective members of each family were identified by tandem NMR and K^+ IDS mass spectroscopic procedures. For comparison, relevant mass spectral data are tabulated in Table I.

Preliminary analysis of our fluoral oligomer data has suggested that the early stages of fluoral chain growth are *less* stereoselective than those observed for the chloral case. For example, a gas chromatogram for the *tert*-butoxide-initiated fluoral family is furnished in Figure 8. Here, several diastereomeric components are clearly present in the pentamer fraction, in stark contrast to the single peak observed for the chloral pentamer in Figure 1. A more detailed inspection of the GC data for the fluoral hexamer and heptamer adducts revealed a similar trend, as did the study of the (-)-bornyl oxide-initiated fluoral oligomer series.²² These observations are consistent with the fact that the anionic polymerization of fluoral often leads to the formation of atactic, nonhelical polymer samples.²⁴ Thus,

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to answer our third question posed in the introductory section, it would seem that the sterically demanding trichloromethyl side group does indeed play a central role in promoting the formation of isotactic, helical structure in polymers of this kind.

In contrast, we have found the oligomerization of bromal to be characterized by a very different kind of limitation. Here, the tribromomethyl side group is so large that chain growth is hampered to an extent that only traces of higher oligomers are usually formed.²³ Preliminary GC analyses have hinted that early propagation steps are highly stereoselective as observed for the chloral case. However, a more accurate determination of bromal oligomer stereostructure will have to await further refinements in our isolation and characterization techniques.

Concluding Remarks

The oligomerization of chloral has provided an unprecedented opportunity to map the origins of helical structure along a growing polyaldehyde chain. Our studies have demonstrated that the early stages of chloral chain growth are remarkably stereoselective, such that an isotactic, helical "embryo" is the only species propagating by the tetramer-pentamer stage. With 4_1 helical symmetry, this embryonic adduct possesses a geometry not unlike that found along a short stretch of polychloral in the crystalline state. In contrast, the oligomerization of fluoral appears to proceed in a more stereorandom fashion, presumably due to the smaller trifluoromethyl side groups which reside in this system.

At this juncture, it remains to be determined whether the methodology developed here can be broadly extended to the study of other polymerization processes. A major advantage to our approach is derived from the fact that low molecular weight products generated during an oligomerization reaction are amenable to an array of modern analytical procedures which often fail on larger, more intractable polymer samples. And finally, although our helical chloral oligomers prepared to date have been utilized exclusively for diagnostic purposes, it has not escaped our attention that the use of initiators and end-capping reagents bearing latent reactive functionalities could provide access to a series of "helical synthons" containing small segments of the isotactic polychloral backbone. It is our belief that the incorporation of these novel building blocks into larger macromolecular or supramolecular structures would represent an exciting area for future study.

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