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L. Steven Corley^{ab}; Gary D. Jaycox^{ac}; Otto Vogl^a

^a Polytechnic University, Brooklyn, New York ^b Shell Development Co., Houston, Texas ^c Department of Chemistry, Dartmouth College, Hanover, New Hampshire

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HALOALDEHYDE POLYMERS. XXX.* MACROMOLECULAR ASYMMETRY AS THE BASIS OF OPTICAL ACTIVITY IN POLYMERS

L. STEVEN CORLEY,[†] GARY D. JAYCOX,[‡] and OTTO VOGL

Polytechnic University
Brooklyn, New York 11201

ABSTRACT

The synthesis of polymers characterized by a preferred helical screw sense (macromolecular asymmetry) is a subject of considerable experimental interest. Here, we summarize our efforts toward the preparation of optically active polychloral in which asymmetry at the macromolecular level is the only factor contributing to the polymer's chiroptical properties. Through the use of chiral initiating species, we have prepared optically active polychloral with specific rotations reaching 4500° at the sodium D-line. The results of this work and the prospects for further investigation are outlined.

BACKGROUND

Optical activity arises from the electronic interaction of plane-polarized light with a molecule that lacks symmetry [1-3]. This asymmetry can arise

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[†]Present address: Shell Development Co., Houston, Texas 77251.

[‡]Present address: Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755.

from the primary structure of the molecule (i.e., a tetrahedral carbon atom with four different substituents). It also can arise from the secondary structure of the molecule (i.e., a helix). Optical activity arising from the primary structure depends on the molecule's configuration (an asymmetric or chiral center). Optical activity originating from the secondary structure, on the other hand, depends on the molecule's conformation (molecular or, more frequently, macromolecular asymmetry). Either case requires that an optically active molecule not be superimposable on its mirror image. This means that it may not contain either a plane of symmetry or an alternating rotation-reflection axis of symmetry.

There are three important aspects of optical activity with which we shall be concerned. First, the secondary structure of a molecule can lead to optical activity just as can the primary structure. Second, specific rotation is wavelength-dependent. Third, there are empirical relationships describing specific rotation as a function of wavelength (Drude equation [4], Yang-Doty plot [5], and Moffitt equation [6]).

Optically active synthetic polymers can be divided into three major groups: 1) polymers with optical activity arising from asymmetric centers in the side or main chain (primary structure), 2) polymers with optical activity arising from both asymmetric centers and macromolecular asymmetry, and 3) polymers with optical activity arising from macromolecular asymmetry (secondary structure). Only the first two cases are reasonably well known. Our work is concerned with helical polymers in which macromolecular asymmetry is the only factor contributing to optical activity. Our ultimate goal is to demonstrate that conditions can be established to produce polymers containing exclusively one type of helix.

It was once thought that isotactic polymers, *per se*, would be optically active since each of the tetrasubstituted carbon atoms of the polymer chain is surrounded by four different substituents where two of the substituents are varying lengths of the polymer chain. Attempts were made to prepare this kind of optically active polymer [7-10], but all polymers prepared by this approach were optically inactive [11] because the substituted carbon atoms are actually only pseudoasymmetric. That is, long-chain substituents which differ only in chain length do not behave as "different" substituents for the purpose of inducing optical activity at an atom to which they are joined in common.

Polymers in Which Optical Activity Is Caused by Chiral Centers

There are two approaches by which optically active polymers with asymmetric centers can be prepared. The first is to generate an asymmetric center

during the polymerization of a monomer. The second is to polymerize a monomer (mixture of enantiomers) which already contains an asymmetric center. The former of the two approaches is called "asymmetric induction," while the latter is called "asymmetric selection."

The first successful experiment that led to asymmetric induction [8, 12] was the copolymerization of *L*(-)- α -methylbenzyl methacrylate with maleic anhydride. The optically active polymer was initially levorotatory. After all of the optically active side group was removed by hydrolysis, the copolymer was still optically active, but was then dextrorotatory.

Three methods are used in asymmetric selection polymerizations. The first is to polymerize an optically active monomer to obtain an optically active polymer. The second is to polymerize a racemic monomer by a single initiator into two types of polymers, each formed exclusively or preferentially from a single enantiomer (stereoselection). The third is to polymerize a racemic monomer with an optically active initiator which selectively polymerizes only one antipode, leaving the other enantiomer unpolymerized. This is called "stereoelection."

The first method of polymerizing an optically active monomer has been used in the past to obtain optically active polymers. The following optically active polymers have been prepared by chain reaction polymerization of optically active monomers: polyacrylamides [13, 14], polyacrylates [15], polyaldehydes [16], poly(alkenyl ethers) [17], poly(alkylene oxides) [18, 19], poly(alkylene sulfides) [20], polyalkynes [21], polyamides from lactams [22, 23], polyaciridines [24], polyesters from lactones [25, 26], polyisocyanides [27], polymethacrylates [28], poly- α -olefins [29, 30], poly(vinyl ethers) [31, 32], and poly(vinyl ketones) [33, 34].

The second asymmetric selection process is stereoselection, where the growing chain-end exclusively selects monomer of the same configuration. The polymer from such a process consists of a mixture of two homopolymers—one of *D*-configuration and one of *L*-configuration. This mixture has no measurable optical activity, but if resolution is performed, the resolved polymers are optically active and have opposite signs of rotation. Stereoselective polymerizations reported in the literature include the polymerization of propylene oxide [35] as well as of racemic 4-methyl-1-hexene, 3-methyl-1-pentene, and 3,7-dimethyl-1-octene [36].

The third method used in asymmetric selection processes is stereoelection, where an optically active initiator polymerizes only one antipode of a racemic mixture of the monomer. One of the first reported stereoselective polymerizations was that of *D,L*-propylene oxide initiated by dialkylzinc/(+)-menthol [37, 38]. The resulting mixture consisted of levorotatory polymer and unre-

acted dextrorotatory monomer. Other similar claims of preparing optically active polymer by a stereoelection process have been reported [39-42].

Polymers with Optical Activity Arising from Both Asymmetric Centers and Macromolecular Asymmetry

A significant number of polymers exist with optical activity due to both macromolecular asymmetry and asymmetric centers. In these polymers the asymmetric center of the monomer (a chiral group near the polymer main chain) induces the formation of short sequences of helices (macromolecular asymmetry).

Probably the most thoroughly studied classes of polymers which have both asymmetric centers and macromolecular asymmetry are proteins and polypeptides. For these polymers, the partial helical conformation (macromolecular asymmetry) is caused by the intramolecular hydrogen bonding of the amino acid moieties which contain the asymmetric centers.

Stereoregular synthetic polymers often exist in a helical conformation, especially in the solid stage [43]. It is recognized that the preferred conformation of an isotactic polymer in the solid state is helical (*tg+*, *tg-*), while syndiotactic polymers usually have a planar zigzag [44, 45] conformation. Consequently, a synthetic polymer must be isotactic in order to develop macromolecular asymmetry. However, more than isotacticity is required for a polymer to have optical activity due to macromolecular asymmetry. For example, isotactic polypropylene is helical in the solid state. However, it is not optically active because the polymer consists of a 50:50 mixture of left-handed and right-handed helices with the same conformational energy.

In order for an isotactic polymer to have optical activity originating from helicity it is necessary to introduce into the polymer some group which makes one screw-sense of the helix more favored (i.e., with a lower conformational energy). Typically, this group has an asymmetric center in the side chain. This asymmetric center can lead to a predominance of one helical form. This means that the polymer is also optically active due to helicity.

Pino [29] studied macromolecules which contain side-chain asymmetric centers which induce a preferred helical screw-sense in the main chain. He found that moving the asymmetric center closer to the polymer backbone increased the optical activity, presumably due to more and/or longer helical segments. Higher isotacticity produced the same result. He also found that the polymer's optical activity decreased with increasing temperature both in solution and in the melt. This was presumably caused by the loss of the rigidity of conformation that led to optical activity.

Abe and Goodman [46] conceptualized the induced molecular asymmetry in these polymers as being caused by a varying number and length of helices. Also, the summation of the product of helical length and the number of molecules having that length should be equal to a constant. One implication of this was that the polymer chains are constantly moving in and out of helical conformations (i.e., the polymer does not have a "fixed" or permanent helical segment).

It should be pointed out that there are probably no isotactic polymers known today [with the possible exception of the example of the polychloral described below or poly(triphenylmethyl methacrylate) in which isotacticity is 100%]; one single racemic placement in the chain could change the screw-sense of the remainder of the chain and destroy any optical activity based exclusively on macromolecular asymmetry.

Optical Activity Based on Macromolecular Asymmetry

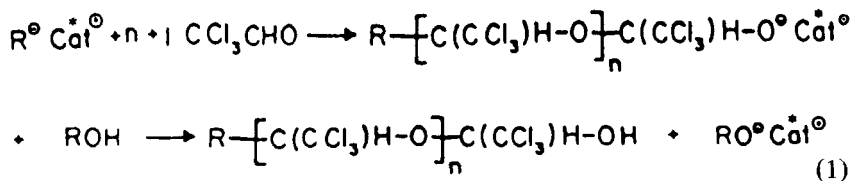
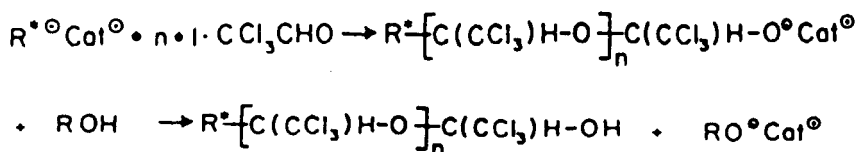
It has only recently been conceptualized and demonstrated that optically active synthetic polymers can be prepared in which the optical activity arises exclusively from the secondary structure of the polymer (i.e., a helix). One of the first syntheses (though of a nonpolymer) which resulted in a "pure" helical structure was the preparation of hexahelicene [47]. Hexahelicene could be resolved into a right- and a left-handed helix having opposite signs of rotation. The specific rotation was very large, $[\alpha]_D^{25} = (+)$ or $(-)$ 3700°. This high optical rotation caused by a helix was one of the driving forces which encouraged us to synthesize optically active polymers based on chloral. These chloral polymers possess only macromolecular asymmetry.

As we noted above, helicity can contribute to the optical activity of polymers containing chiral centers. This observed additional optical activity, although numerically high (100-200°/dm), may reflect a quite low percentage of preferred helicity. In comparison, the optical activity that has been observed in helical inorganic crystals, such as quartz, may be over 10 000°/dm [48]. It is estimated that the actual contribution of helicity to the optical activity of previously studied polymers may be a fraction of the actual theoretical and achievable values that could be obtained if all the polymeric helices were of only one screw-sense.

Over the last 20 years, we have been interested in the preparation of optically active polymers 1) whose structure is completely helical without any conformational reversal, 2) where helicity is the only source of optical activity in the polymer, and 3) whose barrier of rotation along bonds in the main chain is very high or infinite. It has been found that polychloral is

such a polymer and fulfills this concept. Over 20 years ago, we prepared for the first time optically active polychloral with lithium cholesten-3 β -oxide as the anionic initiator [49]. That was the first time that any polymer had been made whose optical activity was based entirely on macromolecular asymmetry.

Haloacetaldehydes, especially chloral, are subject to polymerization through their carbonyl group. In anionic polymerization of chloral, the nucleophile (e.g., alkoxide) attacks the carbon atom of the carbonyl group and by further anionic propagation forms isotactic helical polychloral:



Polychloral prepared by "cryotachensic" polymerization (in which liquid chloral is mixed with initiator above the polymerization threshold temperature and then cooled to initiate polymerization) is completely isotactic, insoluble in all solvents, and crystalline according to x-ray diffraction [50-52]. This technique allowed the preparation of polychloral samples that could be studied for their optical activity in the solid state.

Polychloral samples were prepared by cryotachensic polymerization. Chloral monomer was initiated above the threshold temperature of polymerization, placed between glass plates and then polymerized to polychloral in film form by immersing the assembly in ice water. By this technique, films of about 0.1-0.2 mm thickness were prepared. The films were taken out of the assembly, trimmed, and stabilized by treatment with methanolic hydrogen chloride. The hydroxyl-terminated polychloral film was extracted to remove residual monomer and other impurities. Birefringence in the polymer was minimized by soaking the film in diphenyl ether, which has approximately

the same refractive index as the polymer and reduced or eliminated the crystallinity of the polychloral.

The first successful experiments that resulted in polychloral with measurable optical activity were performed by Vogl in 1963 and by Vogl and Hatada in 1972 [53]. However, the optical activity was first measured by Corley [54, 55]. He used the optically active anionic initiator tetramethylammonium (+)ketopinate to initiate chloral polymerization and obtained a polymer with a specific rotation of $(+)3700 \pm 800^\circ$ at 589 nm. In another case, (+)-methyl-*n*-propylbenzylphenylphosphonium chloride, in which the counteranion rather than the anion is optically active, was used to prepare optically active polychloral with a specific rotation of $(-)1800 \pm 200^\circ$ at 589 nm.

We next used chiral mandelate initiators to obtain polychloral of high optical activity [56]. We converted *L*-(-)-*O*-acetylmandelic acid of $(-)153^\circ$ specific rotation into the tetramethylammonium salt with a rotation of $(-)86^\circ$. *D*-(+)-*O*-Acetylmandelic acid of specific rotation $(+)151^\circ$ was neutralized to the tetramethylammonium *O*-acetylmandelate with a specific rotation of $(+)88^\circ$. These initiators were used in 0.5 mol% concentration for the preparation of polychloral. Optically active polychloral was obtained with a maximum specific rotation of $(-)1860 \pm 70^\circ$ when initiated with tetramethylammonium (+)-*O*-acetylmandelate and $(+)1180 \pm 90^\circ$ when initiated with tetramethylammonium (-)-*O*-acetylmandelate. When the initiator was tetramethylammonium (+)-*O*-methylmandelate ($+52^\circ$), the resulting polychloral had a maximum specific rotation of $(-)190^\circ$. The other antipode (-56°) gave rise to polychloral of specific rotation $(+)210^\circ$. (All these measurements refer to specific rotations at 589 nm.)

The lithium alkoxide derived from methyl mandelate yielded polychloral of higher optical activity [57]. The specific rotation of the initiator precursors was $(+)142^\circ$ for methyl *D*-(+)-mandelate and $(-)141^\circ$ for methyl *L*-(-)-mandelate. Optically active polychloral initiated by the lithium salt of methyl mandelate had a maximum value of rotation of $(+)3600 \pm 110^\circ$ when prepared from the *D*-(+) initiator, and $(-)4670 \pm 240^\circ$ when prepared with the *L*-(-) initiator. The lithium alkoxide made from *R*-(-)-2-octanol gave polychloral with a maximum rotation value of $(+)4200^\circ$, while polychloral made from *S*-(+)-2-octanol prepared under slightly different conditions had a rotation of about $(-)2000^\circ$ [59]. The latter material was obviously not fully of one helical screw-sense. Lithium cholestan-3 β -oxide gave a polychloral sample having an optical activity of about $(+)3000^\circ$, and lithium cholesten-3 β -oxide a value of $(+)3400^\circ$ [59].

Subsequently, we varied the holding time of the initiated mixture (initiator and chloral monomer) above the polymerization temperature prior to cooling the mixture to prepare polychloral films. The holding time had a strong effect on optical activity.

Most polychloral optical rotation values mentioned above were taken from films made from initiated monomer held for about 10 min at 65°C before polymerization. When initiated chloral monomer was held at 65°C for several hours or for shorter times at a higher temperature (i.e., 85°C) prior to polymerization, the polychloral obtained was optically inactive. Optical rotation values were obtained for polychloral made from a number of different initiators after different holding times. Extrapolation to zero time yielded a specific rotation of about 4000° for polychloral prepared from all "strong" initiators, such as alkali alkoxides.

It has been shown by NMR equilibrium studies [58] that strong nucleophiles, such as alkoxides, add the first chloral monomer unit essentially quantitatively above the threshold polymerization temperature. With weaker nucleophiles, such as acetate and chloride, the nucleophile-chloral addition product exists at a level below the detection limit of NMR spectroscopy. Our data show that all polychloral samples with low optical activity were obtained with initiators whose anions carrying the chiral center were weak nucleophiles, such as carboxylates. In addition, these anions often had a chiral center that was one or two atoms removed from the nucleophilic site.

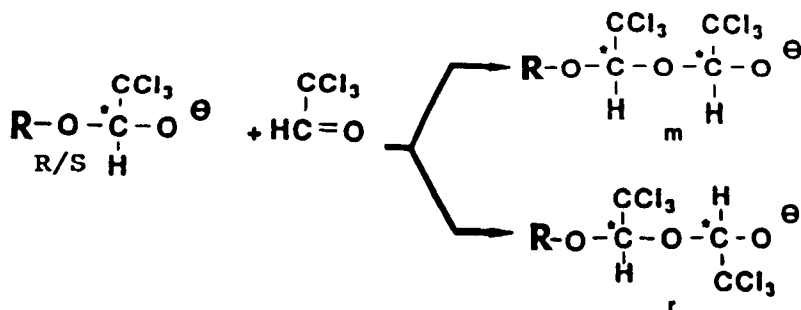
Only in one case did a very "weak" initiator, such as carboxylate, lead to polymer of high optical activity. In this case the chirality was in the counter-cation [55] with the initiating anion being a weak nonchiral nucleophile. Ultimately, this approach of having the asymmetry in the chiral cation may be the initiation technique of choice to prepare optically active helical polymers.

One of the possible reasons for the disappearance of the polymer optical activity with increased holding time above the threshold polymerization temperature is that the chiral centers of the initiator might become racemized. We carried out some experiments to shed light on this problem. We found that, for optically active tetramethylammonium acetylmandelate or lithium cholestan-3 β -oxide, this was not the case. We heated these initiators under initiation conditions for 1 h and then isolated acetylmandelic acid or cholesterol from the carboxylate or alkoxide. The specific rotation values of the acetylmandelic acid and cholesterol were unchanged.

However, in the case of lithium cholestan-3 β -oxide and the two lithium 2-octanoxides [(+) or (-)], we found that polychloral samples made with these initiators, after holding the reaction mixture at 85°C for several hours, were optically inactive [59].

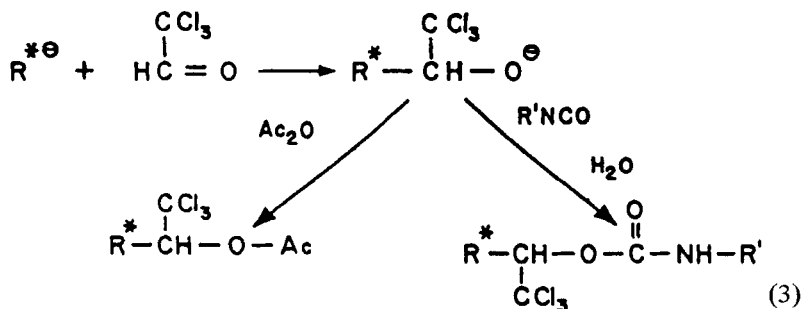
We showed above that the chiral initiator is not racemized under these conditions. Hence, the stereochemistry and the equilibrium of the addition of the first chloral unit, and more likely the stereochemistry of the addition of the second and possibly the third chloral monomer units, are the key to

the optical inactivity of the product polychloral. The polymerization of chloral to isotactic polychloral requires that all chloral units be added in *meso* fashion. The formation of optically inactive chloral polymer from chiral anionic initiators therefore demands the occurrence of both *meso* and *racemic* placements, either in the addition of the first chloral unit or subsequent additions:

**D****L**

(2)

This scenario could explain how chloral initiated with strong nucleophiles and polymerized immediately after mixing gave polychloral with the highest optical activity. On the other hand, when this mixture (with strong nucleophiles as initiators) was held for some time at a higher temperature (85 vs 65°C), inactive polychloral was obtained [60, 61]. Attempts to measure this equilibrium above the threshold polymerization temperature of polymerization have now been successful by quenching the initiated mixture with acetic anhydride or isopropyl isocyanate [62]:



It has become clear that the addition of the second, third, and fourth chloral monomer units also plays an essential role in the stereospecificity of the chloral polymerization and ultimately in the formation of optically active polychloral [62-65]. The steric hindrance caused by the bulkiness of the trichloromethyl groups after the addition of four chloral monomer units forces exclusive subsequent *meso* addition to form helical isotactic polymer [66].

Another possible route to inactive polychloral is that the adduct of a strong nucleophile (such as a lithium alkoxide) with one chloral unit decomposes to yield alkyl formate and trichloromethyl anion on long heating. The trichloromethyl anion would then decompose to yield dichlorocarbene and chloride ion, an optically inactive initiator for chloral polymerization. This also would explain the absence of optical activity in polychloral prepared with optically active alkoxides kept in warm chloral solution for long time periods.

Other polymers have since been prepared whose optical activity seems to arise from macromolecular asymmetry. They are polyisocyanides and poly-(triphenylmethyl methacrylate).

Polyisocyanides were prepared by cationic polymerization of isocyanides and are believed to have a helical structure. The polyisocyanide is in a helical conformation because each carbon atom in the polymer backbone is substituted, which causes a great deal of steric hindrance. Polyisocyanides with a bulky substituent like a tertiary butyl group should be capable of being separated into the two types of optically active polymers. Using a column packing of insoluble poly[(+)-*s*-butyl isocyanide] which had only one screw-sense, poly(*t*-butyl isocyanide) could be resolved in part into the (+) and (-) antipodes [27].

Attempts were also made to use the optically active initiator nickel(II) *L*-alaninate to promote the formation of polyisocyanides having helices with only one screw-sense [27]. However, only an insignificant predominance of one helical form occurred (i.e., nominal optical rotation).

Triphenylmethyl methacrylate was anionically polymerized [67, 68] to optically active polymer. With the optically active initiator, lithium (*R*)-*N*-(1-phenylethyl)-anilide, triphenylmethyl methacrylate homopolymer was prepared having a specific rotation of $(-)$ 104° at 589 nm in toluene. When triphenylmethyl methacrylate was polymerized with *n*-butyllithium (where the lithium counterion was complexed with sparteine, a naturally occurring alkaloid) as the anionic initiator, poly(triphenylmethyl methacrylate) was obtained with a specific rotation in toluene of $(+)$ 363° at 589 nm [69-71]. The optically active poly(triphenylmethyl methacrylate) could be used for the partial resolution of compounds such as hexahelicene, Troeger base, 1-phenylethanol, and others [71-73].

PROSPECTS

The research on optical activity based on macromolecular asymmetry has as its clear and ultimate objective the preparation of optically active polymers of one screw-sense. We wish to demonstrate clearly the feasibility of this basic idea by using the proper chiral initiator and the most suitable monomer. We hope ultimately to obtain optically active polymers with an achiral anionic initiator under the "catalytic" influence of polarized light. We have selected the aldehyde polymers, particularly perhaloaldehyde polymers, and anionic polymerization to achieve this task. The first step was the selection of chloral as the monomer. Chloral polymerizes well under anionic cryotachensic polymerization conditions. It forms exclusively isotactic polymer. No amorphous or atactic polymer, even in oligomeric form, has ever been observed or isolated.

Completely isotactic polymer can also be obtained from other halogenated acetaldehydes. For such to occur, at least two of the three halogen atoms of the trihalomethyl group have to be as bulky as chlorine (but iodoacetaldehydes are too unstable). Increased side group bulk, however, leads to decreased polymerizability and lowers the threshold polymerization temperature, the maximum temperature at which polymer can form from liquid monomer. For tribromoacetaldehyde (bromal) this temperature is -75°C .

Aldehyde polymerization to the polyacetals is readily carried out with anionic initiators and produces a polymer that has a carbon-oxygen bond length of 1.41 Å which, together with the trihalomethyl group, forces the formation of the isotactic polymer configuration in the helical conformation of a repeat unit of about 5.2 Å. Polyolefins with a polyethylene backbone, such as in isotactic polypropylene, form a 3_1 helix based on a 6.65 Å repeat unit. It requires the bulkiness of a cyclohexyl group to force the monomer unit into an isotactic helix during polymerization. Polymers whose backbone chain is isotactic and is

substituted with a very bulky group to provide the rotational barrier [poly-(triphenylmethyl methacrylate)] or that have short bonds with actual or partial double-bond character [polyisocyanates (nylon 1), or polyisocyanides] approach these requirements.

One other approach that we are presently undertaking to achieve the ideal helix is by preparing chiral fluorochlorobromoacetaldehyde and polymerizing it. (The racemic fluorochlorobromoacetaldehyde has been synthesized and polymerized to insoluble, presumably isotactic, polymer [74, 75].) The chiral center on each carbon atom of the polyacetal chain (when only isotactic polymer is formed) should cause exclusive formation of a helical polymer chain of one screw-sense. By subtracting the contribution of the chiral center from the overall rotation, we should be able to determine the contribution of the helical part of the macromolecule.

Recently we showed that not only can optically active polychloral be prepared but that "racemization" occurred when the initiated mixture was kept above the ceiling temperature before the polymer formation was allowed to occur. The immediate perception was that the initiating chiral anion had been racemized by a side reaction, or that the nucleophile had caused a side reaction with chloral to form fragments such as trichloromethyl anion, trichloroethoxide, formate, or ultimately chloride ion, which are achiral initiators for inactive polychloral. If any of these reactions occur, they play a rather unimportant role in the initiation step to form optically active polymer of chloral. We have also shown that the nucleophile used as anionic initiator does not need to be a chiral anion, but that an achiral anion with a chiral cation can also form helical macromolecules with high optical rotation.

In addition to the polymerization of chloral, two additional trihaloacetaldehydes, fluorochlorobromoacetaldehyde (the only perhaloacetaldehyde of the 10 perhaloacetaldehydes not containing iodine that can exist in chiral form) and bromal, will also be studied. Iodine-containing trihaloacetaldehydes are too unstable and undergo side reactions with most nucleophiles under conditions that are needed for the initiation of polymerization.

As nucleophiles, chiral alkoxides can be used as their lithium salts. (In the past, it was shown that other alkali alkoxides undergo undesirable side reactions.) Lithium alkoxides are readily prepared without racemization by addition of *s*-butyllithium to a slight excess (5%) of alcohols, including chiral alcohols, at -78°C . The resultant linear oligomers of chloral initiated by chiral alkoxides ("end capped" with acetic anhydride or with isopropyl isocyanate) should be analyzed by temperature-programmed gas chromatography.

Finally, it has been shown that isotactic (and helical) polychloral of high optical rotation can be made from an achiral anion and a chiral cation. It

would be desirable to explore the polyaddition of trihaloacetaldehydes with salts that have an achiral anion and a chiral cation and ultimately with the "right" chiral anion and the "right" chiral cation.

Ultimately, we would like to see whether it would be possible to prepare chiral compounds (or polymers) from bulky achiral anions and chloral in the presence of polarized light. Results of such experiments would relate to theories of how optical activity first developed on earth. We know that some inorganic crystals, such as potassium chlorate and quartz, exist in an optically active form, based on helical arrangements of the atoms in their crystal lattice [48, 54].

It is known that, in certain cases, the optical activity is a property of the crystal structure and not of the single molecule (quartz, potassium chlorate, potassium silicotungstate); the formation of crystals of one enantiomorph can predominate [76]. Some of those crystals (e.g., quartz) contain atoms arranged in helices. It has been suggested [77] that a possible parallel exists between the discovery by Lee, Yang, and Wu of the nonexistence of parity by weak interactions and the preferential formation of a nucleus of growth of one enantiomeric form.

One other direction of this research suggested and indicated by some unconfirmed experiments is the preparation of highly oriented samples of polychloral and other perhaloaldehydes. One would expect properties similar to those of fibers of typical rigid rod-type materials (though of nonaromatic nature). The optical activity along the fiber axis should be enormous, but it would require the development of a new spinning technique to go from monomer to oriented fiber.

Last but not least, areas of this problem which seem to be suitable for computer simulation are: 1) to establish clearly the space-filling size and size range of the trihalomethyl group required for the isotactic perhaloaldehyde polymer formation; 2) to identify the bulk size and asymmetry required for the initiating anion to add the monomer (e.g., chloral) exclusively in one form (e.g., by *meso* addition); and 3) to identify the energetic conditions for the addition of the first 4-6 monomer units and the stability of the stereoisomers of addition [66].

Finally, it is believed that all helical polymers, not only helical isotactic polymers, could be made into optically active polymers as long as the basic rules laid down in this article are followed: 1) stereospecific addition of the first few monomer units to the chiral initiator until the helix starts forming, and 2) no helix reversal in the helical structure.

We expect that the polymers described in this article should be suitable for a number of applications. These would certainly include the separation

of enantiomers and also optical applications (e.g., as lenses). Of course, many applications may become apparent later that could only be devised with these new types of polymers in hand.

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