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STEREOSPECIFIC POLYMERIZATION AND CHIRAL CRYSTALLIZATION

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ABSTRACT

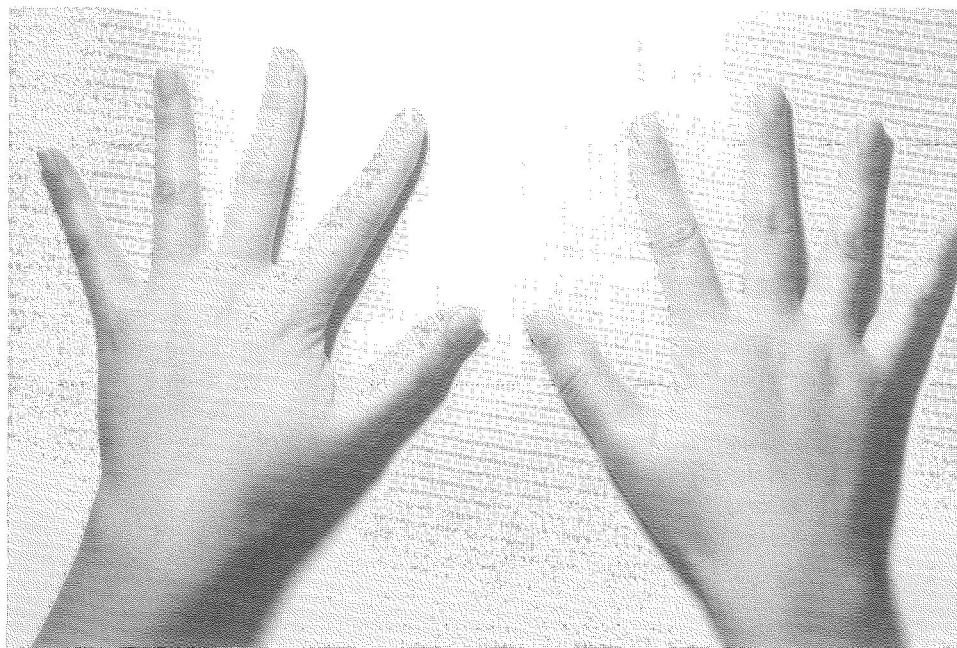
Configurational and conformationally specific polymerization processes which lead to helical macromolecules can be successfully carried out when monomer structure, polymerization mechanism, and spatial restrictions for monomer addition are all carefully considered. Under certain conditions, optically active polymers having a single helical screw sense can be prepared. Surprisingly, the chiral crystallization of certain inorganic salts has much in common with stereospecific polymerization mentioned above. Achiral sodium chlorate and sodium bromate can crystallize spontaneously from aqueous solutions to give a mixture of pure levorotatory and pure dextrorotatory isotropic crystals. The crystallization of these salts can also be nucleated with traces of levo- or dextrorotatory crystals to furnish new crystals with a high degree of chiroptical purity. Our varied efforts within the confines of these two related fields are summarized.

INTRODUCTION

We live in a chiral world [1]. Our hands, our eyes, and our ears each exist macroscopically in two distinct mirror image forms. Within our bodies, the concept of chirality extends all the way down to the molecular level. Here, the intimate association of one chiral molecule with another leads to a high degree of chemical specificity that is ultimately responsible for the maintenance of life itself (Fig. 1).

Widely recognized native chiral structures include the α -helix found in many proteins and polyamino acids [2]. For α -helices comprised of naturally occurring *L*-amino acids, a right-handed screw sense is energetically favored over the left-handed form. Helical "handedness" is also observed among the nucleic acid family of biopolymers [3]. B-form DNA takes on a right-handed double helical geometry while its conformational cousin, Z-DNA, possesses distinct left-handed, "zigzag" symmetry. As for the α -helix mentioned earlier, chirality at the helical or macromolecular level stems from the presence of asymmetric centers which reside within the repeat units, i.e., the nucleosides, of these biopolymers. Helical order encountered among the biopolymers is largely stabilized by hydrogen bonds and other physical bonding interactions, and is thus fragile. When subjected to strong acids or alkali, detergents, or higher temperatures, these macromolecules tend to unfold or denature to a random coil state.

In the early 1960s we embarked upon a novel program to synthesize a *stable*, rigid helix that would possess chirality solely at its macromolecular or helical level [4]. Polychloral was initially selected as our "target" because it is rigid, can be prepared in an isotactic form, and was known at the time to exist as a stable mixture



of left- and right-handed helical screws. Our task was to devise a synthetic strategy which would enable the preparation of polychloral having a single helical screw direction and then to study the chiroptical properties of this new material [5-7]. In the 30 years that have followed, much progress has been made in our laboratory toward attaining these initial goals. We can now prepare optically active polychloral samples having extremely high optical rotation magnitudes in the solid state [8] (Fig. 2).

It is interesting to note that a stereospecific polymerization reaction which leads directly to the formation of a polymer helix in the solid state and the crystallization of smaller molecules share common features. The former process often furnishes polymers with well-defined configurational and conformational geometries, and these species readily pack into higher ordered structures in the solid state [9, 10]. A similar process occurs between smaller molecules during crystallization to again furnish highly organized solid-state structures. Of course, obvious differences exist between these two processes as well. Notably, during polymerization, individual monomer residues are covalently linked together. Moreover, the growth of a linear polymer chain occurs in a unidirectional manner. By contrast, crystallization is devoid of covalent bond formation and crystal growth occurs on the faces of individual crystalline entities.

It is because of the similarities mentioned above that the crystallization of certain inorganic salts has occupied our attention more recently [11-14]. Sodium chlorate (NaClO_3) and sodium bromate (NaBrO_3) both form chiral crystals when



FIG. 2. Single helix.

allowed to crystallize slowly from aqueous solutions. Individual crystals may reach two centimeters in size and exhibit either dextrorotatory (D) or levorotatory (L) optical rotations [15]. Once a crystal begins growing in one chiral "direction," it continues to grow in this manner. No reversal of optical growth has ever been reported. Moreover, crystal growth can often be nucleated with traces of chiral crystals to furnish new crystals having high chiroptical purities. In this sense, chiral crystal growth mimics the polymerization of chloral. Once chloral polymerization begins, the growth of an individual polymer chain proceeds in a stereospecific manner, furnishing one helical screw direction or the other. When the polymerization process is initiated or "nucleated" with a chiral initiator, a *single* helical screw sense predominates and the polymer is optically active [8]. Below, we highlight some of our findings which encompass the related fields of stereospecific polymerization and chiral crystallization.

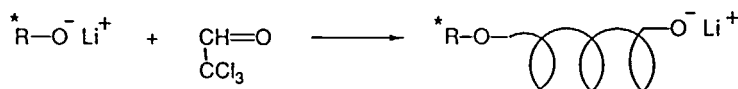
THE SINGLE RIGID HELIX

During the mid-twentieth century, the helical nature of many biopolymers was firmly established. The discovery of the right-handed α -helix and the DNA double helix helped to revolutionize our understanding of life itself. Not surprisingly, in light of these results, synthetic polymer chemists were motivated to synthesize well-defined helical macromolecules which possessed single screw directions. In the intervening four decades, several different approaches have been successfully utilized to accomplish this goal.

Widely exploited has been the polymerization of chiral α -olefins, chiral aldehydes, and other monomers which contain asymmetric centers in close proximity to their polymerizable groups. The first such example of this approach involved the synthesis of chiral 3-methylpentene and its subsequent polymerization to furnish a stereoregular, helical polymer having a predominant screw direction [16]. Here, as for the protein α -helix mentioned above, helical handedness is enforced by chiral side groups residing in the polymer. The resulting polymer is optically active and its chiroptical properties are a direct consequence of asymmetry present at both the atomic and macromolecular levels. Many other examples of this approach have since been reported, including those for the higher chiral α -olefins and chiral aldehydes like citronellal [17–19].

As mentioned in the Introduction, we embarked on a decidedly different path and employed polychloral as the focus for our studies. Since polychloral is isotactic and possesses stable 4_1 helical order in its solid state [20–22], we reasoned that it might be possible to induce the formation of a single screw sense in the polymer using chiral initiating species. Here, the bulky trichloromethyl side groups in the polymer would effectively block unwanted growth steps that would lead to an inversion of the newly formed helical coil. We also speculated that similar results might be achieved if achiral initiating species were used in conjunction with chiral solvents, chiral substrates, or perhaps, even plane polarized light [8].

The structures of polychloral, its cousin polybromal, and a variety of chloral/bromal copolymers were reinvestigated using solid-state NMR techniques [23, 24]. For all polymers, well-resolved peaks were observed, indicating the presence of a isotactic, helical structure, in good agreement with earlier x-ray diffraction and



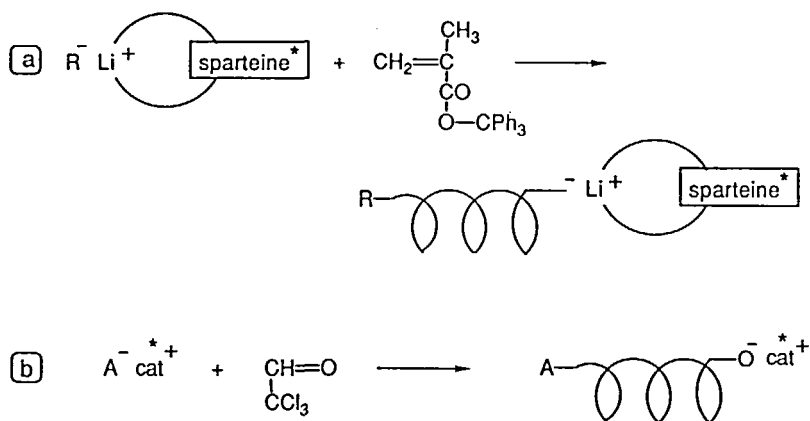
SCHEME 1.

^{35}Cl NQR studies [20–22]. When anionic polymerizations were carried out with chiral alkoxide initiators, optically active polychloral samples were obtained in the solid state [25], as detailed in Scheme 1.

Depending upon the structure of the initiating alkoxide and the polymerization conditions employed, we found it possible to effectively “tune” or adjust both the magnitude and the sign of the optical rotations in our polymers [26–28]. In certain cases, specific rotation magnitudes measured at the sodium D-line reached several thousand degrees. Model endgroup studies confirmed that the presence of chiral-initiating fragments in the polymer had a negligible impact on the rotation magnitudes that we were observing. In other words, the handedness of the rigid polychloral helix was the apparent source of this optical activity.

Helix sense selective polymerizations of the type described above can also be carried out with achiral initiating species if a chiral counterion is utilized. For example, Hatada and coworkers [29–31] successfully polymerized triphenylmethyl methacrylate and other triarylmethyl methacrylates with achiral *n*-butyl lithium complexed to (–)-sparteine or (–)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (Scheme 2a). Their resulting polymers exhibited optical rotations at the sodium D-line of several hundred degrees. Hatada attributed this optical rotatory power to a stable helical conformation with single handedness in which the presence of bulky triarylmethyl side groups effectively prevented the uncoiling of the helical polymer chain produced during polymerization. The use of chiral counterions as effective stereoregulating agents has also been demonstrated in our laboratory for the polymerization of chloral [6, 7] (Scheme 2b).

In the absence of helix sense selective polymerization techniques like those described above, helical polymers devoid of chirality at the atomic level are typically



SCHEME 2.

prepared as racemic mixtures of left- and right-handed screws. In principle, if these helices are relatively rigid and possess high energy barriers to inversion, then their optical resolution on chiral chromatographic supports becomes feasible. This has been achieved for helical poly(butylisocyanide) where optically active materials have been obtained [32, 33]. Of course, this separation technique requires that the polymer be soluble, which is not the case for polychloral.

THE GENESIS OF HELICAL STRUCTURE IN POLYCHLORAL

During the course of our asymmetric polymerization studies with chloral, one question remained largely unanswered. At what stage does the addition of chloral monomer units to the growing polymer chain become highly stereospecific? Or, in other words, when does the first turn in the polymers 4_1 helical coil emerge along the growing polyaldehyde chain? To address this question, we undertook a series of studies that were specifically designed to track the growth of a polychloral chain "from the ground up." By intercepting chain growth at an oligomer stage with an acetic anhydride quench step and then subjecting the resulting products to modern analytical procedures, we were able to witness for the first time the genesis of isotactic helical structure along an emerging polymer chain [34].

For simple alkoxide initiators like lithium *t*-butoxide [35–37] or the chiral lithium (–)bornyl oxide [38], we discovered that the attack of the initiator on the prochiral monomer does not always proceed with a high degree of stereospecificity. A similar trend holds true for the second chloral addition step as well. However, we found that subsequent chloral growth steps become increasingly selective, favoring *meso* addition and helix formation. Indeed, by the time the tetramer stage is reached, competing *racemo* growth steps which serve to scramble nascent helical geometry are completely absent. Interestingly, the same story does not hold true for the oligomerization of fluoral, the trifluoro analogue of chloral [39–41]. In this case, the relatively small trifluoromethyl groups present in this system are apparently unable to endow the propagating chain end with a high degree of stereospecificity. Here, *meso* addition steps never become dominant, and isotactic, helical structure fails to develop in the polymer.

By using a variety of techniques pioneered in our laboratory [34], we isolated individual chloral oligomer fractions after they were endcapped with an acetate group and then grew single crystals for the dimer, trimer, tetramer, pentamer, and hexamer adducts. The x-ray structure [42, 43] for the chloral tetramer proved to be particularly striking. When viewed along its *c*-axis, the tetramer clearly adopts one full helical turn in the solid state. This helical "embryo" has a repeat distance of 4.8 Å (Fig. 3), in close agreement with the 5.2 Å repeat length observed in isotactic, helical polychloral [20]. In essence, this tetramer, when growing in unendcapped form, functions as a kind of helical "template" or "nucleating agent," directing subsequent propagation steps in *meso* fashion and locking in helical geometry with one handedness or the other. As will become apparent later, there are obvious parallels between this process and the chiral nucleation of inorganic salts described below.

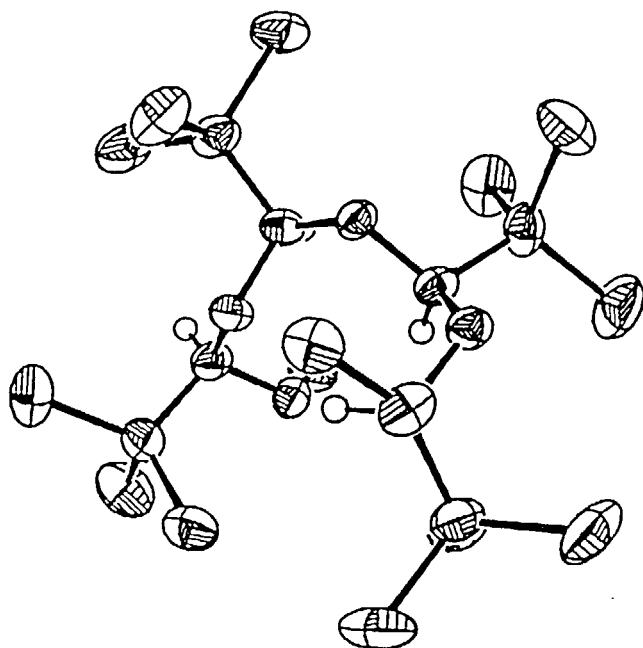


FIG. 3. Tetramer of chloral.

ISOTACTIC POLYPROPYLENE

The most important stereoregular polymer now prepared in large quantities is polypropylene [44]. This polymer is synthesized stereospecifically using transition metal catalysts. In an ideal case, the polymer exists in a *meso* configuration, and when crystallized, adopts a 3_1 helical conformation with a helix pitch of 6.65 Å [9]. When the polymer is melted or dissolved, helical structure is lost. During recrystallization, a racemic mixture of left- and right-handed helical screws is generated and the resulting polymer sample is thus devoid of optical activity. Efforts to demonstrate the existence of optical activity in polypropylene have been unsuccessful because solution measurements were often utilized. Attempts to measure the chiroptical properties of the "native" polymer in its solid state [45] have been thwarted by sample birefringence and other poorly understood variables.

SOME GENERAL CONCEPTS REGARDING STEREOREGULARITY IN POLYMERS

For a number of years, it was believed that the development of stereoregularity, especially in isotactic systems, depended strongly on the initiator's ability to properly orient incoming monomer units undergoing addition to the growing chain end. Indeed, α -olefins like polypropylene require the use of coordinating initiating systems for stereospecificity to develop during polymerization. Suitable initiators

can be based on the original titanium system or may consist of the newer metallocene derivatives.

However, based in part on our own efforts in this area, we now recognize that newer concepts must also be considered.

For example, for polychloral, stereoregular structure is a direct consequence of this polymer's sterically demanding trichloromethyl side groups which force an otherwise flexible polyaldehyde backbone to grow in an isotactic, helical fashion. Here, the size of the trihalomethyl side group is critical [40]. As we have noted earlier, the relatively small trifluoromethyl moieties in polyfluoral are unable to endow that polymer's propagating chain end with a high degree of stereospecificity. As a result, polyfluoral is largely atactic and nonhelical.

OPTICAL ACTIVITY IN SOLIDS

The optical activity of simple organic compounds is normally measured in homogeneous solutions where individual molecules are solvated and well separated. Primarily for inorganic crystals, optical rotation measurements can also be gathered in the solid state. This is particularly useful for chiral crystals, e.g., sodium chlorate, for which optical activity would be lost in solution.

Because isotactic polychloral is totally insoluble in all known solvent systems, we had to devise alternate methods for measuring its chiroptical properties in the solid state. Polychloral film disks with a thickness of ~ 0.1 mm were typically utilized for our studies. However, the presence of microvoids in the polymer sample led to a substantial amount of light scattering and the disks often appeared translucent. Corley [6, 7] and Harris [25, 46], working in our laboratory, found that the polychloral samples could be made transparent for optical activity measurements if they were first soaked in diphenyl ether, a refractive index matching medium. It was with this approach that high quality solid-state measurements were ultimately achieved. However, not all solid samples can be readily prepared in disk or thin film form. Thus, we sought to develop a more general method which could employ suspensions of finely divided powders [11, 47-51]. During the past few years, we have found that the selection of a proper suspension medium is critical for the success of this technique. The densities and refractive indices of the sample and the medium must both be closely matched. Moreover, particle size must be small and the sample cannot be oriented. These rather stringent conditions limit rotation measurements to solids that are isorefractive in all three dimensions. Highly crystalline materials and polymers that exhibit birefringence are not amenable to this technique (Fig. 4).

We have further established that samples should be slowly stirred by placing a small stirring device directly under the optical cell. Stirring rates can be conveniently monitored with the aid of a stroboscope. Excessive stirring rates can cause cavitation while too slow a rate will not provide a proper suspension. The refractive index of the suspending medium should be checked at the beginning and at the end of the optical rotation measurement to insure that no change has occurred. The optical rotation of the suspension should be measured as a function of both the change in refractive index of the medium and as a function of the polarimeter's photocell current to insure that measurements are gathered in a region of maximum transpar-

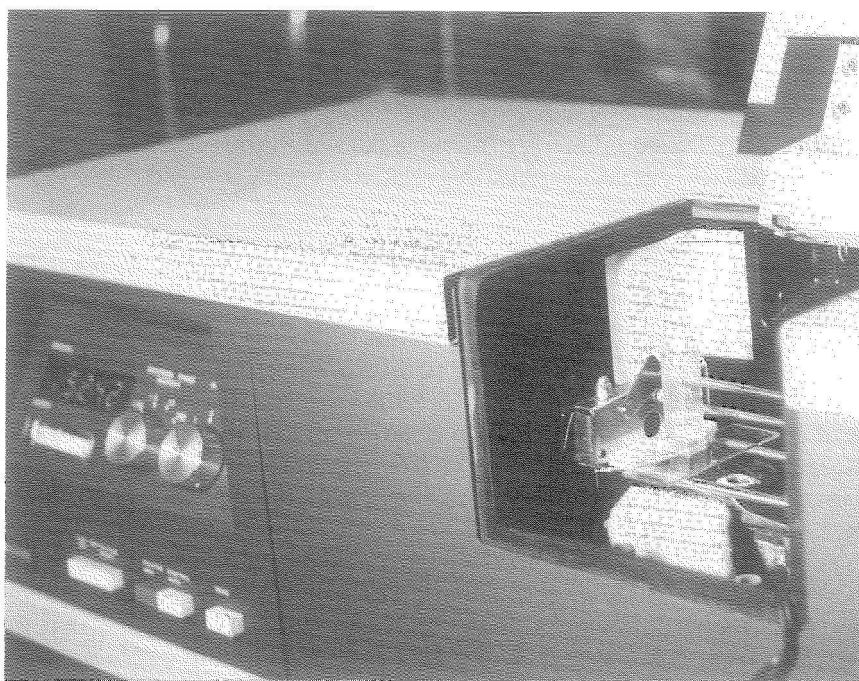


FIG. 4. Apparatus for the suspension measurement of optical rotation.

ency. For a given sample, we have found that chiroptical measurements can be made within 30 minutes with a precision ranging from $\pm 3\%$ to about $\pm 20\%$. It is with the technique described above that chiroptical measurements were made on a variety of different solids [47–55] including inorganic salts, organic compounds, and polymers. Some of our results are presented here.

As will be discussed below, achiral sodium chlorate and sodium bromate both crystallize from aqueous solutions to give chiral, D- and L-crystals [15]. These crystals are isotropic with refractive index and optical rotation being the same in each of the three crystallographic directions. These salts were thus ideally suited for our initial suspension measurements. We isolated these salts as fine crystalline powders with particle sizes below 40 microns. The resulting powders were suspended in a mixture of carbon disulfide and carbon tetrachloride having a matched refractive index with the salt. Chiroptical measurements were then obtained as described above. With some satisfaction, we found that the rotation magnitudes detected in the crystals and in the suspensions differed by no more than $\pm 3\%$. We also repeated earlier measurements of Pino's [16] for the polymer (+)-poly(3-methyl pentene) in suspension with a sample obtained from Professor Pino. Using our technique, we were able to closely replicate reported optical rotation data for this polymer.

Solid-state optical rotation measurements have been performed on a variety of other polymers as well. For optically active poly(triphenylmethyl methacrylate), suspension and solution measurements are in remarkable agreement. In other cases, we've observed significant discrepancies, however. For example, measured specific rotations (sodium D-line) for poly-(R)-lactide are (+) 245° in suspension, (+) 170°

in film form, and (+) 162° in solution. For RNA, we noted rotations of about (+) 20° in suspension and (+) 115° in solution. Here, the physical state of the sample may be important. Furthermore, manipulation of the polymer sample may introduce a number of variables that cannot be accurately accounted for. We recommend that caution be exercised in interpreting some data of this kind, and we present our results to encourage others to explore this relatively uncharted field.

CHIRAL CRYSTALLIZATION AND RELATED PHENOMENA

Crystallization involves the agglomeration of molecules from solution or the melt into solids having highly organized structures. This process can often be initiated by the addition of "seed-crystals" or other nucleating agents. Crystallization has been employed for centuries for the isolation and purification of both organic and inorganic compounds. Some of the most elegant crystals are produced by nature as "minerals" and a number of these are valued by the human race as "precious stones."

Quartz (silicon dioxide), one of the most common minerals, has an asymmetric, i.e., helical, lattice that is not superimposable upon its mirror image. Early work by Biot [56], following an observation by Arago [57], demonstrated that quartz crystals (Fig. 5) can rotate the plane of polarized light. With this discovery was born the notion of "optical activity" and the pioneering efforts of Fresnel [58]. The origins of optical activity in crystalline solids have been extensively studied [59-64]. An excellent account has been published recently by Glazer and Stadnicka [65].

The crystallization behavior of sodium chlorate and sodium bromate has fascinated workers for nearly 150 years [15, 66]. These achiral salts crystallize from aqueous media to give large dextrorotatory or levorotatory platelets that can reach several centimeters in size. An x-ray analysis of levorotatory sodium chlorate has been provided by Abrahams et al. [67, 68]. A helical arrangement of atoms in this solid (Fig. 6) is clearly evident. In our laboratory, large crystals were obtained when saturated aqueous solutions of sodium chlorate or sodium bromate were slowly

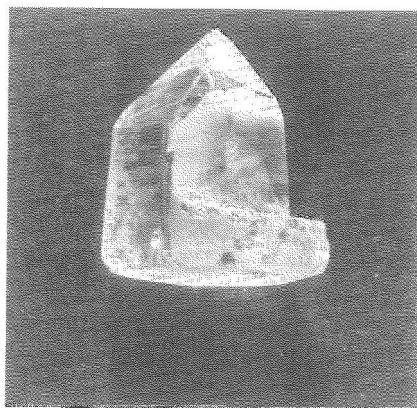


FIG. 5. Quartz crystal.

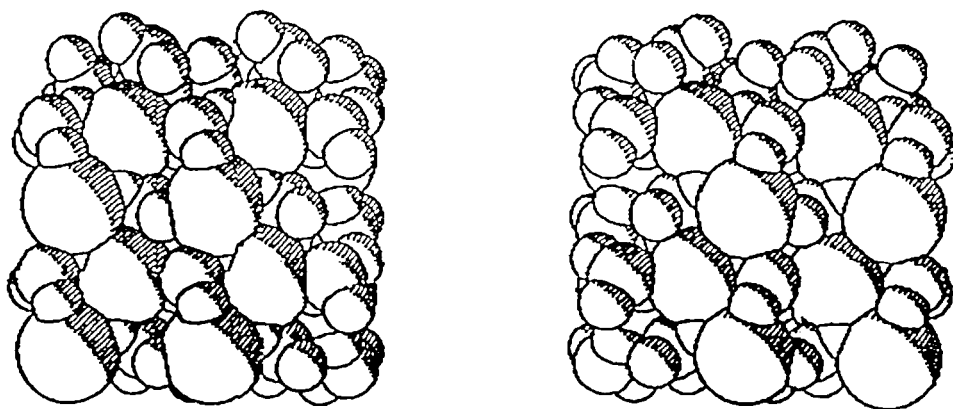


FIG. 6. Molecular models of levo- and dextrorotatory NaClO_3 crystals.

allowed to evaporate under conditions where dust and other particulates were carefully excluded (Figs. 7 and 8). We have confirmed that the chiroptical properties of these solids are isotropic. For example, sodium chlorate possesses a specific rotation magnitude of 122° (sodium D-line) in all three crystallographic directions. Using our suspension technique described above, we've measured similar rotation magnitudes for finely divided crystalline powders. It is interesting to note that nearly a century ago, Landolt [69] attempted to measure the optical activity of sodium chlorate powders and, on finding significant discrepancies between his crystal and powder values (which gave only about 1/3 of the expected value), concluded that his efforts were without merit.

The development of chirality during the crystallization of inorganic salts like sodium chlorate has been studied extensively. In a typical crystallization, statistically equivalent, i.e., racemic, populations of dextrorotatory and levorotatory crystals are usually obtained if experiments are carried out with highly purified salts that are devoid of chiral impurities and other chiral influences [15]. Chiral nucleating

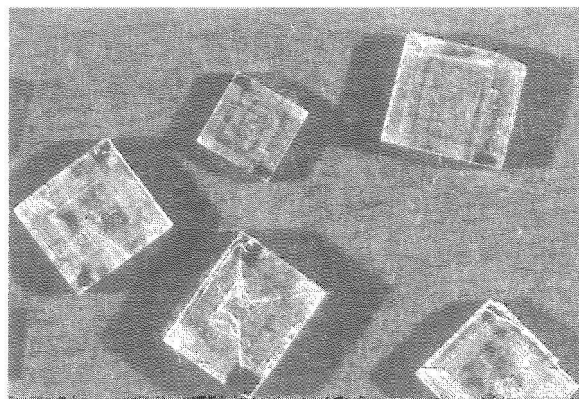


FIG. 7. NaClO_3 crystals.

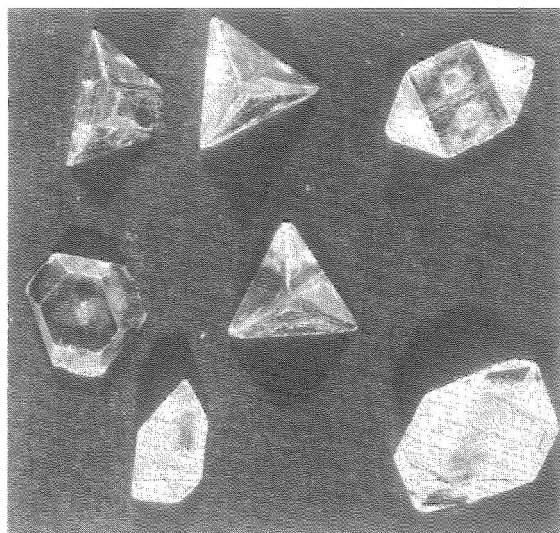


FIG. 8. NaBrO_3 crystals.

agents can bring about enantioselective crystallization of these solutions, however, resulting in a significant excess of either the D- or the L-crystal population.

We nucleated supersaturated solutions of sodium chlorate with D- and L-sodium chlorate powders (Fig. 9) and replicated this phenomenon. In 10 separate experiments using the crystalline D-powder as a "chiral seed," dextrorotatory crystals were always obtained—each with a specific rotation magnitude of about 122° at the sodium D-line. In 10 additional trials with the L-powder, levorotatory crystals were isolated having the same rotation magnitude. Similar results were obtained for

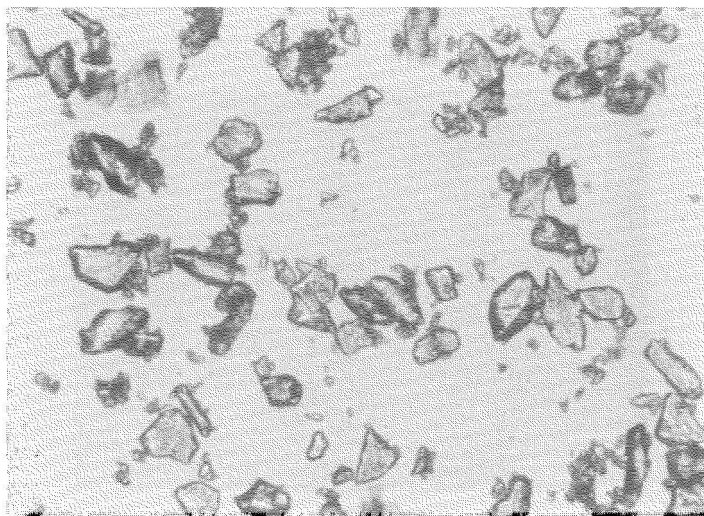


FIG. 9. NaClO_3 seed crystals.

sodium bromate. We then attempted to nucleate sodium chlorate solutions with the isomorphous sodium bromate salt. Interestingly, the D-sodium bromate powder furnished levorotatory sodium chlorate crystals while the L-sodium bromate seed afforded dextrorotatory sodium chlorate crystals. This same "reverse" pattern was observed when sodium chlorate was used to nucleate sodium bromate crystals. Before proceeding further, it is worth noting the obvious parallels between this phenomenon and the use of chiral initiators for the helix sense selective polymerization of chloral described earlier.

Recently, in a startling report [70], spontaneous chiral symmetry breaking during sodium chlorate crystallization was claimed to have been observed in one laboratory. On stirring saturated solutions of this salt, excess populations of D- or L-crystals were reportedly deposited *in the absence of any added chiral nucleating agent*. The authors of this study speculated that their stirring process somehow provided an autocatalytic seeding event which was followed by a successful competition between growing D- and L-crystals to furnish an excess of one chiral crystal population. In about half of their trials, D-crystals *predominated* while in the other half, L-crystals *were favored*. Unfortunately, optical rotation data for the crystals isolated during this investigation were not published. It is important to note that a spontaneous macroscopic resolution of this kind could provide considerable insight into the origins of biomolecular chirality on Earth. The origins of biomolecular handedness, including such problems as chiral synthesis, chiral fields, parity-nonconservation, and chiral symmetry breaking have all been discussed by Mason [71].

Several years before the publication of these findings, we had embarked upon a study using our suspension measurement technique which obviated the need for large crystalline specimens. Our basic experiment was as follows: Into a freshly cleaned 7 mL test tube were placed *highly purified* sodium chlorate (3.0 g) and water (1.8 mL). After capping the tube with a silicone rubber septum, the solution was heated to 85°C in a specially designed apparatus which allowed the tube to slowly rotate at 70 rotations per minute. The apparatus (Fig. 10) containing the tubes was then cooled at 1.2°C per minute while rotation was continued. In most cases, small crystals began to appear at or below 58°C and sometimes as low as 35°C.

Our results are as follows: Of 29 separate experiments, 15 provided samples that contained all (or mostly all) levorotatory crystals while 14 furnished samples that were all (or mostly all) dextrorotatory crystals. Moreover, a total of 76% of the experiments furnished optically pure crystalline powders with rotation magnitudes (sodium D-line) of 122° while 17% of these experiments provided sodium chlorate solids that were greater than 80% optically pure. The remaining experiments afforded solids that were essentially racemic, possessing little or no rotation magnitudes. Interestingly, we observed that solids of the highest optical purity resulted when the crystallizations began within the higher temperature range, generally above 50°C. In those experiments where crystal formation began near 40°C, chiroptical purities of the resulting samples were reduced somewhat. Finally, the racemic compositions resulted from the few experiments where crystalline solids had not formed by the time 35°C was reached. In these cases, the tubes were manually shaken to rapidly induce crystallization which apparently proceeded by completely random nucleation. Identical results were obtained when our tubes were rotated in clockwise or counterclockwise fashion.

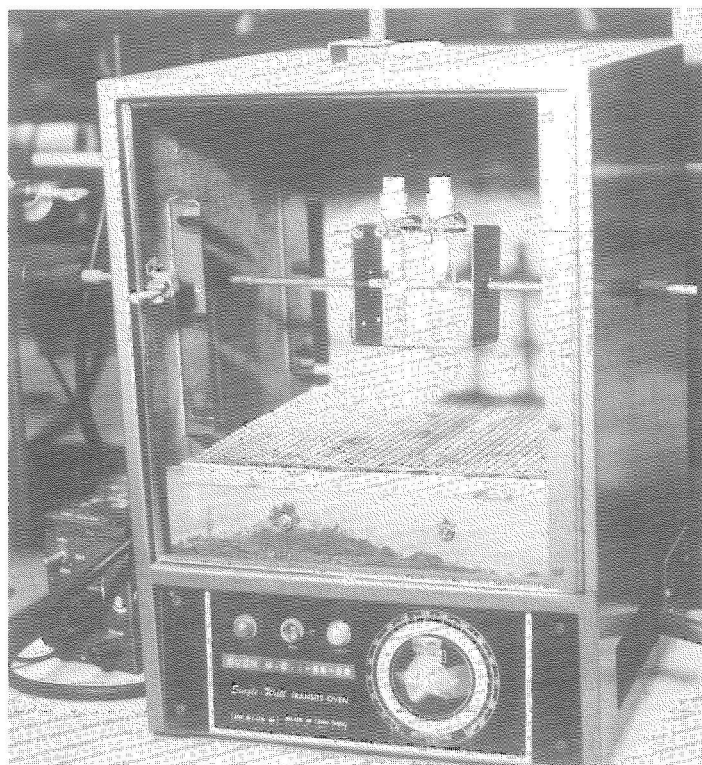


FIG. 10. Tumbling apparatus for chiral crystallization.

We interpret our findings in the following way: The agitation or tumbling action within our tubes generates a chiral "seed" of sodium chlorate having one handedness or the other. The actual mechanism by which this seed is generated is unknown. However, our data do suggest that there exists an equal chance that a given seed will be "right-handed" or "left-handed." No chiral bias is apparent. Further agitation may break *this seed* into a large number of secondary chiral seeds which then go on to rapidly nucleate the solution in chiral fashion. When the sodium chlorate solutions are above 50°C, this process has little competition and crystalline solids having high chiroptical purities are ultimately produced as the solutions slowly cool. For those experiments where crystallization is delayed until lower temperatures are reached, the solutions become increasingly supersaturated. Now, there is a greater tendency for "normal" chiral crystallization to occur and competition with the original seeding process ensues. Depending on the exact dynamics of each system, solids having lower chiroptical purities will generally result. Finally, if the sodium chlorate solutions cool to a point where they are completely supersaturated, a simple agitation event will result in the rapid formation of a nearly racemic mixture of seeds. Here, the normally observed chiral crystallization process will dominate and optically inactive samples will be obtained. *Again, we wish to stress that we are still in the beginning phase; further work on chiral crystallization by chiral nucleation is currently underway.*

SUMMARY

Throughout this paper, we have attempted to draw parallels between chiral crystallization phenomena and stereospecific polymerization processes in an effort to show that there is a common thread linking these two seemingly disparate fields. As we have noted, the chiral crystallization of inorganic salts and the stereospecific polymerization of monomers to give polymeric helices can both furnish chiral entities at a molecular level. However, in our macroscopic world, we isolate these crystals and helices as racemic mixtures. From our perspective, these products are optically inactive.

Moving to a higher level of complexity, we have observed that when these same systems are "challenged" with an external chiral influence, for example, a chiral seed crystal or a chiral initiator, chiral symmetry is broken and optically active materials result. Here, crystals of a single handedness or polymer helices of one screw sense predominate throughout our isolated sample. As chiral beings, we have come to expect that materials of this kind will often behave differently from those described in the previous paragraph.

Finally, when we move to the highest and most poorly understood level of complexity, we find that spontaneous chiral symmetry breaking of the kind observed for sodium chlorate solutions has, apparently, no equal in the current polymer world. This is where our series of analogies must end—at least for now! However, we find it an interesting mental exercise to contemplate the fabrication of a chemically driven, helix growth process that might ultimately exhibit the dual features of spontaneous symmetry breaking and chiral competition.

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