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ALDEHYDE POLYMERIZATION, HELICAL POLYMERS, MACROMOLECULAR ASYMMETRY, AND OLIGOMERS

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ABSTRACT

A historical development of the polymerization of higher aldehydes is presented. It shows the development of the polymerization of the simplest example, formaldehyde, the very ancient and to some extent incorrect history of other aldehyde polymerizations, and actually starts with the full understanding of this field as of the early 1950s. Much of the early work is incoherent and inconsistent, not surprisingly because of the limited knowledge of polymer chemistry that was available at that time. This contribution tries to correlate the polymerization of formaldehyde, the higher aliphatic aldehydes, and the trihaloacetaldehydes within the framework of a comprehensive understanding of the field of polymer science. The extensive progress in the field of trihaloacetaldehyde polymerization has led to the development of cryotachensic polymerization, the concept of optical activity based on macromolecular asymmetry, ultimately the recognition of the importance of the study of oligomers of stereoregular polymers, and the very essence of the embryonic state of addition polymerization.

INTRODUCTION

a. Aldehyde Polymerization

By the middle 1950s it was known that formaldehyde polymers exist, as shown by Butlerov in 1859 and later investigations [1, 2]. Staudinger [3] had made the polymerization of formaldehyde the center of his efforts on polymerization studies beginning in 1919 [4], and he proved that macromolecules are long chain molecules, where small units were held together by sigma bonds.

In 1948 it was found [5] that polyformaldehyde could be prepared in high molecular weight. The polymer had useful mechanical properties suitable for its potential as a large-scale polymer and, what we would call it today, as the first engineering-type polymer. With these interesting properties, by 1952 it was decided by DuPont under McGrew's leadership to commercialize polyoxymethylene.

Peculiar macromolecular products had also been observed from higher aliphatic aldehydes [6, 7]. Most products were of relatively low molecular weight and were condensation products, primarily aldol condensation products [8]. Some of these "condensations" of higher aliphatic aldehydes, particularly of acetaldehyde, were later [9, 10] obtained and further investigated by treating acetaldehyde under basic conditions and high pressure. The purpose of these experiments was the direct synthesis of poly(vinyl alcohol) from the "enol" form of acetaldehyde, vinyl alcohol, which *per se* is not stable.

It was also recognized early that formaldehyde [11], haloacetaldehydes [for example, trichloroacetaldehyde (chloral)] [12], and aliphatic aldehydes [13] form cyclic trimers. Formaldehyde [14] and acetaldehyde also form tetramers [15]; higher cyclic oligomers of formaldehyde have also been isolated [16–18]. These oligomers have the structure of cyclic acetals, with the six-membered trimers (trioxane, paraldehyde) being particularly stable; the eight-membered tetramer of formaldehyde, tetroxane, as well as the tetramer of acetaldehyde, were also found to be stable.

Trioxane, discovered in 1886 [11], was found in 1922 [19, 20] to form a linear high molecular weight polymer of formaldehyde, polyoxymethylene (POM), which has the same structure as the polyoxymethylene prepared from formaldehyde.

In 1929, investigations of the effect of high pressure on small organic molecules was undertaken by Bridgeman and Conant. It included the study of the behavior of aldehydes at high pressures. It was reported that higher aldehydes gave highly viscous liquids [21] and waxy solids [22, 23]; the waxy solids were obtained from the sterically hindered isobutyraldehyde.

In 1934, two papers appeared almost simultaneously, one authored by Travers [24] and the other by Letort [25]. Both reported the transformation of acetaldehyde to a rubbery material upon cooling acetaldehyde below its melting point and then melting the crystalline acetaldehyde ("crystallization polymerization"). Shortly thereafter, Staudinger [26] suggested, based on IR measurements, that the structure of this polymer was that of a polyacetal.

The discovery of the polymerization of acetaldehyde was an accident, and the understanding of why this polymerization occurred was the subject of an extensive investigation of Letort and his group for the next 20 years [27–30]. Details of the crystal structure of acetaldehyde, the rate of cooling, and even the influence of ultraviolet light [30] were believed to be possibly responsible for the polymerization. We know today [31] that only a temperature below −40 or −50°C in the presence of an acidic surface or impurities on this surface, which act as initiators of the acetaldehyde polymerization, are responsible for the "crystallization polymerization."

Chloral, the most commonly known trihaloacetaldehyde, was known to give an insoluble material called metachloral [32, 33] under certain conditions. Even in the first report on the synthesis of chloral by chlorination of ethyl alcohol by Liebig in 1832, he described a horn-like mass which was insoluble [34]. Investigation of this peculiar form of chloral can be traced to patents by Erdmann [32] and Gaertner [33] in 1906. Beginning in 1913 a flurry of investigations by Boeseken followed

[35]. In the ensuing years, additional infrequent communications can be found regarding "metachloral" [35, 36].

This was the status on aldehyde polymerization when I became interested in the subject. Cationic and anionic polymerizations of formaldehyde were known, and formaldehyde polymerization was in the process of commercialization; a semiworks operation was functioning successfully. No work had been undertaken on the polymerization of other aldehydes, and it was believed that the rules for their polymerization, based on literature reports, were quite different from that of the formaldehyde polymerization. Why these polymerizations might act differently was completely unknown.

At this time I will describe the situation of polymer science, and specifically of stereospecific polymerization, as it was known in the open patent literature in 1956.

b. Stereospecific Polymerization

Macromolecules were known to exist as linear and branched polymers and as crosslinked. They were also classified as homo- and copolymers in both the crystalline and amorphous states. While some polymers were crystalline, such as polyethylene, others were semicrystalline or completely amorphous. Propylene was known to give only low molecular weight polymers. Isobutylene had been made by "acid catalysis" for a number of years; today that process is called cationic polymerization.

Polyethylene, known since 1934 [37], was still a curiosity at the end of the 1940s. Its crystal structure had been determined to comprise a planar zigzag molecular structure [38]. Crystallinity and the determination of the crystal structure is not a very sensitive method for understanding the entire structure of a polymer. Only 10 or 20 monomer units arranged in a perfect fashion are often sufficient to observe crystallinity, and crystal structures have been "established" on this basis. Polymerization of ethylene was performed at that time under high pressure (minimum 1500 atm). As a result the polymer was substantially branched and of relatively low crystallinity. In 1948 it was found that when ethylene was polymerized at much higher pressures (10,000 atm), polyethylene samples with much higher melting points were obtained [39]. At about the same time, the structure of "high-pressure polyethylene" was studied in detail, and it was found that polyethylene prepared at about 1500–2000 atm had both long and short branches [40]. The polymer prepared at 10,000 atm was more "linear" and substantially free of branching [41].

Vinyl ethers played an important role in the development of polymer chemistry. In 1948, Schildknecht and his coworkers found that when methylvinyl ether polymerization was conducted with boron fluoride etherate as the initiator at lower temperatures, an elastomeric polymer was obtained that was partially crystalline [42]. The authors suggested that the polymer had some preferred stereochemistry, at least in parts of the macromolecules. Five years later Natta and his school discovered the stereospecific polymerization of propylene using Ziegler–Natta-type initiating systems [43–45].

Ziegler and his school had studied the behavior and reactivity of aluminum alkyls for three decades. They found that reactions with ethylene led to an oligomerization reaction yielding mostly pentamers. In 1952 it was discovered that with transition metal compounds, ethylene could be polymerized to linear polyethylene at atmospheric pressure, and the era of Ziegler-Natta coordination "catalysis" had begun [46, 47].

After the famous ACHEMA meeting in Frankfurt at which Ziegler presented the oligomerization of ethylene with aluminum alkyls, the Natta school applied the transition metal-modified aluminum alkyl catalysts to propylene and successfully generated high molecular weight polypropylene [43]. This polymer was found to be stereoregular. The monomer units were in the *all-meso* position, and the polymer was found to be crystalline and helical in the solid state. The name "isotactic" for this type of polymer was coined. In the next 10 years, essentially all olefins, dienes, and even chiral olefin monomers were polymerized. This was the beginning of a vast expansion in the synthesis and understanding of olefin polymers. It resulted in the very successful, highly lucrative commercialization of low-pressure polyethylene and of crystalline isotactic polypropylene.

Ring-opening polymerization of ethylene oxide in the late 1940s led to the synthesis of low molecular weight ethylene oxide polymers. These low molecular weight polymeric glycols and also similar products from propylene oxide found their greatest utility as soft segments in the preparation of polyurethanes by their reaction with diisocyanates [48].

In 1956 the Pruitt patent [49] appeared. It described the polymerization of propylene oxide with a novel initiating system, including ferric chloride, which gave high molecular weight, crystalline poly(propylene oxide). Although the polymer was never commercialized, it was the first representative of a second class of polymers that were stereoregular, crystalline, and isotactic; the stereoregular polyepoxide family.

In the early development of polymer science very little was known about the details of the thermodynamics of addition polymerization. In fact, the reverse reaction of the equilibrium was largely ignored. The main reason for this, as we now know, is that all the addition polymerization reactions that were then known had ceiling temperatures of polymerization in excess of 300°C. As a consequence, the ceiling temperature of polymerization was never a factor in polymerization reactions. It was not until 1957 when Dainton and Ivin published their classical paper on the ceiling temperature of polymerization that the relationship between enthalpy and entropy of polymerization which commands the equilibrium of polymer and monomer as a function of temperature was recognized [50].

When our work on the polymerization of higher aldehydes started, we were aware of the "crystallization polymerization" of acetaldehyde of Letort, the vinyl ether polymerization, and the propylene polymerization. This background was actually a hindrance rather than an advantage for our own work. During our research the Pruit patent became known; the ceiling temperature paper did not, however, become available until our patents on isotactic, crystalline, higher aldehyde polymers had been filed.

POLYMERIZATION OF HIGHER ALIPHATIC ALDEHYDES

a. Cationic Acetaldehyde Polymerization and Atactic Polyacetaldehyde

I joined DuPont at the end of 1956. After only 6 months in the Exploratory Group of the Polychemicals Department at the Experimental Station, I was transferred to the Delrin group. This was the research and development group that was responsible for bringing polyformaldehyde to commercialization. The decision had been made to synthesize the polymer from purified gaseous formaldehyde. The other form of formaldehyde, the cyclic trimer trioxane, was not considered commercially viable since it was believed to be difficult to manufacture economically and it was considered that it could not compete with purified gaseous formaldehyde.

I was asked to look into the polymerization of higher aldehydes. Together with Dennis Funck, we repeated the old Letort technique of freezing and thawing acetaldehyde in order to make elastomeric polyacetaldehyde. This was not an easy task. Acetaldehyde is a low boiling liquid that is highly reactive, and we had to purify it in large quantities. A low temperature distillation apparatus with a dry ice cooling condenser was used for the purification. According to the literature, only crystallization and thawing of acetaldehyde would generate the polymer. Ultraviolet radiation also seemed to have a beneficial effect [51].

One problem became almost immediately apparent. Even though elastomeric polyacetaldehyde was produced by this procedure, the polymerization yields varied from run to run, and on some occasions no polymer was produced. Letort had described yields as high as 50% polymer; those yields were reported on relatively small runs. When we used a larger amount of monomer for polymerization, the yields usually decreased. We suspected that the "surface to volume" effect had played a significant role in the "crystallization polymerization."

Our ultimate objective was still to make "stabilized" polyacetaldehyde and to test its commercial possibilities. As a consequence, polyacetaldehyde was prepared in relatively small amounts by the "crystallization polymerization" procedure and the now well-established acetyl or alkyl endcapping stabilization techniques which were known to stabilize polyformaldehyde [52]. Acetate capping in solution of acetic anhydride with a small amount of pyridine gave acetate-capped polymer. Treatment with trimethylorthoformate, usually in a fluidized bed reactor, gave alkyl-capped polyacetaldehyde. The addition of soluble polyamides in 1% quantities and antioxidants in 0.1% quantities substantially improved the thermal stability of polyacetaldehyde. Aromatic amines were much more effective than hindered phenols as antioxidants [53].

This work was accomplished in about 3 months, and I was left to pursue our ultimate goal of the polymerizations of higher aldehydes with less exotic polymerization systems. It soon became very obvious that we had to find a way to carry out the acetaldehyde polymerization with "regular" radical or ionic polymerization initiators in order to have a reliable supply of polymer of adequate molecular weight. At that time our knowledge of ionic polymerization was very limited, but an accidental discovery opened the door for the polymerization of acetaldehyde on a large scale. My technician, Jake Mansure, had broken the low temperature distillation apparatus, and it had to be repaired. In the meantime, I insisted that we borrow a similar distillation apparatus from another group. I further insisted that the apparatus (which was a one piece apparatus, except for the flask and for the receiver) was to be cleaned with fuming nitric acid and dried in an oven at 120°C.

When the cleaned apparatus was used for the distillation of acetaldehyde (the condenser part being filled with a dry ice/acetone mixture), the entire condenser part of the apparatus was filled with a rubbery opaque substance which was soluble in the acetaldehyde that was being distilled. When the condenser was brought to room temperature, the material had disappeared—only acetaldehyde was left in the receiver and the distillation pot. In other distillation experiments we found small amounts of rubbery material in the distillation flask when the acetaldehyde was rapidly evaporated. This rubbery material was identical with the elastomeric acetaldehyde that had been obtained by "crystallization polymerization." Because of this observation, we had demonstrated that acetaldehyde could be polymerized *above* its melting point [54–61] and that "crystallization" was not essential for the polymerization of acetaldehyde. It was then October 1957.

From this essential observation it was now easy to progress further to the actual development of the cationic polymerization of acetaldehyde. The basic principle was very simple: the polymerization had to be carried out at low temperature (practically speaking, below −40°C [56]) to avoid the competitive reaction of the trimerization of acetaldehyde to paraldehyde, the cyclic trimer, or to metaldehyde, the cyclic tetramer [60]. While the polymerization was later found to be subject to the ceiling temperature principle, the cyclotrimerization is not; however, it would be more accurate to say it is not subject to the same ceiling temperature principle. In fact, these cyclic compounds can even be made at room temperature.

We had recognized that a temperature below −40°C was essential for the polymerization. The famous paper of Dainton and Ivin [50] on ceiling temperature did not become available until the inventive phase of our acetaldehyde polymerization was completed.

After finding that the polymerization did not require crystalline acetaldehyde, it was easy to realize that we could readily carry out the polymerization at low temperature in a simple test tube capped with a rubber septum. This technique allowed extensive and rapid screening of initiators and solvents. One key hurdle turned out to be essential not only for the preparation of the polymer but even more importantly for its isolation. We had seen many times that a highly viscous solution of the polymer, or even a plug of the polymer, had formed when acetaldehyde was cooled in a solvent and treated with an acid initiator. When the sample was then allowed to come to room temperature, the contents of the tube lost all their viscosity and no polymer could be isolated [56]. It became imperative to completely "neutralize" the acidic initiator residues *at the reaction temperature* (i.e., the dry ice temperature) before allowing the temperature of the reaction mixture to rise to room temperature. When this was done, polyacetaldehyde of high molecular weight could be isolated in nearly quantitative yield [56]. The NMR spectrum of elastomeric polyacetaldehyde was obtained for the first time (Figs. 1 and 2). In this case it was also for the first time demonstrated that "pentads" could be identified by means of a 200-MHz NMR spectrometer (Figs. 3 and 4) [57].

One additional problem for the efficient preparation of elastomeric polyacetaldehyde had to be solved; it had to do with local temperature control. When the polymerization was carried out in the reaction vessel inserted in a dry ice/acetone bath, on some occasions a portion of the acetaldehyde was transformed to the trimer paraldehyde and not to the desired polyacetaldehyde. This was particularly noticeable when "good solvents" for the polymer were selected for the polymerization of acetaldehyde [58]. Apparently the heat of polymerization increased the local temperature above the ceiling temperature and prevented, in part, polymerization to a high polymer, which resulted in cyclotrimerization. The entirely successful polymerization of acetaldehyde to polyacetaldehyde without the formation of paraldehyde could readily be accomplished in liquid ethylene as the solvent due to the low boiling temperature of ethylene (−104°C). Even in propylene, which has a boiling point of −68°C, some paraldehyde was formed with the normal boron

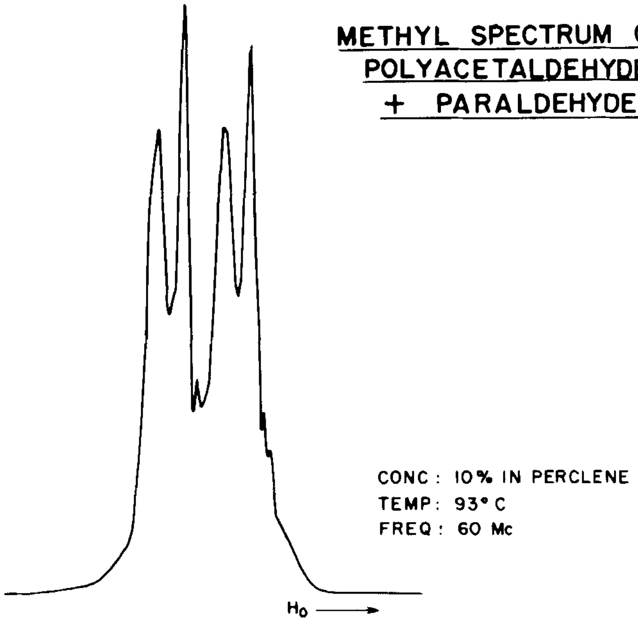


FIG. 1. 60 MHz methyl spectrum of polyacetaldehyde at 93°C.

trifluoride as the initiator. Paraldehyde and metaldehyde formed as side products of the reaction of acetaldehyde with acids at "higher temperatures" are stereospecific cyclotrimers and cyclotetramers; they have the *all-meso* configuration [59, 60]. The other cyclotrimer has been described but has to be prepared in a different way. It is interesting to note that polymerization of acetaldehyde beyond the cyclotrimer state would lead to an isotactic polyacetaldehyde.

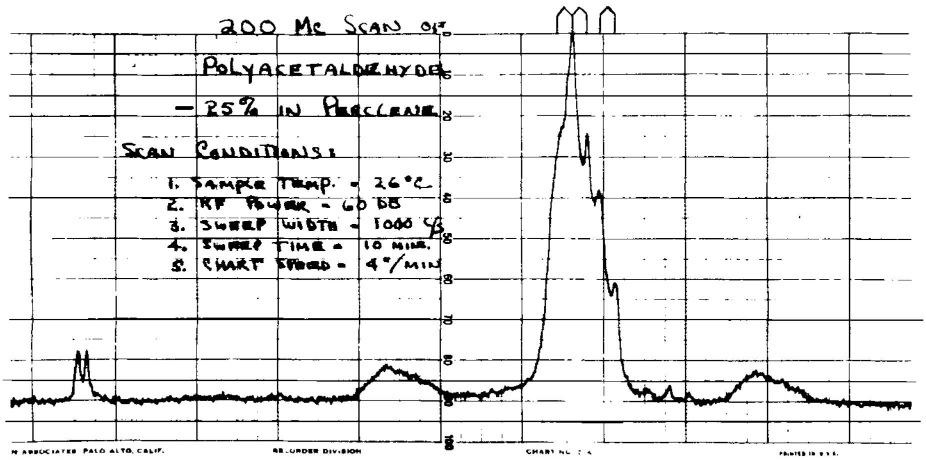


FIG. 2. 200 MHz methyl spectrum of elastomeric polyacetaldehyde at 26°C.

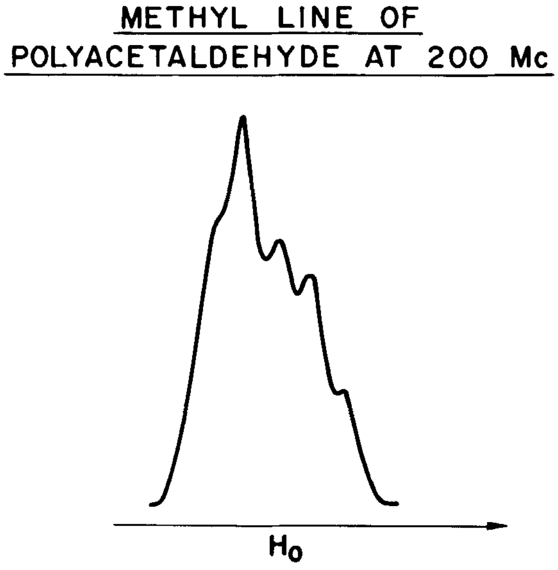


FIG. 3. 200 MHz methyl spectrum of polyacetaldehyde.

As indicated above, our best process for preparing elastomeric acetaldehyde was carried out in liquid ethylene. This solvent gave a homogeneous mixture with acetaldehyde at the polymerization temperature, and the heat of polymerization could be dissipated by the boiling of ethylene. The most convenient initiator was boron trifluoride. Acetaldehyde is not soluble in lower boiling hydrocarbons at very

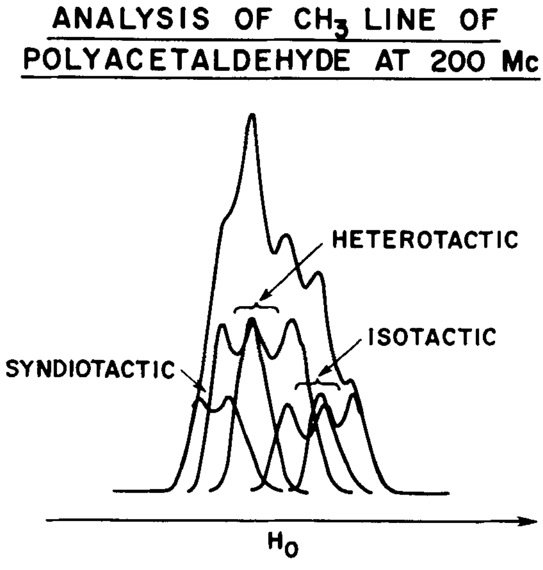
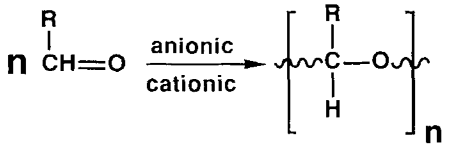


FIG. 4. Curve resolver analysis of the 200-MHz spectrum of polyacetaldehyde.

low temperatures but is soluble in olefins. Polymerizations in low boiling saturated hydrocarbons are two-phase systems, similar to conditions of polymerization in neat acetaldehyde.

b. Isotactic Polyaldehydes

Up to this point in our research on the polymerization of higher aldehydes, only acid-type initiators had been used for the reaction. Under similar conditions and with cationic initiators, *n*-butyraldehyde had also given an amorphous polymer [56]:



$$n\,\overset{\displaystyle R}{\overset{|}{C}}H{=}O \xrightarrow[\text{cationic}]{\text{anionic}} \left[\sim\!\!\sim \overset{\displaystyle R}{\underset{\displaystyle H}{C}}-O\sim \right]_n \qquad (1)$$

R = aliphatic, trihalomethyl

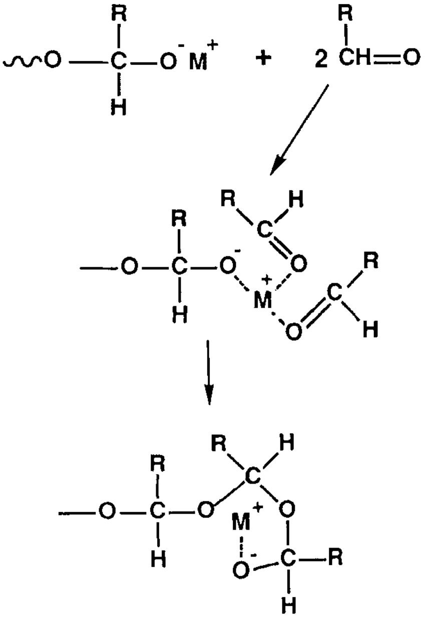
I now turned our attention to the use of anionic initiators for the polymerization of acetaldehyde. We had argued that acetaldehyde with its substitution on the polymerizable double bond, similar to propylene, should be capable of producing an isotactic polymer if the right polymerization conditions were met. I knew that the polymerization had to be carried out at low temperatures. To think in these directions was not easy because it had become common knowledge that stereoregular polymers [isotactic polyolefins, particularly polypropylene and the recently discovered poly(propylene oxide)] could only be made with coordination initiators, preferable of the transition metal type. To think otherwise was heresy.

In my first successful attempt to polymerize acetaldehyde with an anionic initiator, I used lithium aluminum hydride. From about 3 mg initiator, I obtained perhaps 400–500 mg product (about 10% yield) which was very different from anything I had seen previously. It was a solid, appeared to be crystalline, *and* was stable at room temperature [61–64]. It was so different that I set it aside because I thought it was a mixture of some aluminum compounds. A short time later I thought of a method of characterizing the polymer structure: treating the polymer with 2,4-dinitrophenylhydrazine appeared to a chemist as a simple solution. The preparation of the 2,4-dinitrophenylhydrazone of an aldehyde (or a ketone) is done in a solution of 2,4-dinitrophenylhydrazine in sulfuric acid [63]. By then I had also isolated from a large run of an acetaldehyde polymerization with boron trifluoride etherate, in 0.5% yield, an insoluble fraction which I knew was polyacetaldehyde. A typical sample of our now easily available elastomeric polyacetaldehyde, the insoluble fraction from the large run of acetaldehyde polymerization with boron trifluoride etherate and the sample from the "attempted" polymerization of acetaldehyde with lithium aluminum hydride were subjected to the 2,4-dinitrophenylhydrazine treatment. We expected the strong acid medium to degrade the polymer and, at the same time, the "freed" acetaldehyde to react with the 2,4-dinitrophenylhydrazine reagent. All three experiments gave a quantitative yield of acetaldehyde 2,4-dinitrophenylhydrazone. These simple experiments proved the basic structure of the polymers as polyacetals and as polyacetaldehydes. They also demonstrated a convenient method of analyzing the polyaldehyde structure as that of a polyacetal.

Such experiments were necessary prior to the development of NMR spectroscopy and at a time when IR spectroscopy was still not very reliable [65].

After this discovery of the polymerization of acetaldehyde to the elastomeric polyacetaldehyde, the effect of the ceiling temperature on the polymerization, the ease of the isolation of the polymer, and the polymerization of acetaldehyde to what was believed to be the isotactic polymer, a frantic period followed. It was clear that we had discovered a general method of aldehyde polymerization and also a method to synthesize a new type of stereoregular polymer, i.e., stereoregular polyacetals. Soon we recognized that we could use alkali metal alkoxides as initiators for the polymerization to isotactic polymers. Alkoxides with larger, more "organic" groups were found to be more desirable because they were more "soluble" or compatible. Alkali alkyls were found to be too reactive and gave side reactions.

In the next 2 months, insoluble and presumably isotactic polyaldehydes up to the decaldehyde were prepared, stabilized [66], and the most probable polymerization mechanism worked out [64] (Eq. 2).



(2)

We also found that aldehyde polymers with side chains more than three methylene groups long gave a "double melting" point. Much later we determined that the lower melting point was that of the aliphatic side chain and the higher melting point was that of the polyacetal main chain [67, 68]. Within 1 year we had gone from our first studies of the Letort polymer to the filing of patents on stabilized elastomeric polyacetaldehyde [53] and crystalline, presumably isotactic, polyacetaldehyde stabilized by acetate endcapping [62]. The latter patent became the basic patent of acetaldehyde polymers—an important scientific achievement. However, the polymer was found to be too unstable to justify commercialization. The polymerization of valeraldehyde, *n*-hexaldehyde, *n*-heptaldehyde [69–71], *n*-octaldehyde [72], *n*-nonaldehyde [73], *n*-decaldehyde [74], and *n*-undecaldehyde [75] to isotactic polyacetals was later worked out in great detail.

Some early work on the vapor-phase copolymerization of trioxane and ethyl glycidate [76] led to the discovery of polyoxymethylene-based ionomers.

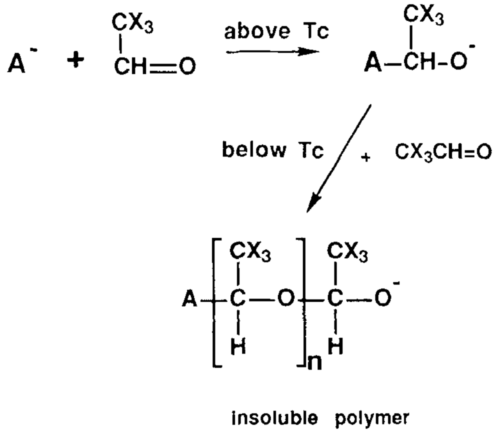
POLYCHLORAL

During our work on the polymerization of higher aliphatic aldehydes, it became apparent that a suitable capping method was needed to stabilize the polyaldehyde produced. All the higher aldehydes have a low ceiling temperature of polymerization and revert to monomer when the polymerization mixture is allowed to come to room temperature. This reversion is somewhat less for crystalline isotactic polyaldehydes. I hoped that the rate of depolymerization could be overcome by acetate endcapping with acetic anhydride which might have a faster rate than depolymerization. Vapor capping was the technique of choice because this method was being used for the endcapping of polyformaldehyde which was soon to be prepared commercially by this method. Keith Brinker, my lab partner, had a laboratory model of a vapor-capper he used for polyformaldehyde capping in which 5 g polyformaldehyde could be used. It consisted of a course fritted filter funnel, modified with a heating element in order to pass overheated acetic anhydride over a sample that was essentially in a fluidized state. The first experiments with isotactic polyacetaldehyde were failures; the polymer samples very quickly and completely depolymerized. I do not remember that we ever had one successful run with this apparatus. However, these experiments accomplished one thing for us. It became clear that we needed a polyaldehyde other than polyformaldehyde on which we could practice our vapor-capping experiments, and one that would survive these capping conditions. We thought that polychloral (PCh) would be slightly more stable, so we chose this material for our capping experiments. Indeed, PCh survived the capping procedure, and 30–50% of the capped polymer was recovered.

PCh had been known since 1832 [34] when Liebig, in an attempt to prepare chloral by chlorination of ethyl alcohol, also isolated a “horn-like” substance. It was later called metachloral [32] and was quite extensively studied after 1900 [33–36]. To us it was clear that it was a high polymer, and in late 1959 Nowak and Whalley, based on infrared data, suggested that metachloral was a polymer [77–79] and, importantly, an isotactic polymer. This observation turned out to be correct.

The polymerization of chloral in late 1962 became the main objective of my research. Soon I found out that *all* the controversial reports on the preparation of the metaldehydes had some merit. The polymerization of chloral was very rapid, but PCh was insoluble in every solvent, including chloral monomer. It was impossible to find suitable mixing devices to bring monomer and initiator solutions together without polymerization. The yield of PCh depended on how effectively the initiator solution was encased with insoluble polymer, but low yields were always obtained.

Although I had been allowed to continue working on the project that I liked and that I thought had many unusual and novel aspects, the time of reckoning was rapidly approaching. On March 15, 1963, I had to present the results of my work to the Steering Committee of the Central Research Department, and I had nothing to report except one-half year of failures. In desperation, I went to the laboratory at 5 o’clock in the morning to make a final attempt to polymerize chloral to a homogeneous piece of polychloral. Within an hour, I had found the solution. The initiator and monomer had to be *heated* before mixing, and when both solutions were above the ceiling temperature of polymerization, they could be safely mixed without polymerization. Cooling formed homogeneous pieces of PCh. By the time of the Steering Committee meeting, I not only had a story but I could also show a most convincing demonstration. The PCh samples were homogeneous and could be stabilized by treating them with phenylisocyanate (Figs. 5, 6, 7, and 8). We called the method of preparation "cryotachensic polymerization" (Eq. 3).



$$A^- + \overset{\displaystyle CX_3}{\overset{|}{CH{=}O}} \xrightarrow{\text{above Tc}} A{-}\overset{\displaystyle CX_3}{\overset{|}{CH}}{-}O^- \xrightarrow[\text{below Tc}]{+\ CX_3CH{=}O} A{-}\left[\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CX_3}{|}}{C}}{-}O\right]_n{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CX_3}{|}}{C}}{-}O^- \quad \text{insoluble polymer} \tag{3}$$

FIG. 5. First solid pieces of polychloral; initiator, lithium cholesteryl oxide; end-capped with phenylisocyanate.

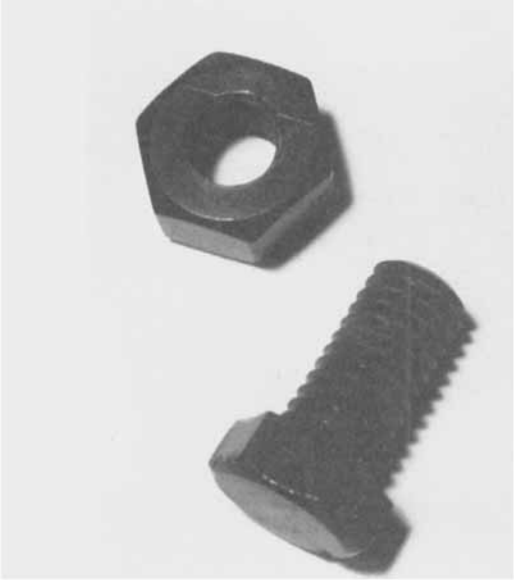


FIG. 6. Machined screw of polychloral

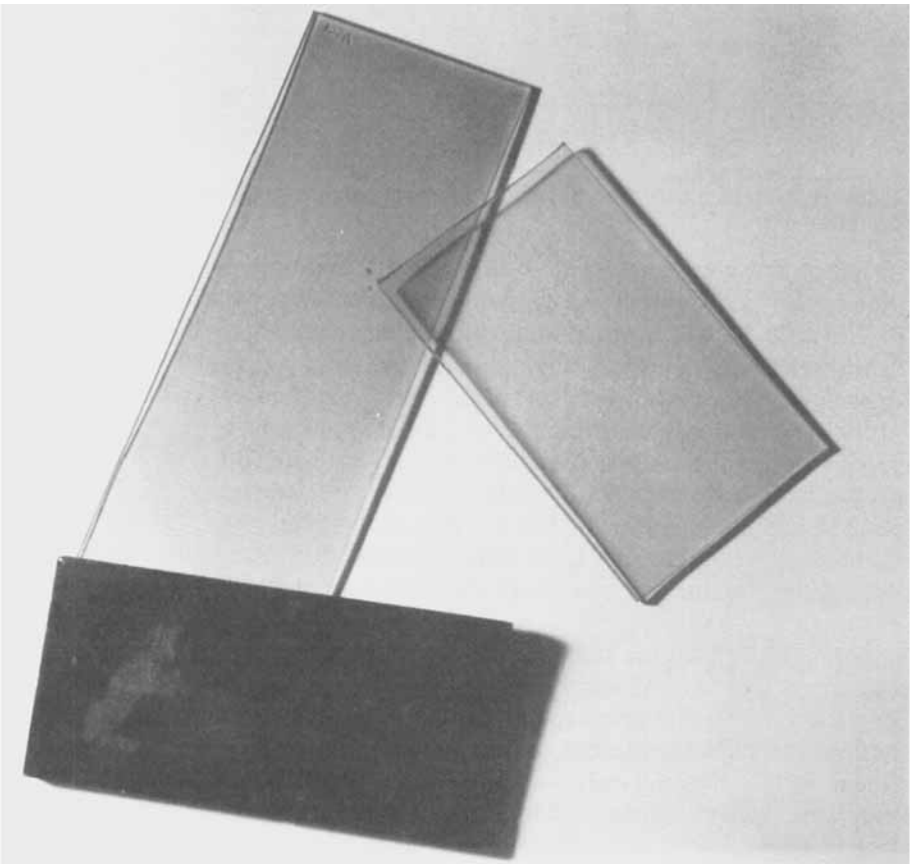


FIG. 7. Sheets of chloral/*p*-chlorophenylisocyanate copolymer.

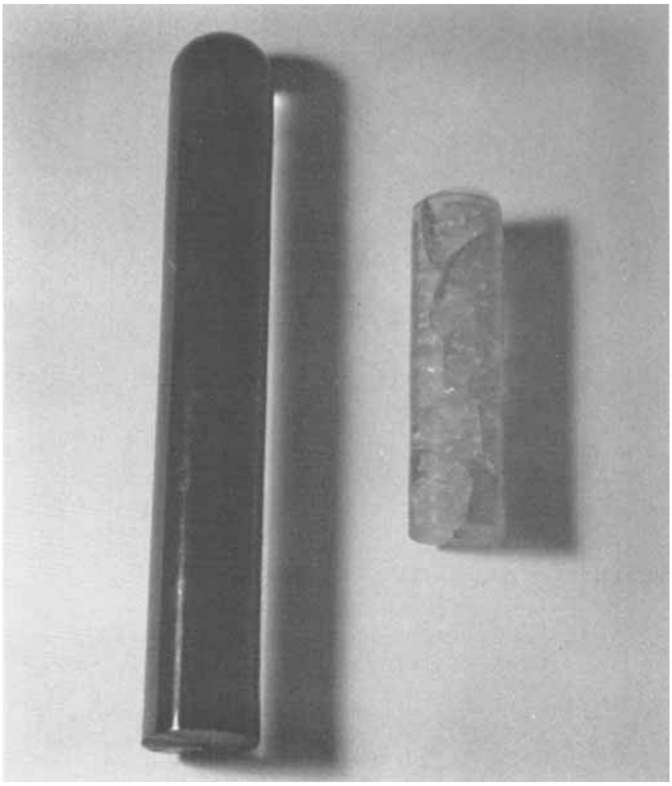


FIG. 8. Test-tube pieces of chloral/*p*-chlorophenylisocyanate copolymer.

In the next few days and weeks quite a few round-bottomed flasks were broken! We needed solid samples to prepare for testing of the basic mechanical properties. Not only did we prepare testbars by machining the PCh samples, but we also produced small cups and even a nut and bolt [80, 81].

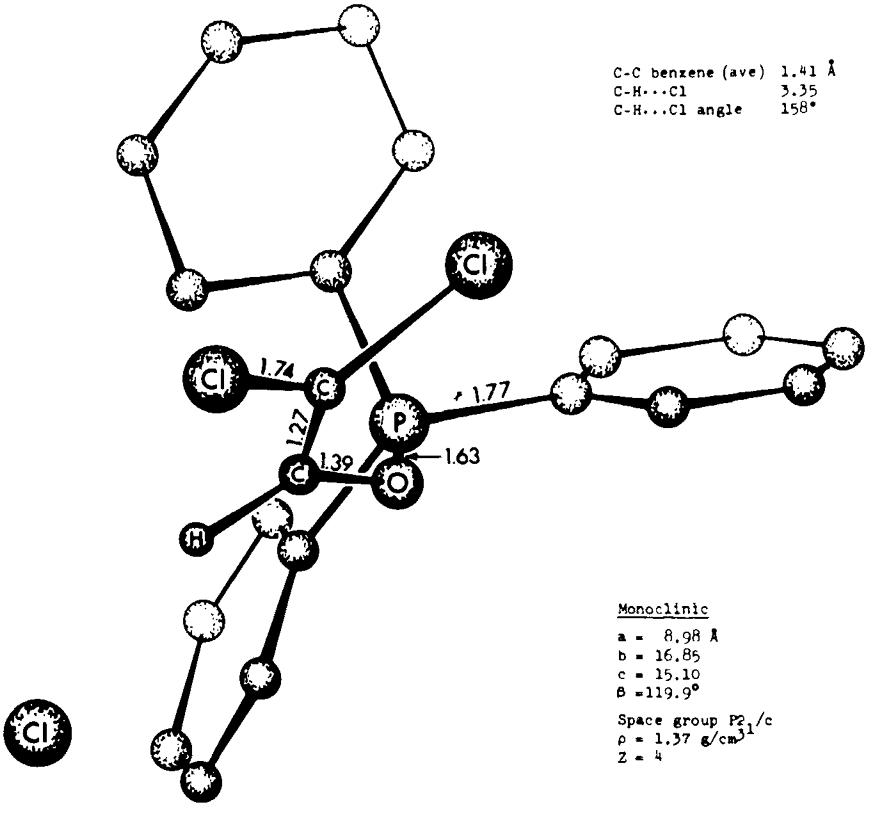
A vigorous period of work followed in an attempt to discover the most effective initiator for chloral polymerization. We ultimately settled on triphenylphosphine; actually, on the reaction product of triphenylphosphine with 1 mol chloral, the initiating anion is a chloride ion. Among the initiators tried was lithium cholesteryl oxide. This was the initiator used in our first experiment, and it was the first experiment to produce an optically active polymer whose optical activity was based on macromolecular asymmetry. It took almost 15 years before we could actually prove this phenomenon.

Many other objectives had to be met as the project shifted into the status of potential commercialization. Almost immediate answers were needed for a number of questions: monomer purification and purity; knowledge of the initial step of the polymerization; the ultimate thermal, oxidative, and hydrolytic stability of PCh samples; the most effective and instant stabilization; the fabrication of samples for ultimate use. I was helped significantly by Henry Miller and by some other people. Henry was a veteran scientist of CRD, who thought of everything that would have to be done to make this project not only a scientific but also a commercial success.

Polychloral shrinks by almost 25% during the monomer casting technique (Fig. 8). H. C. Miller thought of how to make solid pieces without faults. He just cooled the sample slowly from the bottom as we made sheets and films between glass plates with flexible spacers, gum rubber for 3-mm sheets and Lycra yarn for 1–2-mm films. The film thickness was determined by the strength of the clamps which held the assemblies together [81a].

Many problems were not worked out or were not considered because they did not contribute to the ultimate objective. We studied the polymerization of large sheets with 5% ferric oxide to simulate Spanish tiles, we made glass-reinforced sheets, and we successfully encased entire small radioapparati which required castings of 1 kilo and more. Much of the work was done with 5% *p*-chlorophenylisocyanate copolymers [82, 83].

Rather important work was done on the structure of the triphenylphosphine chloral reaction product (with Lloyd Guggenberger) (Figs. 9 and 10), which showed that the "triphenylphosphine initiation" was actually a chloride initiation. It was not until 10 years later that it became clear that the polymers with lithium tertiary butoxide initiation were brittle because they were more like a "living polymerization" with a narrow molecular weight distribution. The chloride initiation of chloral apparently gave a broad MWD polymer with much greater toughness.



C-C benzene (ave)	1.41 Å
C-H···Cl	3.35
C-H...Cl angle	158°

Monoclinic

a = 8.98 Å
b = 16.85
c = 15.10
β = 119.9°

Space group $P2_1/c$
ρ = 1.37 g/cm^3
Z = 4

FIG. 9. X-ray structure of chloral/triphenylphosphine reaction product.

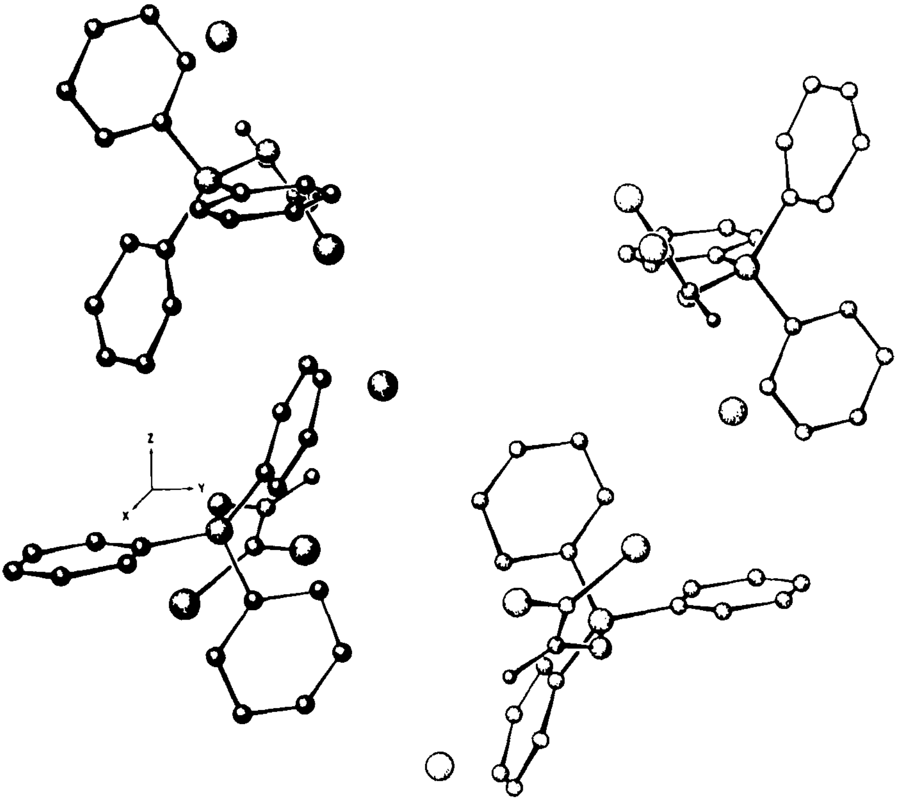


FIG. 10. Unit cell of chloral/triphenylphosphine reaction product.

Shortly after I went to the University of Massachusetts, the polychloral project was abandoned at DuPont as a commercial possibility (and correctly so) for the applications we had envisioned. Things had changed from the time the project was conceived. Initially, it was highly desirable to have a polymer that was completely nonflammable (72% chlorine), that did not melt and drip (had no liquid phase on heating), but decomposed. In the end, disadvantages such as phosgene formation on burning and the monomer being placed on the controlled substance list made the polymer completely unacceptable as a commercial product.

In a way, the failure to commercialize the polymer was unfortunate, but from the scientific point of view many problems had been recognized and partially solved. It turned out that polychloral is a most unusual polymer and could be used as an excellent and invaluable example for the study of macromolecular engineering.

In the following 10 years many points were clarified, among them copolymerization; initiation with various categories of initiators; endcapping; the existence of dormant, buried ends as the source of instability of the polymer samples; the strong attachment of the monomer onto the polymer "as prepared"; cationic chloral polymerization, initiation, and "self-stabilization"; and the thermal stability of stabilized polychloral samples which were similar to those of polyoxymethylene [84–95]. Interpenetrating networks of PCh with a number of polymers were made by homo- or copolymerization of chloral in the presence of polymers dissolved in the monomer chloral prior to polymerization [96].

OTHER PERHALOACETALDEHYDE POLYMERS

Polychloral is a semicrystalline polymer. When we first became interested in it in 1958, nothing was known about its structure except that it was a polymer of chloral. The question of whether "metachloral" was a cyclic oligomer or a polymer had not been resolved. Shortly after the beginning of our work, the Nowak–Whalley paper came out and showed that metachloral is a polymer of chloral and, according to IR analysis, is isotactic [97, 98]. A few years later, x-ray work suggested that the polymer had a 4/1 helix with the repeat distance equal to polypropylene, namely 6.65 Å [84]. We subsequently corrected this value after finding that the actual repeat distance was much shorter, about 5.1 Å [85]. (See also Fig. 11.) A model of isotactic helical polypropylene is shown in Fig. 12.

There are 10 possible perhaloacetaldehydes, with chlorine, bromine, and fluorine and various combinations as the halogen atoms. We have made a detailed study of the synthesis and characterization of all of them, and we have also investigated their polymerization. All 10 trihaloacetaldehydes polymerize under conditions similar to those for chloral, but with some subtle differences. The polymerization is readily carried out with anionic initiators but not so readily with cationic initiators. However, we did not study the cationic polymerization in great detail in all cases.

The ceiling temperatures of polymerization for the trihaloacetaldehydes were found to range from a high of +85°C for fluoral to −75°C for bromal [99–108]. This was to be expected, with the larger bulk of the tribromomethyl group as the substituent causing the most steric crowding as the polymer was formed. On the other hand, the larger size of the trihalomethyl group guaranteed an increased stereospecificity of polymerization. Considering the van der Waals radii, it was not surprising that the trihalomethyl group almost guaranteed complete stereospecificity in the polymer. Hence, only isotactic helical polymers are formed. It also demon-

FIG. 11. Model of isotactic polychloral.

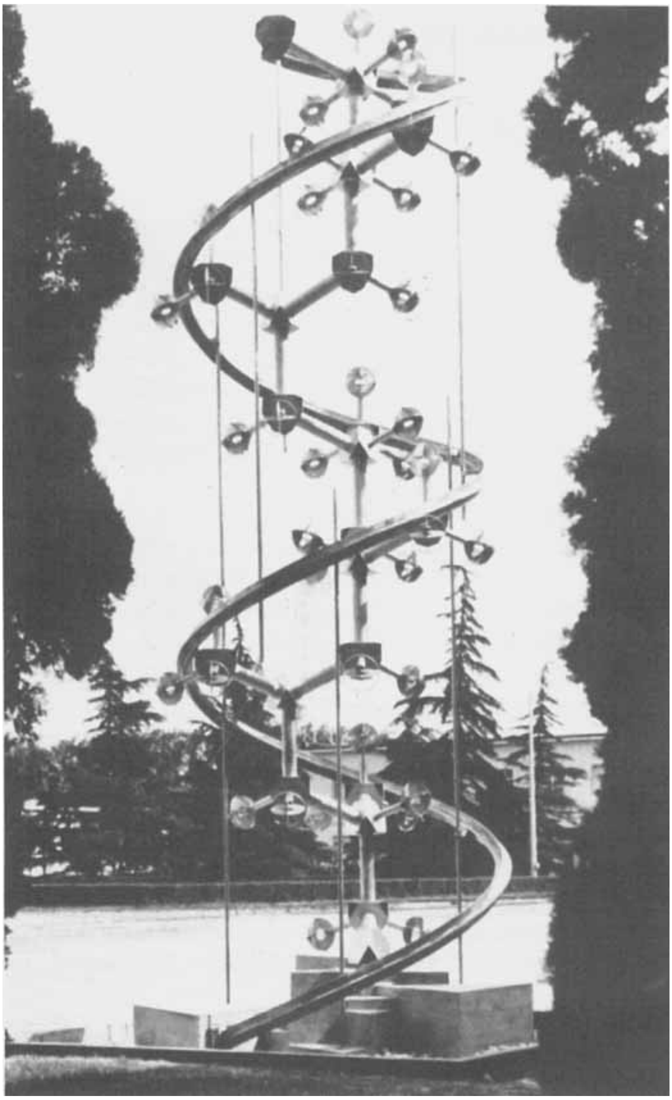


FIG. 12. Polypropylene helix, Giulio Natta Research Laboratory, Montecatini, Ferrara, Italy.

strated for the first time that stereospecific polymers may be formed without "stereospecific catalysts!" Any initiator can give stereospecific polymers if the monomer structure and the resulting polymer have the proper spatial relationship.

The last trihaloacetaldehyde polymers that we studied was fluorochlorobromoacetaldehyde and its polymers [106–108]. It is the only trihaloacetaldehyde containing a chiral center. It could be prepared in its racemic form or in a highly enriched enantiomeric form and could then be polymerized. In this case we were trying to synthesize an isotactic polymer that had not only optical activity based on the contribution of the monomer unit but also optical activity based on macromolecular asymmetry. However, the optical purity of the monomer was not high enough to test this hypothesis [108].

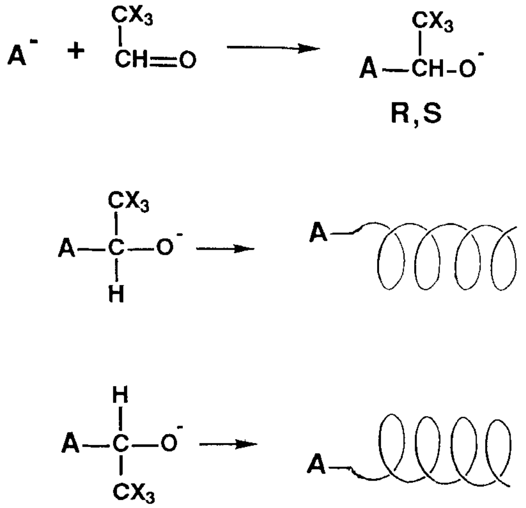
We have, however, been able to prepare fluorochlorobromomethane with an optical purity of about 85% from the intermediate of the antipode separation, e.g., fluorochlorobromoacetic acid, by decarboxylation, which was found to be similar to the optical purity of the starting acid. Fluorochlorobromomethane was previously prepared only in about 7% optical purity [109].

OPTICAL ACTIVITY BASED ON MACROMOLECULAR ASYMMETRY

Optical activity, defined as the rotation of the plane of polarized light passing through a material, is a property found in molecules and macromolecular structures. The organic chemist normally thinks of optical asymmetry on an individual molecule. Most optically active compounds have asymmetric carbons or other central atoms, or are structures that have rotational restrictions as in the substituted biphenyls.

Some macromolecular structures also show macromolecular asymmetry; for example, sodium chlorate and quartz. Macromolecular asymmetry based on helicity was also known for cholesteric liquid crystals and the oligomeric helicenes. Macromolecular asymmetry was suspected to exist in rigid helical structures. None were known 30 years ago, nor was it possible to conceive how to make them.

When polychloral was suggested to be isotactic and presumably not capable of existing in an atactic structure, the thought of synthesizing a helical structure of a single handedness became a real possibility. It should be remembered that when helical structures exist in the solid state [110–112], such as in polypropylene or many other polymers in the crystalline state, these structures exist as 50:50 mixtures of right- and left-handed helices (Eq. 4).



(4)

In 1963 we started working on this principle of synthesizing a single-handed helix of polychloral. In April, shortly after the discovery of cryotachensic polymerization, we used the lithium salt of cholesterol as the anionic initiator for the polymerization of chloral and for the copolymerization of chloral with isocyanates. The samples prepared by this type of initiation were superior in their mechanical properties to other chloral samples prepared with other initiators. Indeed, the nut-and-bolt sample was made from cholesteryl-oxide-initiated chloral polymerization, fortuitously "finished and stabilized" by soaking the sample in phenylisocyanate (Figs. 5–8).

At that time we did not know how to measure the optical rotation of a solid semicrystalline compound, and this aspect of the project was temporarily abandoned. Most organic compounds are measured in solution. Chiroptical measurements in the solid state could only be made when perfect and relatively large crystals were available such as for quartz, the first compound whose optical activity was determined (by Biot in 1812 [113]). We looked at the problem of how to measure the optical activity of polychloral initiated with cholesteryl oxide again 10 years later. Koichi Hatada spent a substantial part of 1 year carefully preparing machined samples of polychloral and polished them with great skill but to no avail and without success—the sample remained highly birefringent.

We were just not ready to solve this problem, and we still do not have a general technique to measure optical activity of polychloral in bulk or in suspension, although in thin films the optical rotation of polychloral could be measured. By 1977, Steve Corley [114] in our laboratory succeeded in making thin polychloral films that did not have any birefringence, which was the key for successful measurements of the optical rotation. Since that time, stacks of randomly rotated films of polychloral samples have been measured after being soaked with solvents that are isorefractive with the polymer; optical rotation values in the thousands of degrees have been measured [114–122]. The samples were prepared by initiating chloral polymerization with chiral alkoxides and/or by salts whose countercations are chiral. One of the enantiomers used as the initiator gave the dextro- and the other the levorotatory sample of polychloral. It was also shown that a column filled with chiral polychloral would partially separate a mixture of isotactic polymers of *R*-(+)- and *S*-(−)-alpha-methylbenzyl methacrylate [123, 124].

Preparation of polychloral films with alkoxide initiators, including several steroid alcohols [120–122] and also with the ammonium salts of several derivatives of mandelic acid [116–118], have also been accomplished. By the middle 1980s the hypothesis that optically active polychloral, whose optical activity was based on macromolecular asymmetry, was firmly established, and Hatada's group had shown convincingly the phenomena of optical activity based on macromolecular asymmetry on poly(triphenylmethyl methacrylate) [125].

We recently developed a technique for measuring the optical activity of solids in suspension, including the measurements of polymer [126–131].

STEREOCHEMISTRY OF TRIHALOACETALDEHYDE OLIGOMERS

Oligomers have been known to be part of many polymer compositions for decades; they were usually "impurities" of a polymer obtained by condensation polymerization. Much less was known about oligomers of addition polymers which are always formed in minute amounts, especially in commercial processes, but were generally ignored. Many oligomers were prepared under abnormal conditions and were synthesized by normal chemical reactions as "model compound studies." Examples include the classical work of Caraculaca on the oligomers of poly(vinyl chloride) (PVC), which were prepared by classical chemical methods; dimers, trimers, and even pentamers were prepared. Oligomers of propylene were also prepared for different reasons, actually starting from initiator systems used for stereospecific polymerizations of propylene.

Some of the most significant work on oligomers, including their correct characterization, was done on methyl methacrylate oligomers. These were prepared by anionic polymerization that allowed the synthesis of isotactic or syndyotactic oligo(methyl methacrylates) [131a]. Other attempts have been made to synthesize specific oligomers such as the codimers of styrene and acrylonitrile. These cooligomerizations have been carried out by classical chemical procedures which attempted to mimic the start of actual polymerization reactions.

Our attempts to study oligomers were based on our interest in trihaloacetaldehyde polymerization, specifically in chloral polymerization. After a successful beginning with this monomer, we extended our studies to the polymerization of fluoral and bromal. Based on our former experience with trihaloacetaldehyde polymerization, we started to study the oligomerization of chloral using tertiary butoxide or bornyl oxide as the initiator. Lithium tertiary butoxide is soluble in hydrocarbon solvents, such as in methylcyclohexane, which makes the initiation much simpler and provides initiation in a homogeneous phase [132–138]. Lithium bornyl oxide, as the initiator, although it was initially "insoluble," afforded a clear solution after initiation, giving oligomers that could be handled readily by GC after acetate capping.

We found that lithium tertiary butoxide initiation, followed by acetate endcapping to "freeze" the initiation equilibrium, gave an oligomer mixture that could be readily analyzed by GC, HPLC, K^+IKS mass spectrometry, and high resolution NMR spectroscopy. Individual oligomers were isolated, crystallized, and the absolute configuration determined by single crystal x-ray analysis [139–142] (Figs. 13 and 14).

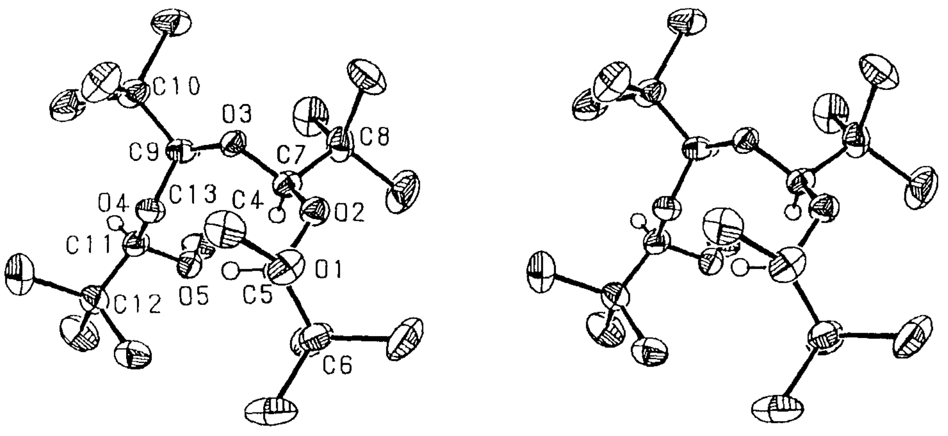


FIG. 13. Tetramer of tertiary butoxide initiated, acetate capped chloral oligomer; first turn of the isotactic polychloral helix.

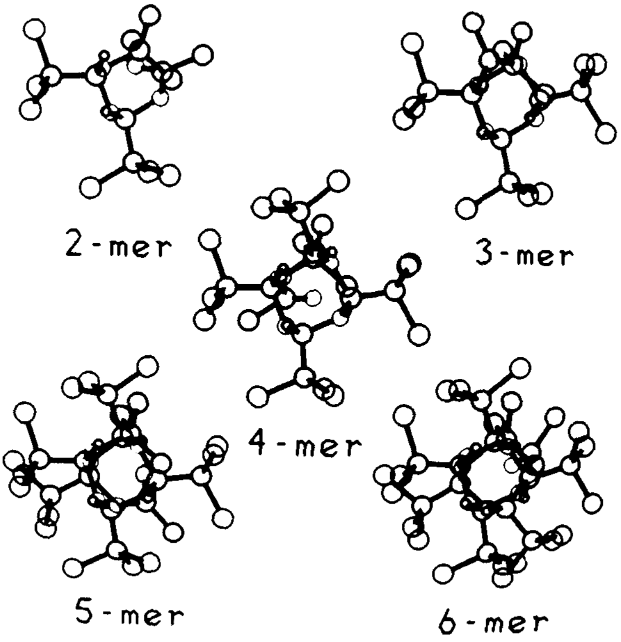


FIG. 14. Computer model of helical oligomers of chloral.

GC confirmed the existence the oligomers up to the heptamer, HPLC followed by NMR spectroscopy up to the nonamer and K^+IDS up to the heptamer [143–152]. The bornyl oxide initiated chloral oligomerization showed similar results [153–155].

Initiation by tertiary butoxide and bornyl oxide of fluoral [156, 157] gave very interesting results: K^+IDS mass spectrometry was able to identify oligomers up to the undecamer, but due to the large numbers of oligomers obtained by random addition without a substantial selection of the stereospecificity, structural assignments could only be done on the basis of NMR spectral assignments.

Bromal, initiated by tertiary butoxide or bornyl oxide, gave oligomers similar to those of chloral and fluoral. It appears that the equilibria of the oligomers is more in favor of fluoral, followed by chloral and bromal, which correlates with the steric bulk of the trihalomethyl moiety in the aldehyde monomer. This may reflect the difference in the ceiling temperature in some respects [158–166]. The oligomerization studies of bromal initiated with tertiary butoxide and bornyl oxide showed that the existence of the dimers was less pronounced than in the case of the chloral oligomer [160, 163]. The percentage of the trimer was even less. A pentamer could still be observed for the bromal oligomers. Under similar conditions the nonamer of chloral and the undecamer of fluoral could be identified.

From our studies, the stereochemical consequences of the first addition of the trihaloacetaldehyde monomer to the initiating alkoxide is now very clear. All three trihaloacetaldehydes, fluoral, chloral, and bromal, started propagating in a stereorandom fashion. Chiral initiators gave an almost 50:50 mixture of meso- and racemo-addition for the unimer. In the case of fluoral oligomerization, not much stereospecificity developed during the oligomerization; chloral became stereospecific after the trimer (three monomer units added). The on-set of stereospecificity of the bromal oligomerization has not been determined [160, 164, 165].

The cooligomerization of chloral and bromal has also been recently investigated [163, 166–168]. In this case K^+IDS was of primary importance for the identification of the individual oligomers. Analysis of the cooligomers showed very clearly that they could be detected up to the pentamer. They showed interesting directions for the process of the addition of the individual monomer units.

As indicated earlier, many individual chloral oligomers were isolated and crystallized, they were studied by single crystal x-ray analysis, and the absolute configuration of these compounds was established. Some of the lower bromal oligomers were also prepared, analyzed, and characterized. We found that the bromal oligomers were much more difficult to handle even though they crystallized more readily [161, 162].

Finally, most chloral oligomers were found to exist in the solid state or in solution in a rigid helical conformation. Some individual higher oligomers have been separated on chiral columns into left- and right-handed helices that are stable at room temperature. They do not undergo helical inversion at room temperature. Chloral oligomers with small end groups, such as methoxy end groups, show limited thermal stability against helical inversion. We have clearly demonstrated by NMR spectroscopy that the pentamer is stable below 70°C, but the hexamer (the oligomer with a helix of 1½ turns) is stable up to 130°C [169]. This result is in excellent agreement with our proposal of many years ago that helix formation in chloral polymerization becomes stereospecific somewhere between one turn (4 monomer units) and two turns of the helix as it is formed during polymerization.

Several other developments in this type of oliger research have been written recently [170–173].

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