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### Review and Future of Ionic Polymerization with Special Emphasis on Carbonyl Polymerization

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## Review and Future of Ionic Polymerization with Special Emphasis on Carbonyl Polymerization

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### REVIEW

Ionic polymerization received prominence about 35 years ago when isobutylene was commercially polymerized by two processes which, with some modifications, are still used today [1]. One process uses aluminum chloride as the initiator and the other uses boron trifluoride; both cationic polymerization processes are carried out at low temperatures. A number of additional commercial processes based on cationic and anionic polymerization have since been developed. Cyclic ethers, most prominently tetrahydrofuran, are polymerized cationically to relatively low molecular weight hydroxyl terminated polyethers which have found important uses in polyurethanes. Trioxane is copolymerized with a small amount of ethylene oxide to form a useful copolymer of polyoxymethylene. Other products which are of interest are the polymers of caprolactone and epichlorohydrin and polymers of various epoxides, mainly those of glycidyl ethers which are most commonly known as epoxy resins. Anionic polymerization on a commercial scale has developed along the lines of styrene and isoprene polymers. Stereorubber, stereoregular 1,4-cis isoprenes, are based on lithium initiators and were introduced in the middle 1950s. Triblock polymers based on A-B-A block polymers of

isobutylene with styrene as endblocks and prepared from living polymers have been known since the early 1960s.

Some of these developments in ionic polymerization were the results of fundamental scientific investigations, but others, particularly the earlier work, were based on intuitive work of ingenious inventors.

It is clear that the general scope of ionic polymerizations involves a number of different fields of interest. It is the purpose of this symposium to bring together investigators involved in investigations of various disciplines in order to disseminate the information and cross-fertilize the ideas developed in their own area of interest.

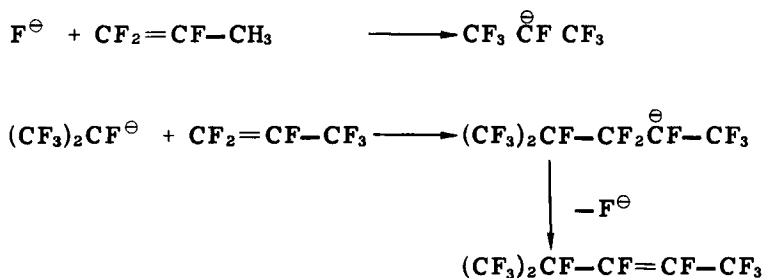
Ionic polymerization can be looked upon from the traditional mechanistic or historical as well as from the practical point of view, and it has been treated in numerous ways. In cationic polymerization, isobutylene polymerization has often been compared with styrene polymerization; carbenium ion (carbocation) polymerization has competed or coexisted with oxonium polymerization; and coordinative ionic polymerization has profited from classical ionic polymerization.

Cationic and anionic polymerization are chain growth polymerizations which frequently involve bond-opening reactions of carbon-carbon double bonds with carbenium (carbocations) or carbanions as polymeric propagating species. Heteroatom-containing monomers, such as aldehydes, polymerize by bond-opening polymerization of carbonyl groups, and cyclic ethers by ring-opening polymerizations with oxonium ions or alkyoxide ions at the end of the growing polymer chain. Lactam and lactone polymerizations involve the ring opening of the carbonyl group, but the methylene group attached to the ether oxygen may also be the point of attack [2].

In addition to the above-mentioned chain growth polymerization to form high molecular weight polymers by ionic processes, polymer formation by a step growth polymer process which involves ionic intermediates has frequently been investigated. It involves electrophilic and nucleophilic substitution reactions on aliphatic or aromatic compounds to form high molecular weight polymers. Discussions of these polymerizations are usually not included when ionic polymerization is discussed.

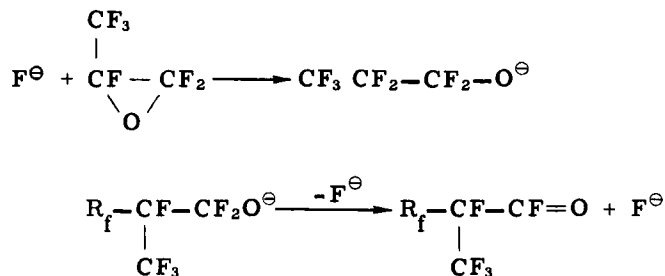
Cationic polymerization of olefins is carried out with olefins which are substituted with electron-donating groups. The best studied examples are isobutylene, styrene, butadiene, and isoprene. Methyl substitution, especially disubstitution on one carbon atom, as for example in isobutylene, causes the carbon-carbon double bond to be properly polarized for the addition of the electrophile.





This reaction is very similar to the oligomerization of propylene in the presence of protic acid.

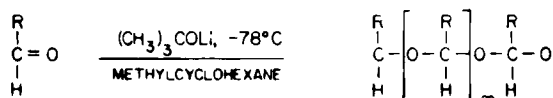
Ring-opening polymerizations proceed only by ionic mechanisms, the polymerization of cyclic ethers mainly by cationic mechanisms, and the polymerization of lactones and lactams by either a cationic or anionic mechanism. Important initiators for cyclic ethers and lactone polymerization are those derived from aluminum alkyl and zinc alkyl/water systems. It should be pointed out that substitution near the reactive group of the monomer is essential for the individual mechanism that operates effectively in specific cases; for example, epoxides polymerize readily with cationic and anionic initiators, while fluorocarbon epoxides polymerize exclusively by anionic mechanisms [9]. Polymers of fluorocarbon epoxides can be readily obtained but fluoride transfer is sometimes excessive; hexafluoropropylene oxide polymerizes anionically with a growing alkoxide which easily loses a fluoride ion to form acid fluoride-terminated polymers with the fluoride initiating a new polymer chain. This is a severe limitation to obtaining high molecular weight materials.



Another example of the importance of substitution near the reactive group of the monomer is exemplified by the polymerization of  $\beta$ -propiolactone as compared to dimethyl- $\beta$ -propiolactone (pivalolactone).

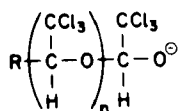
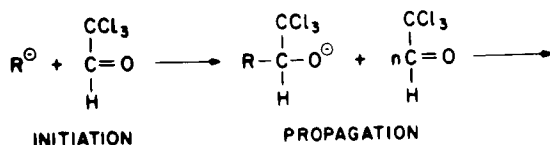
While  $\beta$ -propiolactone polymerizes with both cationic and anionic initiators, pivalolactone apparently polymerizes with typical anionic initiators but not with aluminum alkyl/water systems as initiators.

The polymerization of aldehydes can be accomplished by cationic and anionic initiators [10, 11]. Substitution in the  $\alpha$ -position of the carbonyl group determines which polymerization mechanism is more facile or predominant. In the case of formaldehyde polymerization, weak nucleophiles are capable of polymerizing formaldehyde to polyoxymethylene but relatively strong acids are necessary for its polymerization. Aliphatic higher aldehydes are easier polymerized with cationic initiators, and relatively weak electrophiles will produce high molecular weight polymers; however, strong nucleophiles such as alkoxides must be used for the initiation of the anionic polymerization of aliphatic aldehydes.



The stereochemistry of the aldehyde polymers is also influenced by the nature and type of initiators. Ionic initiators generally favor the formation of crystalline isotactic polymer while most cationic initiators produce amorphous polymers of low tacticity. The tacticity increases, especially in the case of cationic initiators, when the length of the aliphatic side chain is increased.

On the other hand, when the  $\alpha$ -position of the aldehyde is substituted with an electron-withdrawing group, such as a trichloromethyl group as in the case of chloral, the anionic polymerization of haloaldehydes becomes more facile. Chloral polymerizes readily with weak nucleophiles, and even chloride ions are very effective initiators. Many other alkoxides, amines, and phosphines are effective initiators for the anionic polymerization of chloral [12].



Strong acids, such as sulfuric acid and particularly trifluoromethane-sulfonic acid as well as selected Lewis acids, have been found to be initiators for the polymerization of chloral [13].

In all cases, polychloral has been obtained only in its isotactic form.

Fluoral, on the other hand, can be polymerized with anionic and cationic initiators to the crystalline polymer or a mixture of crystalline and amorphous polymer.

The replacement of oxygen by sulfur in aldehydes leads to thioaldehydes which have a substantially different electron density in the thiocarbonyl bond and also a longer C—S bond length. In general, the thiocarbonyl compounds are easier to polymerize than the corresponding carbonyl compounds. For example, thioformaldehyde is so reactive that it has not been prepared in its pure form; even at  $-120^{\circ}\text{C}$  thioformaldehyde polymerizes rapidly. It is apparently initiated by the trace impurities which are normally present during its preparation. On the other hand, many thiocarbonyl compounds can be polymerized whose corresponding carbonyl compounds have resisted polymerization. Examples of the polymerization of such thiocarbonyl compounds are thioacetone, thiohexafluoroacetone, thiocarbonyl fluoride, and a number of fluoroacyl fluorides.

Few cases of established radical polymerizations have been reported involving thiocarbonyl compounds, for example, thiocarbonyl fluoride and thioacetone.

## NEW DEVELOPMENTS

### Cryotachensic Polymerization of Chloral

Many years ago chloral was polymerized with such typical anionic initiators as pyridine or other tertiary amines to an insoluble and infusible powder which could not be formed into a useful shape. Cationic polymerization with aluminum chloride and sulfuric acid as initiators gave the same polymer.

We have now found that chloral may be initiated above the threshold temperature of polymerization which, in the case of neat chloral, is  $58^{\circ}\text{C}$  [12]. Above the threshold temperature initiated chloral can be handled and transferred and no polymerization occurs. However, as soon as the initiated mixture is

cooled below the threshold temperature, polymerization occurs (cryotachensic polymerization):

cryos	tacheitis
cold	acceleration

- (1) Initiate above  $T_c$  (ceiling temperature)
- (2) Polymerize by cooling (removal of heat of polymerization)

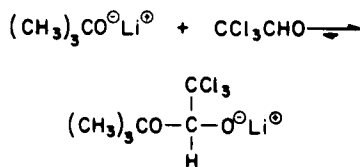
Chloral polymerization can be carried out neat or in the presence of inert diluents (solvents) which do not interfere with the polymerization.

The threshold temperature depends on the concentration of chloral. The ceiling temperature of a 1-M solution of chloral in methylcyclohexane has been determined to be 18°C.

The rate of chloral polymerization depends on the efficiency of the cooling bath which surrounds the container or mold containing the initiated chloral solution; it also depends on the thickness of the piece and consequently on the heat transfer through the already polymerized polychloral.

Polychloral is formed from the initiated monomer in the form of a homogeneous gel. At about 2 to 5% conversion the gel is already rigid, and during the course of the polymerization the polychloral matrix becomes more and more rigid until polymerization is complete. Above 50 to 60% conversion the polymerization of chloral becomes strongly diffusion controlled, and it comes to a complete stop at approximately 85% conversion if no diluent is used for the polymerization. With about 20% diluent, such as hexane, conversions of more than 95% may be obtained. The progress of the polymerization can be very conveniently followed by the disappearance of the chloral monomer signals by nuclear magnetic resonance spectroscopy (Fig. 1).

Numerous nucleophiles are initiators for chloral polymerization. Good nucleophiles such as lithium t-butoxide add quantitatively to 1 mole of chloral above the threshold temperature of polymerization and no further addition to more chloral occurs.





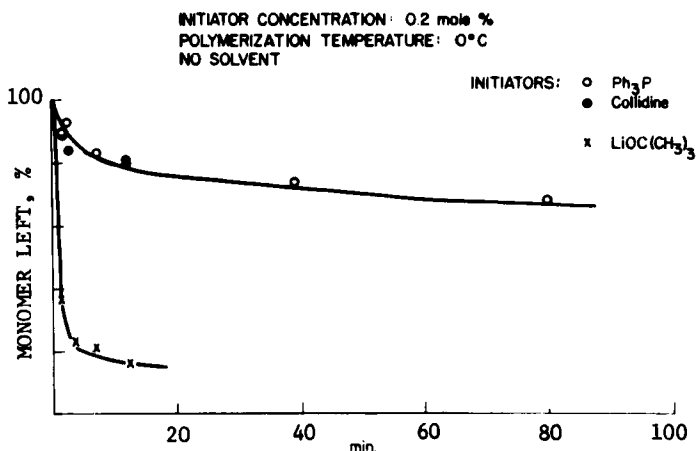


FIG. 1. Rate of chloral polymerization (determined by NMR). Initiator concentration: 0.2 mole %. Polymerization temperature: 0°C. No solvent.

Poor nucleophiles such as chloride ion or 2,4,6-collidine do not add to a significant degree to chloral monomer and no addition product could be identified by NMR in the mixture. However, when the initiated chloral mixture is cooled, polychloral is formed rapidly, indicating that although the equilibrium of the initiation reaction does not favor addition, propagation proceeds rapidly.

Triphenylphosphine is also a good initiator for chloral polymerization, but triphenylphosphine is not the actual initiator. It reacts almost instantaneously with 1 mole of chloral to form a quaternary phosphonium salt whose anion, chloride, is the actual initiator.

Polymers of chloral prepared under various conditions and with various initiators have identical IR spectra and according to x-ray studies are isotactic; no soluble atactic form has ever been isolated.

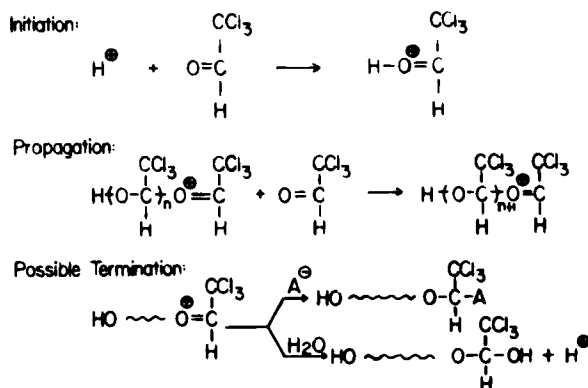
Chloral has also been polymerized cationically with strong acids, particularly trifluorosulfonic acid and sulfuric acid, as the initiator. A few selected Lewis acids such as aluminum chloride and antimony pentachloride also act as initiators for the chloral polymerization, but many other typical cationic initiators, Lewis acids, and cationic salts are ineffective (Table 1).

TABLE 1. Polymerization of Chloral with Lewis Acids<sup>a</sup>

Initiator	Yield (%)	Remarks
AlCl <sub>3</sub>	78	Rate comparable to anionic rate
FeCl <sub>3</sub>	4	—
TiCl <sub>4</sub>	2	Time: 14 days
SbCl <sub>5</sub>	13	Gel
SbCl <sub>5</sub> + CH <sub>3</sub> COCl (5 mole %)	8	Gel
SbCl <sub>5</sub> + Et <sub>2</sub> O (5 mole %)	—	Dark solution

<sup>a</sup>Initiator concentration: 2 mole %. Polymerization: Bulk.  
Temp: -5°C. Time: 3 days.

A proposed scheme for the initiation, propagation, and termination of cationic chloral polymerization is described in Scheme 1.

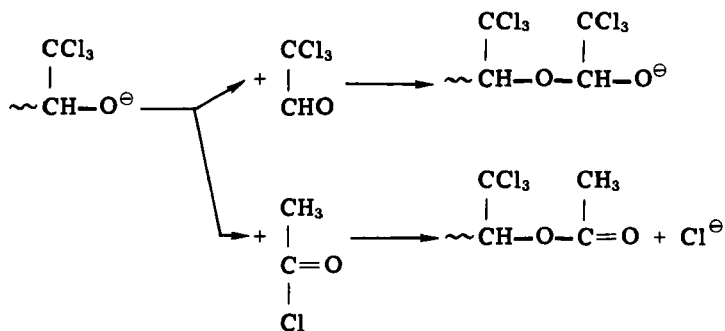


SCHEME 1. Cationic polymerization of chloral.

Very little is known about the end groups of chloral polymers prepared by cryotachensic polymerization. Some of the polymers are quite unstable and have a maximum degradation rate temperature near 150°C while the best stabilized polychloral samples show a maximum degradation rate at 385°C. On the other hand, homopolymers of chloral cannot be endcapped by the usual acetylation techniques known to be effective for the stabilization of hydroxyl-terminated polyoxymethylene. Earlier reports by other investigators seem to have demonstrated that chloral polymers also have hydroxyl end groups which can be acetylated. We have prepared many chloral polymers under different conditions but our acetylation attempts under various conditions were unsuccessful.

Since polychloral is insoluble, few techniques for the characterization of polymer samples are available. One of the most convenient techniques to compare various polymer samples is the determination of the thermal stability of individual chloral polymers by differential thermogravimetric analysis (DTG). Polychloral samples prepared with different initiators and under different reaction conditions gave a distinct and characteristic spectrum of polymer stability. In this way general types of end groups could be identified on the basis of the thermal degradation pattern of the polychloral samples. Generally, anionically prepared polychloral samples were less stable to thermal degradation, and it is believed that these samples may have occluded living ends which have not terminated but are not accessible for the capping reagents and consequently cannot be acetylated.

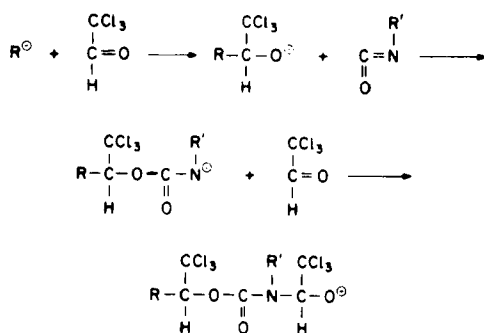
Since the acetylation was not possible, we attempted to increase the thermal stability of the polychloral sample by trying to carry out chain transfer reactions during the polymerization. To our surprise we found that anionic chloral polymerization can be carried out in the presence of up to 2 mole % of acyl chlorides, for example, benzoyl chloride and acetyl chloride, when the polymerization is initiated with triphenylphosphine.



Lithium tertiary butoxide could not be used as initiator for these systems because it reacted immediately with the acid chloride and acetylation of the tertiary butoxide anion occurred.

It was initially believed that polymerization of chloral in the presence of benzoyl chloride, acetyl chloride, or acetic anhydride was governed by a chain transfer reaction whereby the growing alkoxide reacted with the carbonyl carbon of the acetyl chloride or the acetic anhydride to form an acetyl-terminated polychloral with the loss of chloride or acetate ion which then initiated a new polymer chain. More extensive studies showed that termination and virtually no chain transfer actually occurs toward the end of the polymerization [14]. In a mixture containing two types of carbonyl compounds, the monomer chloral and chain transfer agent acetyl chloride, there is competition throughout the reaction for the growing alkoxide to add to the carbonyl carbon of either of the two carbonyl compounds. Apparently the chloral very effectively competes with the acetylating agent for the addition because analysis of the polymers at different conversions showed that although the conversion of monomer to polymer is high even after a few minutes, the concentration of carbonyl end groups in the polymer increases very slowly and the maximum acylation is not obtained for several hours. An estimation of the number-average molecular weight showed that a DP of about 300 of the stable fraction was obtained.

Chloral can be successfully copolymerized with isocyanates, particularly with aromatic isocyanates, and with ketenes [15].



This polymerization is carried out with anionic initiators to form polymers containing urethane or ester linkages. As expected, copolymers of chloral with isocyanates and ketenes have a substantially improved thermal stability. Recent studies indicate that even the more reactive isocyanates, aromatic isocyanates,

are not incorporated into the polymer from the very beginning of the copolymerization but are incorporated in the later stage.

Homopolymers of chloral prepared under various conditions and with various initiators have identical IR spectra and consequently have the same chemical structure and stereochemistry. According to x-ray studies, polychloral is isotactic and no soluble atactic form of chloral has yet been observed.

### Sequential Polymerization and the Formation of Interpenetrating Networks

Chloral polymers cannot be mixed with other polymers by melt or solution blending because they are insoluble and infusible. We were, however, able to produce polymer blends and interpenetrating networks [16] of polychloral on the basis of a sequential polymerization. Chloral is first ionically polymerized or copolymerized with an isocyanate, for example phenyl isocyanate, which is then followed by a second polymerization of an addition monomer with a radical initiator.

### Composites of Chloral Polymers and Copolymers with Addition Polymers

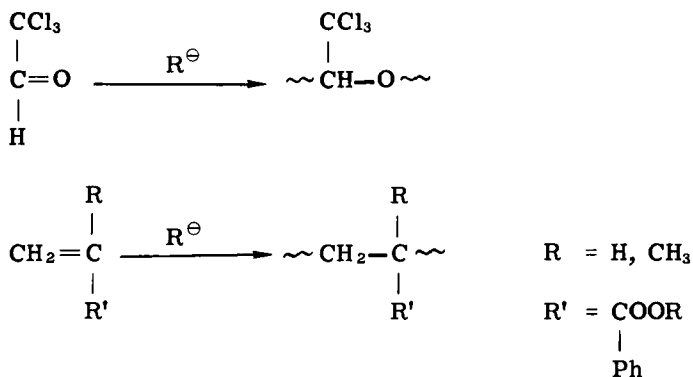
- A. Dissolve addition polymer in chloral and polymerize chloral.
- B. Prepare chloral polymer, soak with addition monomer (containing initiator), and polymerize monomer.
- C. Mix addition monomer (and its initiator) with chloral.
  1. Carry out chloral polymerization.
  2. Carry out polymerization of addition monomer.

In principle, polymer blends can also be prepared by dissolving a chloral soluble polymer in chloral, initiating the chloral polymerization above the threshold temperature of polymerization and then cooling the mixture to perform the actual chloral polymerization. Polymers of up to 10% of their weight can be incorporated into chloral polymers; they include ethylene/propylene rubber, various acrylates, and soluble polyolefins. One of the limitations of this technique is the solubility of the high molecular weight addition polymer in chloral monomer.

Another method of preparing polymer blends with polychloral consists of the preparation of appropriate polychloral samples, imbibing the polymer with the addition monomer, and then polymerizing the addition monomer within the polychloral matrix. This

method also has its limitations because the amount of monomer which can be imbedded into the polychloral matrix does not exceed 30%. Addition monomers which can be used for this technique are of a much wider scope because it does not make any difference if these monomers interfere with the chloral polymerization. Acrylates, styrene, and dienes have been used with radical initiators, and cyclic ethers with cationic initiators.

The most flexible and chemically unique technique is the sequential polymerization of chloral followed by the polymerization of the addition monomer. As mentioned earlier, chloral can be polymerized in the presence of inert solvents. Potential monomers which do not interfere with the polymerization of chloral can be used for the sequential polymerization.



It has been found that homopolymerization of chloral or copolymerization of chloral with isocyanates can be carried out in the usual manner in the presence of monomers which can then be polymerized in a second step, preferably by a radical mechanism.

The actual preparation of the polymer blends is carried out as follows: Chloral, a monomer which can be polymerized by a radical mechanism, and a corresponding radical initiator, for example, AIBN, are mixed and heated above the threshold temperature of chloral polymerization. The chloral initiator is then added and chloral polymerization, which is carried out by cooling to 0°C, proceeds rapidly to a homogeneous gel. It is believed that the chloral polymerization goes to more than 95% conversion because it has been determined in different experiments that chloral polymerization in the presence of 20% of heptane gives a 96% conversion to polychloral. After the chloral polymerization is complete, the sample

is heated to the temperature at which the radical initiator is activated and the second polymerization proceeds by a radical mechanism.

Polymer blends of chloral with a number of addition polymers were prepared by the sequential polymerization technique. They include styrene, methyl methacrylate, methacrylate, and  $\alpha$ -methylstyrene. No grafting occurred during this polymerization and an intimate mixture of polychloral with the addition polymer was obtained. The addition polymer could be extracted from the polychloral matrix to more than 95%. The initiated monomer mixture may be cast directly in films or sheet, and the composite compositions may be translucent to opaque depending on the exact reaction conditions and also depending on the individual addition monomers used to prepare these blends.

Some time ago, Bamford [17] described a grafting of addition monomers by radical mechanism onto polychloral. In this work, manganese carbonyls were used as the grafting initiators and their reaction with the trichloromethyl group of the polychloral initiated the radical graft polymerization. We have used AIBN and similar radical initiators and have found no evidence of grafting in our system.

Sequential polymerization, the anionic polymerization of chloral followed by the radical polymerization of addition monomers, also permitted the preparation of interpenetrating polymer networks [18]. Instead of preparing a linear polymer from the radically initiated monomer, it was only necessary to use cross-linking agents to cross-link the second polymer network within the polychloral matrix. We have been able to prepare interpenetrating networks of polychloral as one phase and polystyrene cross-linked with divinylbenzene or poly(methyl methacrylate) cross-linked with ethylene dimethacrylate as the other phase. It should be mentioned, however, that our attempts to prepare interpenetrating networks required the use of 8 to 10 mole % of cross-linking agents in order to form a properly cross-linked second phase; with less than 5% cross-linking agent, the polymer can still be extracted. This amount of cross-linking agent is substantially greater than normally needed to form a lightly cross-linked polymer if this cross-linking reaction is carried out in solution.

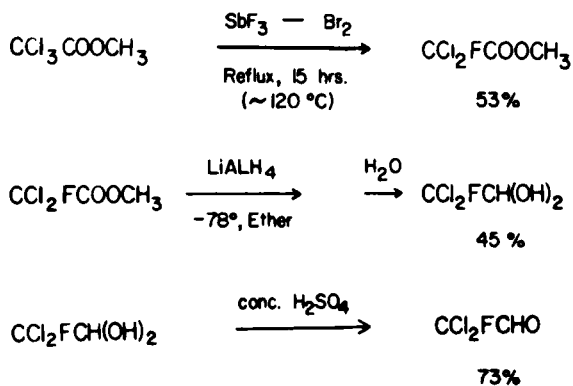
We believe that it is remarkable to perform a sequence of two polymerizations, one ionic polymerization or copolymerization of chloral followed by a radical polymerization of a suitable addition monomer, without interference of either polymerization with each other and without observing radical grafting on polychloral.

### Preparation and Polymerization of Other Haloaldehydes

Aliphatic aldehydes polymerize to isotactic polymers primarily with alkali metal alkoxide and to some extent with specific aluminum organic compounds and to atactic polymer. Chloral polymerizes to one type of polymer only—*isotactic* polychloral. The polymerizations may be initiated by anionic or cationic initiators. Simple initiators such as tetranalkyl ammonium chloride or pyridine as well as metal alkoxides are efficient initiators. Since there is no coordination necessary to form *isotactic* polymer, it is believed that the size of the trichloromethyl side group is alone responsible for the formation of the *isotactic* polymer. Bromal (tribromoacetaldehyde) has not yet been polymerized, and fluoral (trifluoroacetaldehyde) has been polymerized to crystalline, presumably *isotactic* polymer, and under different conditions to an amorphous soluble polyacetal.

It was of interest to change the size and shape of the side groups of halogenated acetaldehydes in order to determine the size and shape of the trihalomethyl side groups which can be tolerated to form *isotactic* polymers. We were interested in determining basically two limits: how many chlorine atoms in trichloroacetaldehyde can be replaced by bromine before the side group becomes too sizeable and the corresponding haloaldehyde does not polymerize any more, and how small can the trihalomethyl side group be made without the formation of atactic polyhaloaldehydes. This can be readily done by systematically substituting chlorine atoms in chloral by fluorine [19].

Difluorochloroacetaldehyde and fluorodichloroacetaldehyde were prepared by lithium aluminum hydride reduction of the corresponding difluorochloroacetate and fluorodichloroacetate. This reduction must be carried out at  $-78^{\circ}\text{C}$  in order to avoid further reduction.





The aldehydes were initially isolated as the aldehyde hydrates, which were dehydrated with sulfuric acid followed by several careful distillations from phosphorous pentoxide. Both monomers polymerized with cationic and anionic initiators but, as expected, more readily with anionic initiators as indicated in Tables 2 and 3.

Ceiling temperatures of chlorofluoroacetaldehydes and their boiling points are shown in Fig. 2.

TABLE 2. Polymerization of  $\text{CClF}_2\text{CHO}$  with  $\text{Ph}_3\text{P}$

Initiator amount (mole %)	Polymerization		Polymer yield (%), acetone	
	Temp (°C)	Time (hr)	Soluble	Insoluble
0.8	25	1	0	54
0.5	-78	1	19	21
0.02	-78	20	73	0

TABLE 3. Polymerization of  $\text{CClF}_2\text{CHO}$

Initiator	Amount (mole %)	Polymerization		Polymer yield (%), acetone	
		Temp (°C)	Time (hr)	Soluble	Insoluble
$\text{Al}(\text{C}_2\text{H}_5)_3$	0.8	-78	1	0	91
$\text{LiOC}(\text{CH}_3)_3$	0.2	-78	1	11	81
$\text{SbCl}_5$	0.3	-78	1	56	0
$\text{TiCl}_4$	0.3	-78	1	0	5
$\text{H}_2\text{SO}_4$	0.4	25	480	3	0

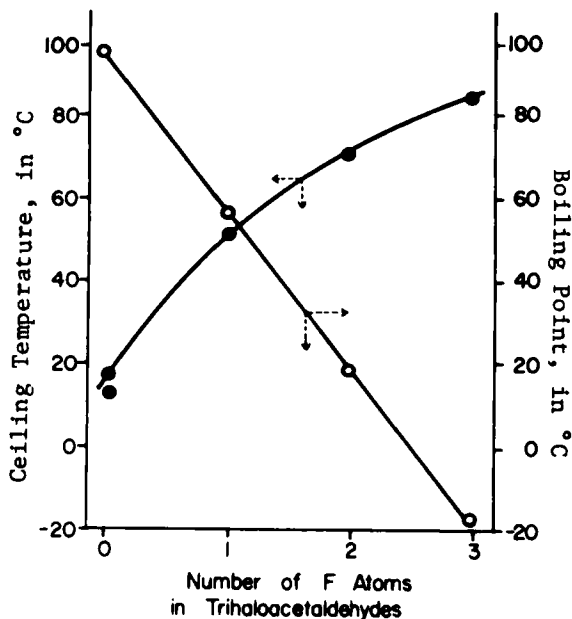
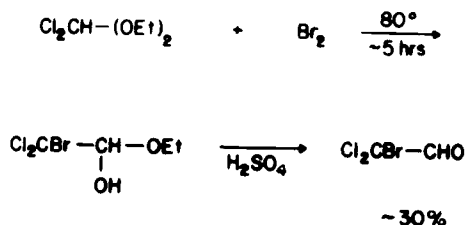
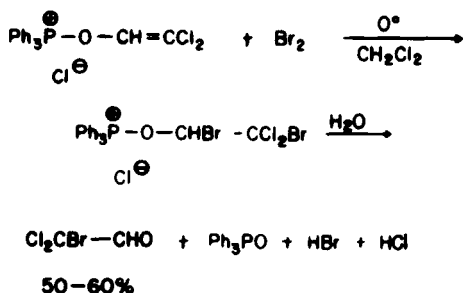


FIG. 2. Ceiling temperatures and boiling points of chloro-fluoroacetaldehydes.

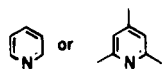
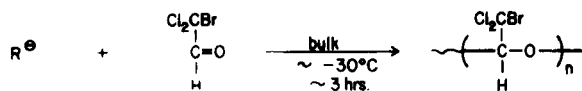
Dichlorobromoacetaldehyde and chlorodibromoacetaldehyde were prepared by bromination of the corresponding chlorinated diethylacetal. The preparation of dibromochloroacetaldehyde via the acetal route is more convenient and gives a much better yield of the pure aldehyde than the dichlorobromoacetaldehyde.



For the preparation of pure polymer grade dichlorobromoacetaldehyde, a more laborious route was found more desirable.



Triphenylphosphine reacts instantaneously with 1 mole of chloral to form triphenyldichlorovinyl oxy phosphonium chloride. This compound could be brominated to the dibromo compound. Upon hydrolysis a good yield of pure dichlorobromoacetaldehyde was obtained in addition to triphenylphosphine oxide. Purification by distillation from phosphorus pentoxide gave a polymer grade material. Dichlorobromoacetaldehyde polymerized with cationic and anionic initiators to an insoluble polymer unlike the gel-like polymer which was obtained during the chloral polymerization and no soluble polymer was found.



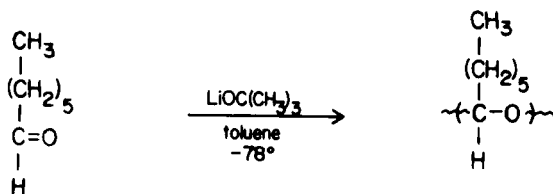
also used as initiators

All attempts to polymerize dibromochloroacetaldehyde have failed.

### Polymerization of n-Aliphatic Aldehydes with C<sub>3</sub> to C<sub>8</sub> Side Chains

Anionic polymerization of aliphatic aldehydes with C<sub>3</sub> to C<sub>7</sub> side groups have been reinvestigated with particular emphasis on the

polymerization of n-heptaldehyde. Reaction conditions have been very carefully defined, and it was found that the polymerization of n-heptaldehyde is most conveniently carried out with lithium t-butoxide as the initiator in methylcyclohexane as the solvent at a temperature of about  $-60^{\circ}\text{C}$ .



The reaction is essentially complete in half an hour; workup and endcapping can subsequently be performed to stabilize the polymer. According to our 300 MHz NMR investigation, the polymer is isotactic.

We had earlier reported in a qualitative way that polyaldehydes with linear aliphatic side chains showed a peculiar melting behavior [20]. This characteristic has now been confirmed and quantitatively evaluated. A careful DSC study and a study of the thermal mechanical behavior of  $\text{C}_4$  to  $\text{C}_8$  isotactic polyaldehydes showed that, beginning with poly(n-valeraldehyde), two major transition regions may be defined [21]: a lower temperature transition which is apparently related to the melting of the aliphatic side chains and a higher temperature transition around  $140$  to  $150^{\circ}\text{C}$  which is related to the melting of the main polymer chain (Fig. 3). Similar characteristics have been observed by other workers in polyacrylates and polyolefins, but the behavior of our polyaldehydes is the first well-studied case of side chain crystallization of stereoregular polymers where both the side chain and the main chain crystallized separately.

### Solvent Mobility in Rigid Polymeric Matrices

The problem of the solvation of a growing polymer chain, especially in ionic polymerization, and the competition of solvent and monomer during the polymerization to become involved in the structure of the transition state has been the concern of almost everyone involved in ionic polymerization. We have recently studied the line width of the proton signals of a number of solvents

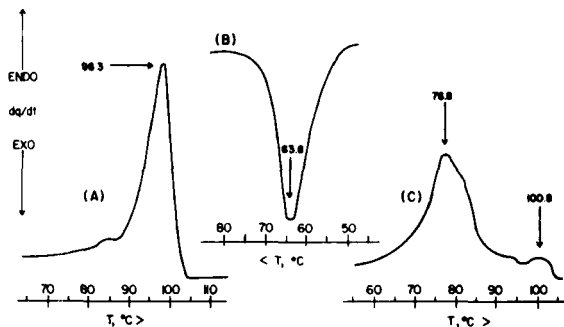


FIG. 3. Poly(*n*-heptaldehyde) DSC studies. First melting endotherms (A and C) and crystallization exotherm (B). Polymer insoluble in  $\text{CH}_2\text{Cl}_2$ .  $\bar{M}_n = 6600$ . Heating rate:  $10^\circ\text{C}/\text{min}$  under nitrogen.

during the polymerization of chloral and found that the line width of various solvents is not constant throughout the polymerization. As the polymer matrix becomes more immobilized, solvent molecules become immobilized in various ways.

The example in Fig. 4 shows that the aldehydic proton of chloral retains the mobility throughout the polymerization even at high conversion. Toluene, on the other hand, shows a distinctly different behavior. The phenyl protons become very restricted after approximately 40% conversion while the methyl group is still relatively mobile.

This finding may give some important insight into the interaction between solvent molecules and particular parts of specific polymer chains.

### FUTURE PROBLEMS

Any attempts to predict future developments are based on the subjective curiosity of the interested person and his own knowledge of needs in a certain area. A few thoughts should point toward unsolved problems and possible future developments in ionic polymerization.

A very recent development [22] describes the preparation of comb-like polymers with the possibility of preparing a variety of microphase

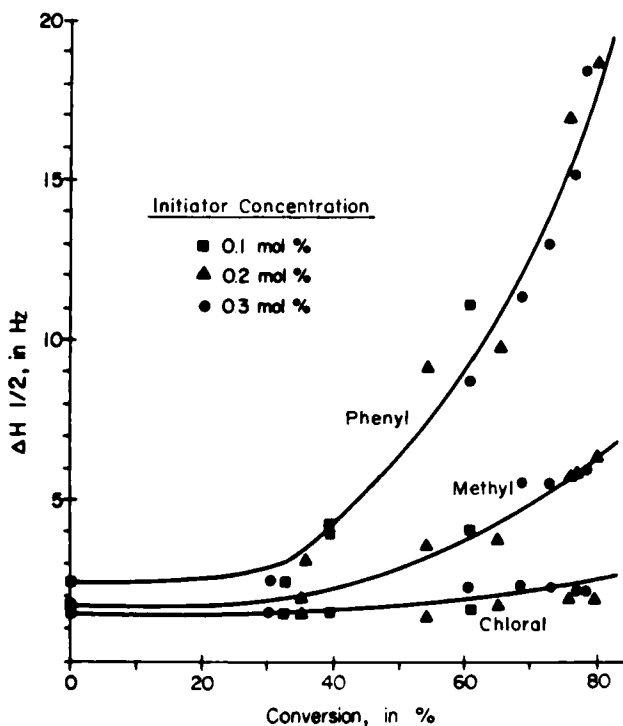


FIG. 4. Polychloral. PMR line broadening of toluene and chloral signals.

separated systems with the potential of new and unusual properties based on new products using established chemistry. Living polystyrene (and other living polymer systems such as polyisoprene) were terminated with reactive halo compounds such as allyl chloride, acrylyl chloride, vinyl chloroethyl ether, epichlorohydrin, and chlorovinyl acetate to form polymeric monomers: olefins, acrylates, vinyl ethers, epoxides, and vinyl acetates. Copolymerization with the appropriate comonomers gave a large variety of new polymers with various properties.

Complete and broad understanding of the influence of substituents of the ceiling temperature in ionic polymerization.

Solvation and definition of solvent spheres around the growing ions and their influence on rate and stereodensity of polymerization.

Control of chain transfer reactions in ionic polymerization.

Mobility and spatial arrangements in the crystal lattice in ionic solid state polymerization.

Diffusion of monomers in polymerization systems where the polymer crystallized during polymerization; effect of polymerization rate and polymerization mechanism on the morphology of the polymer (occlusion of reactive sites).

New anionic and cationic graft and block copolymers of conventional monomers using new techniques to achieve polymers with new properties.

Pure head-to-head polymers and their direct preparation.

Chlorocarbon polymers by ionic polymerization mechanism.

Preparation of stereoregular fluorocarbon polymers. (Previous reports of the successful preparation of stereoregular hexafluoropropylene polymers are doubtful, for they were probably hexafluoropropylene/isobutylene alternating copolymers, the isobutylene coming from relatively large amounts of allyl aluminum used as part of the initiator system.)

Polymerization of acid chlorides and acid fluorides or a reasonable explanation as to why this is unsuccessful.

Much of the immediate work on ionic polymerizations will be related to the preparation of polymers with new and unusual combinations of properties, and truly fundamental work for the search for knowledge without an ultimate goal will be less emphasized than previously.

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#### REFERENCES

- [1] H. Gueterbook, Polyisobutylene, Springer, Berlin, 1959.
- [2] P. H. Plesch, Chemistry of Cationic Polymerization, Pergamon, Oxford, 1963.
- [3] J. P. Kennedy, in Polymer Chemistry of Synthetic Elastomers (J. P. Kennedy and E. G. M. Tornqvist, eds.), Wiley-Interscience, New York, 1969, p. 291.
- [4] J. P. Kennedy, J. Polym. Sci., A-1, **6**, 3139 (1968).

- [5] A. Tsukamoto and O. Vogl, Progr. Polym. Sci., **3**, 199 (1971).
- [6] T. Saegusa, H. Ikeda, and H. Fujii, Macromolecules, **6**, 315 (1973).
- [7] S. Penczek, IUPAC Symposium on Cationic Polymerization, Rouen, 1973.
- [8] W. J. Brehm, K. G. Bremer, H. S. Eleuterio, and R. W. Meschke, U.S. Patent 2,918,501 (1961).
- [9] H. S. Eleuterio, J. Macromol. Science—Chem., **A6**, 1027 (1972).
- [10] J. Furukawa and T. Saegusa, Polymerization of Aldehydes and Oxides, Wiley-Interscience, New York, 1963.
- [11] O. Vogl, Polyaldehydes, Dekker, New York, 1967.
- [12] O. Vogl, U.S. Patent 3,454,527 (1969).
- [13] P. Kubisa and O. Vogl, Vysokomol. Soedin., **A17**, 929 (1975).
- [14] P. Kubisa and O. Vogl, Polym. J. (Japan), **7**, 186 (1975).
- [15] O. Vogl, U.S. Patent 3,668,184 (1972).
- [16] J. R. Millar, J. Chem. Soc., 1960, 1311.
- [17] Bamford et al., Trans. Faraday Soc., **60**, 751 (1964).
- [18] O. Vogl, U.S. Patent 3,707,524 (1972).
- [19] C. Woolf, U.S. Patent 2,870,213 (1959).
- [20] O. Vogl, J. Polym. Sci., **46**, 241 (1960).
- [21] I. Negulescu and O. Vogl, J. Polym. Sci., Polym. Lett. Ed., **13**, 17 (1975).
- [22] R. Milkovich and M. T. Chiang, U.S. Patent 3,786,116 (1974).