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### Polymerization of Formaldehyde

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## Polymerization of Formaldehyde

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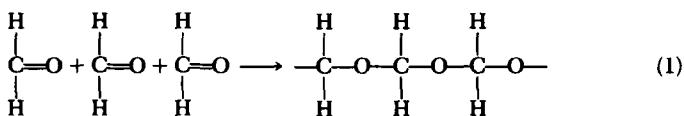
### Synopsis

A review is presented that covers the chemistry of various routes from formaldehyde to high-molecular-weight polyoxymethylenes, and emphasizes recent developments. The requirements of a feasible addition polymerization system are enumerated. The variety of possible polymerization mechanisms is illustrated by discussions of representative anionic, organometallic, and cationic initiator systems.

The fundamental concepts of condensation polymerization of formaldehyde in aqueous or alcoholic media are considered in some detail, the analogy to crystallization is developed, and the effect of temperature, degree of supersaturation, and catalyst on the relative extent of growth versus nucleation is discussed. Techniques are described for preparing active seed polymer and for minimizing end-group occlusion during growth. Examples are given of the preparation of polymer of macromolecular properties from both water and methanol solutions.

The recently discovered metastable orthorhombic form of polyoxymethylene and its preparation from aqueous solutions is described.

This paper is a discussion of the principles of the polymerization of formaldehyde to high-molecular-weight polyoxymethylene, excluding copolymerization, with a critical review of recent developments in the field.





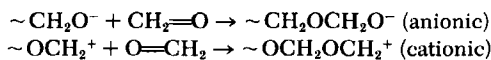
Chemically, the polymer chain appears to be completely linear and to consist exclusively of oxymethylene links. Despite much effort by many investigators there has been no substantiated instance of branch points, in-chain carbon-carbon bonds, or other extraneous in-chain groups in polyoxymethylenes as prepared. The lack of carbon-carbon bonds indicates that no detectable sugar-type polymerization occurs concurrently along with the normal type (Staudinger's classical  $\delta$ -polyoxymethylene, which contained a small amount of sugar linkages, was produced from a normal polymer by a hydrolytic posttreatment). Polymer end groups depend upon the polymerization mechanism, hydroxyl being the most common.

The equilibrium between polymer and monomer is essentially free from side reactions. As noted above, the equilibrium vapor pressure of monomer over crystalline polyoxymethylene is 1 atm at 119°. Strictly thermal depolymerization gives monomer exclusively as a primary product, except for fragments derived from polymer end groups. The depolymerization occurs via an unzipping reaction and is initiated from an unstable end group, if present, or by chain cleavage. These initiating steps are strongly accelerated by catalytic contaminants, such as strong acids. In the absence of catalytic impurities the strictly thermal depolymerization takes place quite slowly, even at elevated temperatures. For example, rates of weight loss of 0.10%/min in vacuo at 282° are routinely obtained in this laboratory on clean acetate-capped polyoxymethylene, without additives.

Concerning solvolytic attack, the polyoxymethylene chain is stable to base but is slowly cleaved by acid. Hydroxyl end groups are attacked by either acid or base. However, this source of instability can readily be eliminated by end-capping to stable groups such as acetate or methoxyl. Following chain cleavage or attack on end groups, unzipping can occur in either acidic or basic media.

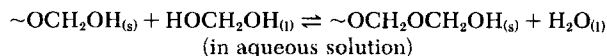
### POLYMERIZATION TYPES

There are two general polymerization routes for producing polyoxymethylene from formaldehyde. The first is by addition to the double bond of the monomer:



This route is followed in the polymerization of essentially pure monomer, either neat or in solution in aprotic solvents. This is a rapid chain reaction, comparable to other familiar addition polymerizations.

The second route is followed in aqueous or alcohol media, where a completely crystalline solid polymer grows by a stepwise equilibration with the solvated monomer. In this case there is essentially no unsaturation remaining in the monomer, and the crystallization process now becomes a major driving force. This may be visualized as a condensation polymerization:



In either case the mechanism can be either anionic or cationic, depending upon the environment. There has never been a verified example of free-radical mechanism. Even radiation-initiated polymerizations have been shown to proceed by an ionic mechanism. Likewise, polymerizations occurring in the presence of conventional free-radical initiator types can invariably be attributed to ionic impurities.

In a consideration of the fact that ionic mechanisms, of both anionic and cationic types, are possible the relationship of the rate of depolymerization of paraformaldehyde in water versus pH is pertinent (9). This shows a decided minimum at pH of about 4, indicating that the neutral point is definitely on the acid side. Thus, relatively strong acids are needed to produce oxymethylene carbonium ions, but only relatively weak bases are needed to form the oxyanions. This relationship, derived from the condensation polymerization system, carries over into catalysis for addition polymerization, in which strong Lewis acids, such as tin halides, are needed to obtain good rates, but in which, on the other hand, even such a weak base as pyridine can be quite effective.

### ADDITION POLYMERIZATION: GENERAL

Chemically, the addition polymerization of formaldehyde differs from that of vinyl compounds in the limitation in possible termination modes. The most common modes for either anionic or cationic mechanisms on formaldehyde are (1) reaction with protonic impurities (water, etc., usually with reinitiation), (2) chain transfer to

monomer, yielding methoxyl and formate end groups (similar to the Cannizzaro reaction on monomer), and (3) occlusion of growing ends. In the latter instance precipitation or growth of a new polymer particle covers over the growing end, preventing the access of monomer. Many termination modes common in vinyl polymerizations have not been detected in this system: for example, dimerization or disproportionation of growing ends, reaction with solvent (saturated hydrocarbon or halogenated derivative) or, in cationic systems, expulsion of a proton. In the usual method of operation, involving continuous feed of monomer, the proportion of nonterminated living ends will be extremely low.

The polymer as produced by the addition polymerization in a liquid medium is about 90% crystalline. The small but definite amorphous content is sufficient to render this material readily distinguishable from the 100% crystalline polymer produced by the condensation mechanism.

The physical relationships in a formaldehyde polymerization introduce many added variables not present in a homogeneous polymerization. The most frequently used systems operate at room temperature or above and utilize an inert solvent, in which formaldehyde (b.p.  $-19^{\circ}$ ) is but sparingly soluble, with the continuous introduction of gaseous monomer as it is consumed. Thus, three phases are present: formaldehyde gas, its solution, and the solid polymer. The rate-determining step will often be the mass transfer from the gas into the liquid phase. Such a system is not very amenable to kinetic studies, particularly since the actual operating monomer concentration in the liquid is very difficult to determine.

A variable of critical importance in any practical application of a polymerization system is the physical nature of the solid polymer as formed. The particles can exhibit at least a tenfold range of bulk density and surface area, can range from dense, granular, sandy material, forming readily poured and filtered suspensions at up to 50% solids, to feathery aggregates that set up in the medium as immovable gel at 5% solids or less. Likewise, the extent of adhesions to the reactor walls can vary to a marked degree. Much of this is an electrostatic phenomenon and is strongly affected by the chemical nature of the initiator, solvents, and contaminants and by reactor design and operational variables.

The chemical nature of the product polymer, however, is not significantly affected by its physical form. The most satisfactory over-

all mechanistic picture of addition polymerization seems to be a hybrid between being homogeneous and being heterogeneous, the growth occurring in the liquid phase on a chain end, which emerges a few monomer units out of the solid surface, and crystallization occurring concurrently these few units behind the growing end.

A convenient practical system for the production of high-molecular-weight polyoxymethylene by this route utilizes highly purified monomer, which keeps the concentration of extraneous chain transfer agents at a controlled low level. A hydrocarbon medium is employed at 25 to 75° with continuous addition of gaseous monomer in the presence of an initiator of sufficient activity to keep the concentration of dissolved formaldehyde low during the polymerization. This low concentration minimizes chain transfer to monomer and probably minimizes end-group occlusion as well (10,11). MacDonald has given a laboratory synthesis procedure for a polymerization of this type (12).

Thermodynamic calculations have given the following approximate values in kilocalories for the hypothetical steps in the polymerization at 35° (3):

	$\Delta H$	$\Delta F_{35^\circ}$
(1) $\text{CH}_2\text{O}_{(g)} \rightarrow \text{CH}_2\text{O}_{(l)}$	-5.0	+1.06
(2) $\text{CH}_2\text{O}_{(l)} \rightarrow \frac{1}{n}[-(\text{CH}_2\text{O})_n-]_{(l)}$	-10.3	-4.22
(3) $\frac{1}{n}[-(\text{CH}_2\text{O})_n-]_{(l)} \rightarrow \frac{1}{n}[-(\text{CH}_2\text{O})_n-]_{(s)}$	-1.7	-0.54
Total:	-17.0	-3.70

Steps 2 and 3 cannot be separated in practice in the preparation of high-molecular-weight polymer, because the polymer invariably precipitates as it is formed.

A voluminous body of patent literature covering a wide variety of initiator types has been produced in recent years. A description or tabulation of these references is outside the scope of this paper; instead, discussion will be limited to a few representative systems.

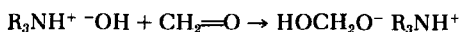
A variety of basic and acidic substances are effective initiators. Within the broad framework of anionic and cationic mechanisms there appear to be gradations in the mechanism of action of an

individual initiator, which range from a pure ion pair to an insertion type, with gradations in between, depending upon the extent of polarization of the bond joining the initiator fragment or counterion to the growing end.

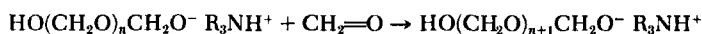
### ANIONIC INITIATORS

What is probably the most clearly defined type of initiator is the anionic ion-pair type, exemplified by a tertiary aliphatic amine. The active initiator is the ion pair derived from reaction with water or other protonic contaminant. The polymerization mechanism has been pictured as follows (11):

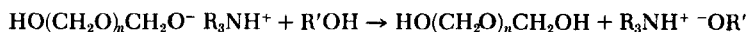
Initiation:



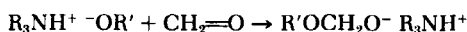
Propagation:



Transfer:



Reinitiation:



Almost any basic material will initiate polymerization to some extent. Besides the amines, among the most effective are phosphines (example, triphenyl), ammonium, sulfonium, phosphonium salts, nitrogen heterocycles, amides, amidines, and polymeric products with the above-given functions. With the onium salts the accompanying anion must be capable of forming a covalent bond as an initiating end, such as chloride or acetate. Perchlorate salts, for example, are inactive.

Kinetic data are difficult to obtain in polymerizations carried out near room temperature. In du Pont studies (13) chain-transfer activities were determined from analytical data on feed stream and on product molecular weights. More recently a study at low temperatures was made by Mejzlik et al. (14). Under the latter conditions the reaction can be followed dilatometrically. Table 1



**TABLE I**  
Effect of Contaminants: Amines and Ammonium Initiators<sup>a</sup>

	Molecular-weight reduction		Rate retardation
	+40° <sup>b</sup>	-60° <sup>c</sup>	-60° <sup>c</sup>
H <sub>2</sub> O	1	1	—
CH <sub>3</sub> OH	0.5	3	—
CO <sub>2</sub>	—	21	14
CH <sub>3</sub> COOH	—	22	1
HCOOH	21	24	6

<sup>a</sup> Figures in each column are relative among themselves, with reference compound as unity.

<sup>b</sup> du Pont (13).

<sup>c</sup> Mejlík et al. (14).

gives the relative effect of common contaminants for chain transfer and reaction retardation in the two studies. The marked effect of the acidic species is visualized as derived from modifying the action of the initiator. In the studies of Mejlík and in more recent work by Shaginyan et al. (15) complex kinetic mechanisms were reported.

### ORGANOMETALLIC INITIATORS

Of particular interest in this class are carboxylate soaps and other hydrocarbon-soluble complexes of many metallic elements. The propagating species with these agents probably exhibits very little charge separation, so in effect they operate by an insertion mechanism. Studies in the laboratories of Farbenfabriken Bayer A.G. (16) indicate that derivatives of divalent tin are outstanding compared to those of other metals. These initiators are in the form of either basic soaps of carboxylic acids or—apparently preferred—derivatives of phenols, carbamates, or xanthates. The latter complexes are more readily purified from structures having undesired catalytic effect in the polymerization. The feature of interest with these initiators is that, whereas, chain termination is largely by reaction with hydroxylic species, the activity of these com-

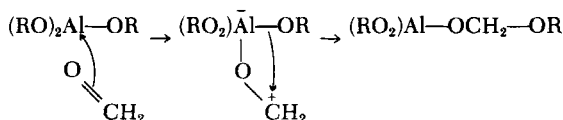
ponents is extremely low. As a result, the production of polymer of satisfactorily high molecular weight for good physical properties is reported from monomer containing up to 5% water. The tin residues remain as end groups on the raw polymer or are adsorbed thereon, but they are removed in subsequent end-capping reactions, if the polymer is taken into solution and reprecipitated.

Tomaszewicz et al. (17), studied the polymerization with calcium stearate initiator in a room-temperature hydrocarbon system. A similar low chain-transfer activity of the common contaminants was observed: one out of 95 molecules of water terminated growth, one out of 32 of methanol, and one out of 23 of formic acid. High-molecular-weight polymer was produced from monomer containing up to 1% methanol. Polyoxymethylenes produced with calcium stearate initiator were found by Majer (18) to have a broad molecular-weight distribution from a comparison of  $\bar{M}_n$  versus  $[\eta]$ .

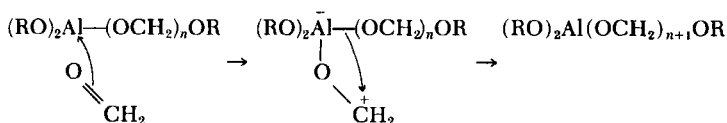
A larger number of other organometallic types have been found to be effective initiators: for example, many metal alkoxides and alkyls, orthotitanates, orthosilicates, Fe, Co, Ni carbonyls, and mercaptides. Most metal alkyls or Grignard-type compounds are quickly converted into alcoholates by reaction with formaldehyde. Therefore, the Ziegler-Natta class of complex initiators cannot function unchanged in this environment.

A study of the action of aluminum isopropoxide has been made by du Pont workers. This agent shows to an extreme extent the tendency of many metal-containing catalysts, including some Lewis acids, to produce polymer containing a high concentration of methoxyl and formate end groups. An insertion mechanism is proposed, as follows:

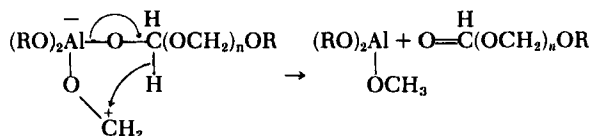
Initiation:



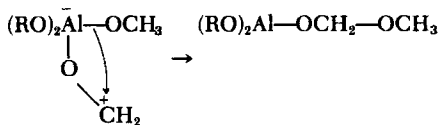
Propagation:



Transfer:



Reinitiation:



### CATIONIC INITIATORS

Formaldehyde is also polymerizable by cationic initiators; however, only fairly strongly acidic species are effective in producing high polymer at good rates. Lewis acids of the metal halide type show a large degree of individuality in their catalytic activity. Some are extremely active at quite low concentrations. The complexity, we believe, stems not only from their varying electronic nature but also from their individual tendency to coordinate with the chain end and with polar constituents in the medium, whether intentionally or adventitiously present, and, possibly, the tendency to replace halide by solvolysis. The coordinated molecules may act as coinitiators. In general, there may be a variety of simultaneously active catalytic species with a given Lewis acid initiator, and the end result from a product standpoint may be relatively sensitive to operating conditions. The action of  $\text{SnCl}_4$  and  $\text{SnBr}_4$ , both in activity and product characteristics, is very similar to that observed for the anionic ion-pair initiators. Water, etc., undoubtedly act as coinitiators. On the other hand, agents such as  $\text{AlBr}_3$  and  $\text{FeBr}_3$  give the largely methoxyl-formate termination suggestive of the insertion type.

Acetal-interchange reactions may also occur in the presence of these Lewis acids. However, the rates are relatively slow compared to that of the polymerization, except at relatively high temperatures.

### POLYMERIZATION ON SOLID SURFACES AND FROM VAPOR PHASE

High-molecular-weight polymer has been produced from gaseous monomer in the absence of a liquid medium. In such

a system the primary concern is removal of the heat of reaction, temperature control, and physical handling of the product. Examples of this type of process include that of St. Gobain (19), in which temperature control is effected by vaporization of a low-boiling hydrocarbon such as pentane or by the use of a rotary reactor charged with preformed polymer plus steel balls for heat transfer, with external cooling.

The Bayer divalent tin catalysts (20) have also been used in this type of operation, a fluidized bed system being preferred.

The use of a variety of solid catalysts has also been disclosed in the patent literature. These are of three general types: bulk surfaces, from which the polymer can be scraped physically, ionic salt crystals, which are subsequently dissolved away, and polymeric compounds, which are allowed to remain with the product. Some of these latter, which contain amide or amine functions, act as stabilizers for the product. Some heterogeneous solid catalysts are reported to facilitate the formation of granular high-bulk-density product.

### RADIATION-INDUCED POLYMERIZATION

Polymerization of formaldehyde can also be induced by ionizing radiation, such as gamma rays from  $^{60}\text{Co}$  source or high-energy electrons. In bulk the best results are obtained at temperatures near the melting point of the monomer ( $-118^\circ$ ) from either the liquid or the solid phase. At temperatures below about  $-150^\circ$  only activated species are formed. These cause explosive polymerization when the sample is subsequently warmed. At temperatures above that of dry ice the relative rate of background polymerization becomes appreciable, although this can be minimized by means of a dilute solution in an inert medium such as ether or acetone or a suspension in a nonsolvent. It has been shown that the mechanism is definitely ionic and not free-radical. By copolymerizations with appropriate vinyl compounds the mechanism in ether solvent, which gave the highest molecular weight, was found to be anionic but to be cationic in bulk, toluene, and  $\text{CH}_2\text{Cl}_2$ . Added water increased the rate but decreased the molecular weight. Polymer made from bulk liquid monomer at low conversion was reported to be 100% crystalline, whereas that from solution was partially amorphous (21,22).

Initiation of polymerization by ultraviolet light is reported in

the patent literature, either in the absence or presence of UV sensitizers. A more complete discussion of this topic is given in Furukawa and Saegusa (23).

### CONDENSATION POLYMERIZATION

This discussion of the polymerization of formaldehyde in aqueous or alcohol solutions is based largely upon du Pont studies (24).

The familiar low polymer, paraformaldehyde, and types of historical interest,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -polyoxymethylene, are derived from aqueous formaldehyde (1). These and more recent high-molecular-weight polymers produced in our laboratory are formed by a fundamentally different mechanism from that of the polymer prepared in anhydrous systems. Here the monomer feed is essentially completely in the form of *gem*-diol, or hemiformal in alcohol solution, and the driving force of crystallization is now of major importance and causes the products to be invariably 100% crystalline. The mechanism of this polymerization is quite comparable to a crystallization and is a relatively slow equilibrium phenomenon, not at all like the chain reaction characteristic of addition polymerization.

The condensation polymerization is the end result of a complex family of equilibrium reactions involving solid, liquid, and, thermodynamically, the gas phase. These are all reversible and are catalyzed by either acid or base (neutral point = pH 4).

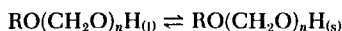
*Homogeneous equilibria* (in solution), R = H or alkyl:



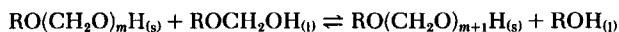
As has been noted above, the over-all solvation of the carbonyl group is extremely high, only about 0.03% of the total formaldehyde being present as free  $\text{H}_2\text{C=O}$  at 30°. The combined formaldehyde is distributed statistically among monomeric and polymeric diols (hemiformals), the relative amounts depending upon total concentration of formaldehyde (that is, upon the sum of all species present as equivalent monomer) and also upon temperature. An increase in temperature favors dissociation of the polymeric diols (hemiformals) and also increases the concentration of free formaldehyde. Calculated distributions between the species have been reported by Ilceto and co-workers (25).

*Heterogeneous equilibria:*

Nucleation:



Growth:



The solubility of the polymeric species in the medium decreases with chain length, and somewhere near DP 10, or a little higher, spontaneous nucleation or precipitation of solid crystalline polymer takes place. Once the solid phase is present, the growth of the chains on the crystal surface by addition of monomer is markedly favored over growth in the liquid phase. This reaction again is stepwise, and may involve free (nonsolvated) monomer as reactive agent. It has been proved that growth by addition of a dissolved polymeric species cannot occur.

Thermodynamic quantities have been calculated for the two separate components of the growth reaction. For the experimental conditions of Example 1 (see next section) the values are as follows (3):

	$\Delta H$ , kcal	$\Delta F$ , kcal
Crystallization of polymer	-1.7	-0.32
Liquid-phase reaction	-0.8	-0.04
Total:	-2.5	-0.36

The solid-liquid relationships are shown schematically in Fig. 1. They are comparable to those of a simple crystallization.

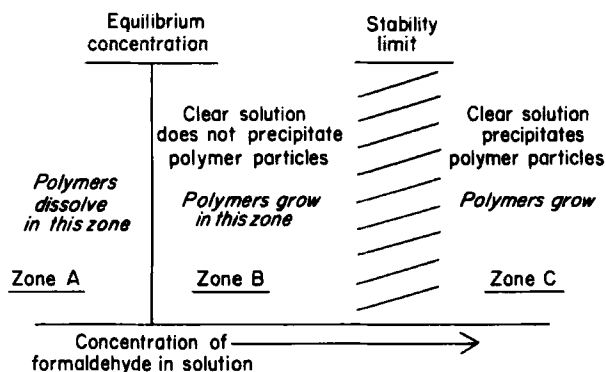


FIG. 1

At a given temperature in solutions of formaldehyde in a given hydroxylic solvent there will be an equilibrium concentration, below which polyoxymethylenes dissolve and above which they will increase in weight. At relatively high concentrations, designated Zone C, spontaneous precipitation from a clear solution will occur. Moreover, there is a narrow range of concentration, usually ranging from 4 to 8 wt-% above equilibrium, designated Zone B, in which preformed polymers will increase in weight but in which the degree of supersaturation is insufficient to cause spontaneous nucleation. The relationships given above do not require a catalyst; an acidic or basic additive, however, must be present, to give significant reaction rates.

### HIGH-MOLECULAR-WEIGHT POLYMER FROM AQUEOUS FORMALDEHYDE

Merely contacting a polymer with a formaldehyde solution in Zone B is not sufficient to produce high-molecular-weight polymer. While much of the monomer adds to the chain ends of the existing molecules, an appreciable amount of induced nucleation of new molecules occurs as well, even under conditions where spontaneous nucleation does not take place. This situation is shown schematically in Fig. 2, a plot of formaldehyde concentration

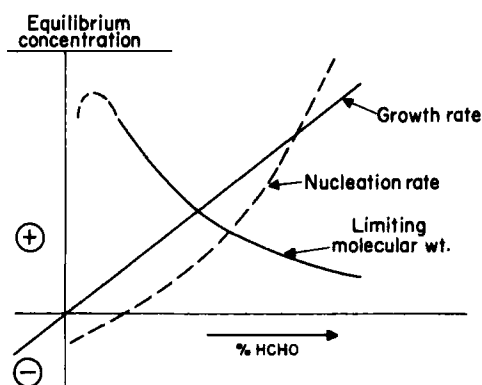


FIG. 2

versus growth rate, which is more or less linear, going through the origin at the equilibrium concentration, and nucleation rate, which is equal to zero net at slightly above equilibrium and then rises rapidly. Conversely, the limiting molecular weight attainable at

steady state increases throughout most of the range as the formaldehyde concentration is reduced closer to equilibrium, with, of course, concurrently decreasing growth rate.

The surface activity of the solid polymer, however, is another variable that requires control. The ideal perfect crystal is born by spontaneous nucleation and then grows exclusively by addition of monomer to the chain ends. It will be a monodisperse system with  $\bar{M}_w/\bar{M}_n$  equal to unity and with all the growing ends lined up on one crystal face. Unfortunately, this condition is impossible to achieve in practice. If the crystal is subjected to conditions of high nucleation, many of the growing ends are buried by the newly deposited chains and so are incapable of further growth. On the other hand, if a polymer is processed at a concentration just barely above equilibrium, it also can become inactive for further growth, probably because of loss by depolymerization of the most active sites.

Many of the classical polymer types produced from aqueous formaldehyde are of relatively low molecular weight because of inadequate control of concentration versus temperature and of nucleation. In particular, many of these materials are characterized by highly occluded end groups. We have developed a technique for measuring the relative availability of end groups. This involves making a sample react with acetic anhydride at relatively low temperature (60°), where only the surface is available to the reagent. The degree of acetylation is measured by the intensity of IR hydroxyl and ester carbonyl bands. By this technique  $\beta$ -polyoxymethylene samples have shown as little as no detectable available end groups, compared to about 80% for polymers made under preferred conditions.

The presence of either acidic or basic catalysts favors the growth reaction over nucleation. Acidic systems, however, are not satisfactory because of complications arising from transacetalization and related reactions. In aqueous media this causes end-group occlusion. Acidic systems in alcohol media are completely inoperable because of formal formation in solution. Therefore basic media are preferred for preparation of high-molecular-weight polymer. The Cannizzaro-type side reaction renders difficult the control of both pH and formaldehyde concentration, especially in basic systems. Fortunately, the relative rates of growth to side reactions can be kept sufficiently favorable by judicious choice of buffered systems and addition of inert diluent when necessary.



The realization of high molecular weights at reasonable rates was made possible by two developments. The first was the use of high temperature, which favored the growth reaction over nucleation. By control of catalyst recipe, so as to minimize Cannizzaro losses, operable systems at 95° and higher in both water and alcohols were achieved. The second development was the technique of seeding the reaction by quick-chilling the mixture or an aliquot thereof to conditions of high supersaturation. After a short period of time, usually 30 min or less, the seed is reintroduced into the high-temperature medium in the concentration region preferred for growth. Such seed and its growth products maintain higher activity than does isothermal seed and grow readily under preferred conditions to products of high molecular weight.

*Preparation of high-molecular-weight polymer from aqueous formaldehyde: Example 1.* The recipe was  $(\text{CH}_3)_3\text{N}/\text{H}_3\text{PO}_4$  (1/0.55 mole ratio), 0.13 g of total catalyst per gram of  $\text{H}_2\text{O}$ , pH 6.5. The initial solution containing 56.8% HCHO at 95° (equilibrium = 52.0%) was chilled to 60° for 30 min to form seed, returned to 95°, and maintained at 95° for 48 hr, formaldehyde concentration decreasing to 52.8% final. The product  $\bar{M}_n$  was 38,000.

### POLYMERIZATION IN ALCOHOLS

The same principles apply to polymerization in alcohols, with appropriate changes in recipes to adjust to the characteristics of the solvent. Of particular practical interest is the system with methanol as solvent, because of the possible direct use of the effluent from a methanol dehydrogenation unit as feed stock. Two further developments in our laboratories have made possible the continuous automatic control of the polymerization environment in this system (26). The first was the discovery that the removal by distillation overhead of methanol from concentrated solutions (up to 85% HCHO) could be readily achieved in the presence of catalytic amounts of basic materials in the still column to accelerate the absorption and reaction of formaldehyde vapor in the liquid phase. Previously, in the absence of such catalyst satisfactory removal of formaldehyde-free methanol could only be obtained from solutions containing less than about 65% formaldehyde.

The second development was the finding that the presence

of small amounts of water, about 0.1%, effected a marked reduction in the losses of formaldehyde to methyl formate and other side-products and thus increased the operable temperature to the region of 110°C. Under such conditions sodium formate at concentrations of about 100 ppm is a preferred catalyst.

*Preparation of high-molecular-weight polymer from methanolic*

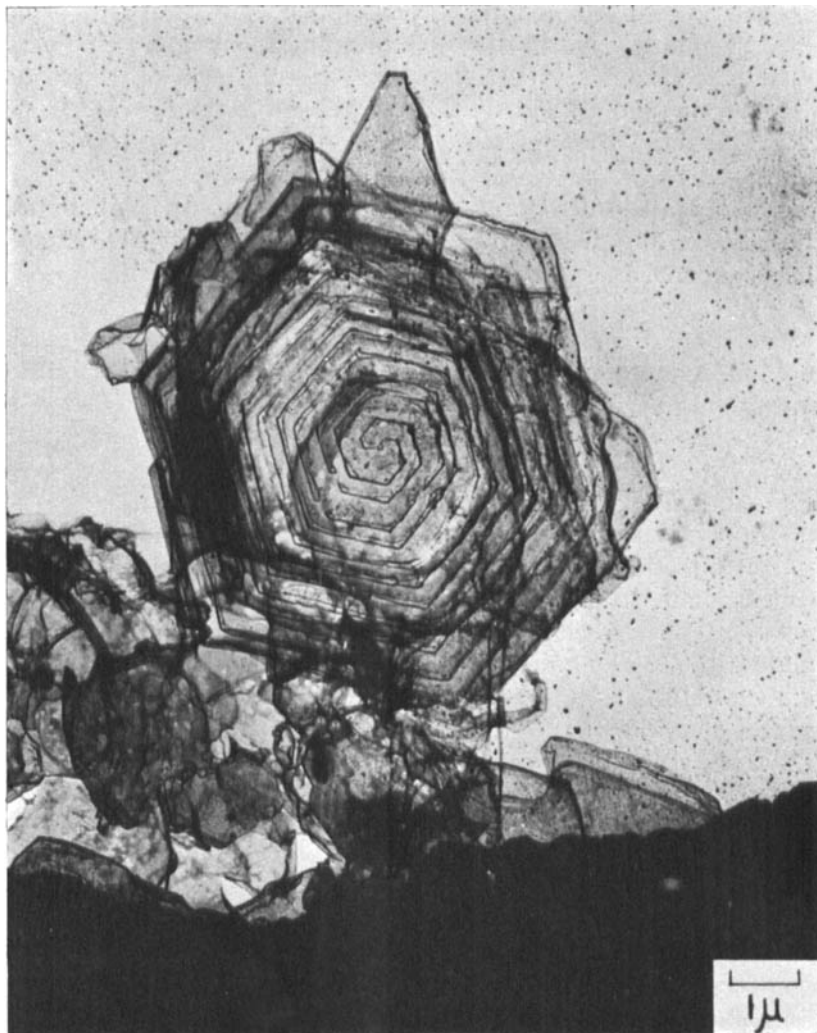


FIG. 3

*formaldehyde: Example 2.* To a flask equipped with a fractionating still column was charged a clear solution containing 75% HCHO, 0.10% H<sub>2</sub>O, 0.50% N-ethylpiperidine, and 75 ppm NaOH, the remainder being methanol. The solution was chilled to 60° for 10 min, to form seed, and returned to 110.0°. Distillation was commenced at this temperature at a pressure of 805 mm Hg absolute. Methanol was removed overhead, and fresh feed was added at such rates as to maintain temperature, pressure, and liquid level. Suitable control devices permitted automatic operation of both feed and distillate draw-off. After 91 hr of operation the slurry contained 21.8% solids, and the product  $\bar{M}_n$  was 46,000. Losses to side reactions were less than 1% of the formaldehyde per day.

An electron micrograph of a crystalline polyoxymethylene produced in the methanolic system is given in Fig. 3. This shows the hexagonal crystalline form and well-developed spiral growth patterns.

End-capped polymers fabricated by conventional plastics-molding techniques have given physical properties and stabilities equivalent to those of commercial formulations.

### ORTHORHOMBIC POLYOXYMETHYLENE

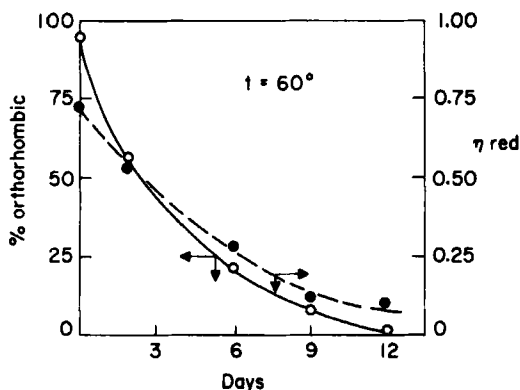
All polyoxymethylenes discussed above and, in addition, material recovered from the melt or from solution exhibit universally a hexagonal crystalline form. Mortillaro and co-workers (27), however, have recently discovered a new, hitherto unknown, modification belonging to the orthorhombic system. This form is metastable, is produced from aqueous formaldehyde under certain conditions at 20 to 35°, and reverts to the hexagonal form above about 50°. The critical condition for preparation of this form, other than temperature, apparently is a relatively high pH (above 10) which, to maintain, requires intermittent addition of caustic. High concentrations (over 20%) of certain preferred salts, such as sodium formate or potassium fluoride, promote high-molecular-weight product. Aqueous solutions at 20 to 35° under conditions other than those mentioned above yield hexagonal polyoxymethylene of low molecular weight. The growth of orthorhombic polyoxymethylene follows the same mechanism as does growth of the hexagonal polymer; therefore, close control of the degree

of supersaturation is required for high molecular weight. Any crystalline polyoxymethylene (even paraformaldehyde) can be used as seed. A typical steady state is reached in about ten days, and productivity is such that the weight of polymer in suspension doubles in about two days at steady state.

**TABLE 2**  
Polymerization of Aqueous Formaldehyde HCOONa  
Catalyst (34 to 38%), pH 10.4 (27a)

Temp., °C	Steady state	
	$\eta_{red}$	Orthorhombicity, %
20	0.8	95
35	1.0	90
50	<0.1	<5
60	<0.1	<1

The effect of temperature in this reaction is particularly striking, as shown in Table 2. At 20° the product is almost completely orthorhombic, as determined by x-ray, the remainder being hexagonal. Raising the temperature to 35° decreases the percentage of orthorhombicity slightly but gives the highest molecular weight for a given production rate. However, at 50 and 60° both molecular weight and percentage of orthorhombicity decrease markedly. In the highest temperature experiments cited orthorhombic



**FIG. 4.** Polymer characterization versus time. [From Table 2.]

polymer was actually used as seed and was converted to the hexagonal, as shown by Fig. 4.

Another characteristic feature is the salt effect. In the high concentrations used the salts have a marked desolubilizing effect on the polymers and thus must be considered both solvent and catalyst. Only certain salts have the desired effect and, likewise, the effect of concentration varies: with some, the molecular weights increase throughout, as salt concentration is increased to saturation; with others, there is an optimal concentration.

**TABLE 3**  
Polymerization of Aqueous Formaldehyde Salt and pH Effect (27*b,c*)  
(35°C, pH 10.4, 30 to 40% salt, unless noted)

Salt		$\eta_{red}$	Orthorhombicity, %
KF	pH 9.4	0.1	10
KF	—	1.0	80–85
HCOOK	—	0.8	80–85
HCOOK (ex KOH)	5% max.	0.4	80–85
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	—	<0.1	<0.1

A few most striking effects are given in Table 3. The first line shows the failure of the system to operate at low pH with the same concentration of salt that gives optimal performance at preferred pH. The fourth line is an experiment in which no catalyst other than KOH, necessary for pH adjustment, was added, producing orthorhombic polymer but of low molecular weight. The final line is an example of a salt which is ineffective in favoring the orthorhombic form.

Comparative crystallographic data show that in the orthorhombic modification the monomer units in a given chain are wound in a tighter helix than in the hexagonal form (2.00 monomer units per turn versus 1.810) and that the distance along the helix axis is shorter (1.78 Å versus 1.92); as a result the calculated density is higher (1.537 versus 1.506). On the other hand, the cross-sectional area between chains is slightly larger. These constants indicate that the conversion between the two forms requires but minor adjustments in position of the atoms.

## ALDOL TYPE OF CONDENSATION

This reaction [Eq. (2)] involves migration of an aldehydic hydrogen to a neighboring carbonyl oxygen with formation of a carbon-carbon bond. It takes place only under rather specific catalytic conditions and does not cross with the polyoxymethylene type of polymerization. The most common method of inducing this reaction is by the action on dilute aqueous formaldehyde of certain metallic hydroxides, notably calcium, and also  $Tl^+$ ,  $Pb^{2+}$  and  $Sn^{2+}$ . Six carbon sugars ("formose") are a common product.

This condensation has been found to be autocatalytic, the primary condensation products accelerating the reaction. The active species has been pictured as a coordination complex between the metallic hydroxide and an  $\alpha$ -hydroxycarbonyl compound. A suggested structure of this complex and a fuller discussion of the reaction are given by Furukawa and Saegusa (28).

The aldol-type condensation can also occur under some conditions with anhydrous formaldehyde: for example, in the presence of certain weak organic acids. In our experience at du Pont we have observed this condensation to take place from gaseous formaldehyde in the presence of many copper and brass alloys at temperatures of about  $150^\circ$ . Pyrolysis of paraformaldehyde at controlled temperature (for example, in a bath maintained at  $160^\circ$ ) yields a residue containing readily water-extracted sugars, which are relatively free from carbonaceous by-products.

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