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The Polymerization and Copolymerization of Trioxane

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Stable high-molecular-weight polyacetals can be prepared from formaldehyde or from its trimer trioxane.

Polyoxymethylene was prepared as early as 1859 by Butlerov (1). In the 1920's Staudinger and co-workers succeeded in producing an unstable formaldehyde polymer of moderately high molecular weight (2). In addition end-capping of a polymer, to prevent hemiacetal degradation from the ends, was accomplished on low-molecular-weight materials. During the last decade du Pont has been marketing a high-molecular-weight end-capped homopolymer (3), and Celanese is marketing a high-molecular-weight polyacetal copolymer prepared from trioxane and a cyclic ether (4).

This paper will be a review of certain aspects of trioxane properties and its polymerization and copolymerization, including some data from our own laboratories.

TRIOXANE PROPERTIES

Trioxane, the cyclic trimer of formaldehyde, melts at 60.3°C and has a boiling point of 114.3. It can be prepared conveniently by treating aqueous formaldehyde with acid and distilling out the trioxane (as the water azeotrope), as it is formed. The compound is remarkably stable, is an excellent solvent, and has found uses as a fuel and convenient source of anhydrous formaldehyde. An interesting characteristic of its stability, which is germane to a polymer-property aspect to be discussed later, is its inertness to bases. The hemiacetal structure, a characteristic of most formaldehyde oligomers, is susceptible to hydrolysis in basic media; this moiety is not present in trioxane.

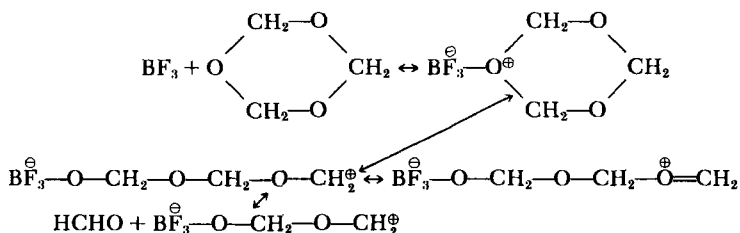
POLYMERIZATION

Homopolymerization

Trioxane is polymerized cationically (5,6).

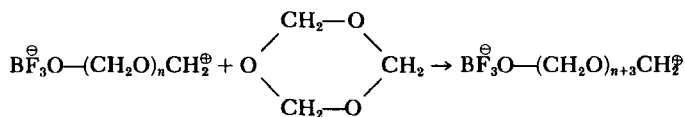
The mechanism of polymerization as discussed by Kern and Jaacks (5) and Leese and Baumber (7) may be described as follows.

BF_3 , for example, coordinates directly with an oxygen in the trioxane molecule, and ring opening is induced to form a resonance-stabilized zwitterion.



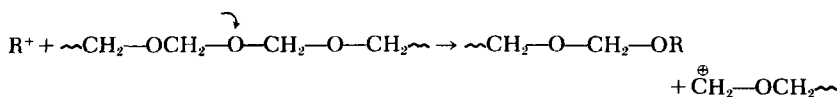
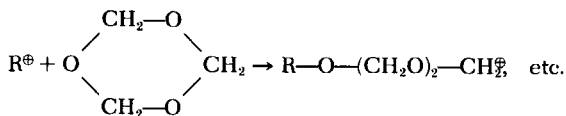
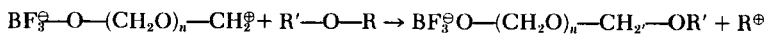
An equilibrium is established between the reactive polyoxymethylene oligomer and formaldehyde. When the equilibrium concentration is achieved (60 mmoles/liter at 30°C) (5), low-molecular-weight polymer develops and forms crystal nuclei and the reaction rate has been shown to be dependent on the surface area (7) available for polymer deposition. Polymerization continues very rapidly thereafter on the surfaces of these nuclei (7). This "induction" period can be eliminated by the addition to the reaction mass of an equilibrium concentration of HCHO.

The propagation step may be depicted as follows:



Terminations and cocatalyst requirements have not been unequivocally settled at this writing. Jaacks and Kern (6) have pointed out that in spite of attempts at thorough drying all polymer chains were transferred by water and contained at least one hydroxyl end group. H_2O , CH_3OH , and $\text{CH}_3\text{---O---CH}_2\text{---O---CH}_3$ have been found to

serve as chain transfer agents (8), supplying a terminus for one molecule and initiating another as follows:



From our studies it has been possible to show that each molecule of chain transfer agent supplies the ends for one polymer chain; see Fig. 1.

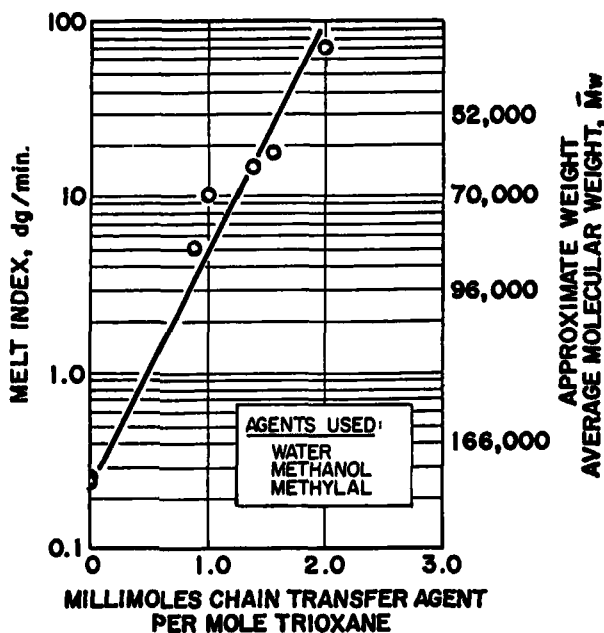


FIG. 1. Effect of chain-transfer agents in acid-catalyzed trioxane copolymerization.

Jaacks and Kern (6) also made an interesting study of the effect of initiator variations on the induction period and reaction parameters. Some of their data are reproduced here in Table 1.

TABLE 1

Initiator	Amount of initiator, mole per mole trioxane	Induction period	Reaction time, hr	Yield, %	\bar{M}_w
CH ₃ COCIO ₄	4×10^{-5}	25 sec	1	47	29,000
FeCl ₃	4×10^{-5}	40 sec	1	38	27,000
SnCl ₄	4×10^{-5}	3 min	1	27	16,000
BF ₃ ·O(Et) ₂	4×10^{-5}	18 min	1	13	8,500
SbCl ₅	4×10^{-5}	ca. 30 min	1	5	3,000
H ₂ SO ₄	4×10^{-5}	24 hr	24	0	—

The authors concluded that the catalytic ability is related inversely to the basicity of the gegenion and that in the absence of chain-transfer agents or terminators "living" cationic species can be said to exist.

Copolymerization

Studies, conducted by Celanese and also by Farbwerke Hoechst (8), of the copolymerization of trioxane and ethylene oxide reveal that an induction period, much longer than observed in the case of the homopolymer, prevails. It has been established that during this period ethylene oxide is converted to 1,3-dioxolane, 1,3,5-trioxepane, and low-molecular-weight linear copolymer. Only after all of the ethylene oxide is so consumed does solid polymer form. Rate data on the disappearance of ethylene oxide conforms with first-order kinetics (actually pseudo), as shown in Fig. 2. Interestingly, this induction period also can be eliminated by the addition of HCHO, at a level equal to the sum of the equilibrium concentration discussed before and the molar concentration of ethylene oxide.

During the preparation of a trioxane-ethylene oxide copolymer (2 wt. % ethylene oxide), if the reaction is quenched by addition of polar solvent, to destroy the catalytic activity, just before insoluble polymer forms, a low-molecular-weight polymer at a yield of about

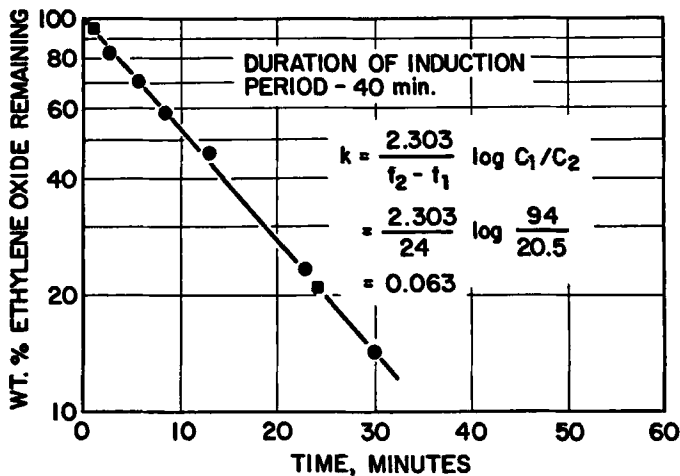


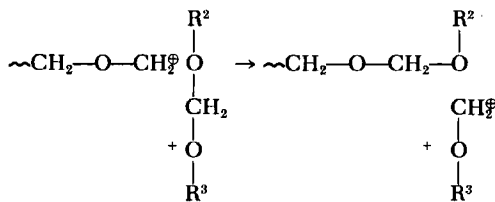
FIG. 2. Rate of disappearance of ethylene oxide during the induction period of a trioxane-ethylene oxide (98 wt-% and 2 wt-%, respectively) copolymerization reaction.

5% can be isolated, which contains virtually all the ethylene oxide charged, as mono-, di-, or triethyleneoxy units.

When 1,3-dioxolane is substituted for ethylene oxide in a copolymerization reaction, a small induction period, analogous to the homopolymerization equilibrium reaction time, is observed. Again, when the reaction is stopped in the early stages, virtually all of the 1,3-dioxolane is found in the polymer as monoethyleneoxy units.

TRANSACETALIZATION

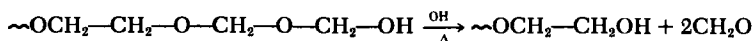
The elaborate reshuffling, leading to random distribution of these concentrated ethyleneoxy units throughout the polymer chain, occurs via a transacetalization reaction (8). Growing chains (carbonium ions) can attack another chain, in a manner similar to that involved in the proposed attack on the acetal oxygen of the trioxane molecule and so create a "new" growing chain:



In this manner the oxyethylene units can be randomly distributed throughout all of the polymer chains. Our studies have shown that when poly-1,3-dioxolane (MW ca. 1000) is dissolved in trioxane and the mixture treated with BF_3 , ethyleneoxy units are randomly distributed throughout the high-molecular-weight copolymer produced. As additional evidence of the transacetalization reaction it has been demonstrated that virtually all of the chain-transfer agent present in the reaction is incorporated as polymer chain ends early in the reaction. Molecular weight thus increases with conversion.

Conversion	Inherent viscosity (0.1% in p-chlorophenol at 60°C)
25%	0.48
40%	1.0
60%	2.0
75%	2.1

A "most probable" molecular-weight distribution ($M_w/M_n = 2$) (9) is another consequence of this equilibrium reaction. In addition, the copolymer possesses good thermal stability, once the short, unstable homopolymer end segments are removed. This may be accomplished by basic hydrolysis, since the ends are hemiacetal structures, or by mild thermal decomposition.



Note that at the terminus of a molecule so treated is a hydroxyl ethyl ether group, a stable moiety.

RECENT TRIOXANE POLYMERIZATION DEVELOPMENTS

Okamura et al. have polymerized trioxane by irradiation (10) with beta and gamma rays. The irradiation, conducted in the crystalline state, results in polymer after mild thermal treatment.

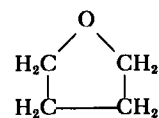
It has been suggested that cationic species trapped in the crystals are reactivated and that these may be the initiators of the polymerization. In a further study Takakura et al. reported (11) that maleic anhydride-benzoyl peroxide acts as a catalyst system for the polymerization of trioxane. This finding is rather interesting, when we consider that benzoyl peroxide is generally regarded as a free-radical initiator, and the trioxane reaction so catalyzed proceeds,

kinetically, in the same fashion as the BF_3 -initiated reaction. However, these researchers felt that hydride ion abstraction and trioxane radical electron transfer to maleic anhydride would be a likely route by which trioxane cations are generated in this system. With this species formed, propagation can occur as described previously.

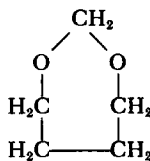
Workers at Continental Oil Co. reported at the last meeting of the American Chemical Society in Atlantic City (12) on the ability of molybdenum diacetylacetonate to polymerize trioxane and formaldehyde rapidly to high-molecular-weight polyoxymethylenes. The authors described a catalytic insertion mechanism which may be involved. Catalyst fragments at the ends of polymer chains would tend to stabilize the molecule and, although they state that their IR evidence is not unequivocal, it does conform with such a hypothesis.

Another interesting catalyst system was that studied initially by Bawn et al. in the homopolymerization of tetrahydrofuran, that is, triphenylmethyl antimony hexachloride (13). We were able to demonstrate that a copolymer of this generally unreactive cyclic ether with trioxane could be prepared conveniently at room temperature.

The copolymer so prepared is similar to that formed by trioxane-cyclic formal of 1,4-butanediol copolymerization. The latter comonomer involves acetal linkages and can readily be copolymerized with trioxane and BF_3 as catalyst.

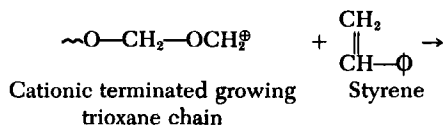


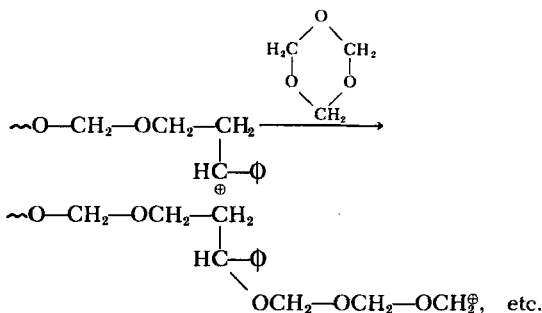
Tetrahydrofuran



Cyclic formal of 1,4-butanediol

Trioxane can polymerize with olefin compounds. Hohr et al. (14) have demonstrated that a trioxane-styrene copolymerization occurs as follows:

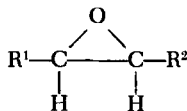




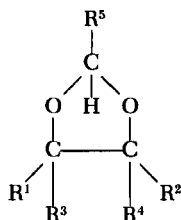
The researchers (14) clearly established that attack on the styrene was at the β carbon.

Other compound types that have been successfully copolymerized with trioxane include (4) the following.

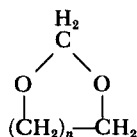
Mono- and disubstituted epoxides:



Mono- and polysubstituted dioxolanes:



Cyclic and linear formals, $R^1-O-CH_2-O-R^2$:



PROPERTIES OF POLYOXYMETHYLENE

The structure of polyoxymethylene homopolymers produced from HCHO and trioxane are identical. X-ray diffraction studies reveal a hexagonal unit cell in the polymer crystal and a helical formation having nine CH_2O units or three trioxane units in the identity period of 17.3 Å (15,16).

A theoretical density of 1.506 g/cm^3 has been calculated (17). The actual density is 1.425, and crystallinity is estimated at 84%.

The commercial copolymer has a density 1.410 and an estimated crystallinity of 80%.

Dynamic mechanical studies of polyacetals (18,19) show the existence of three transitions below the melting point. The gamma transition is observed at about -60°C (100 cyc/sec) for both the homopolymer and the oxyethylene copolymer. The alpha transition at $+130^{\circ}\text{C}$ appears to increase with crystallinity in both intensity and temperature. The beta transition at $+5^{\circ}\text{C}$ (100 cyc/sec) can vary as much as 15°C , depending on comonomer level. The latter transition, which translates to room-temperature region when dynamics associated with impact testing are examined, is pertinent in the explanation of elongation phenomena. The copolymer demonstrates improved elongation and improved tensile impact, whereas the level of increased crystallinity associated with the homopolymer imparts increased tensile strength and modulus

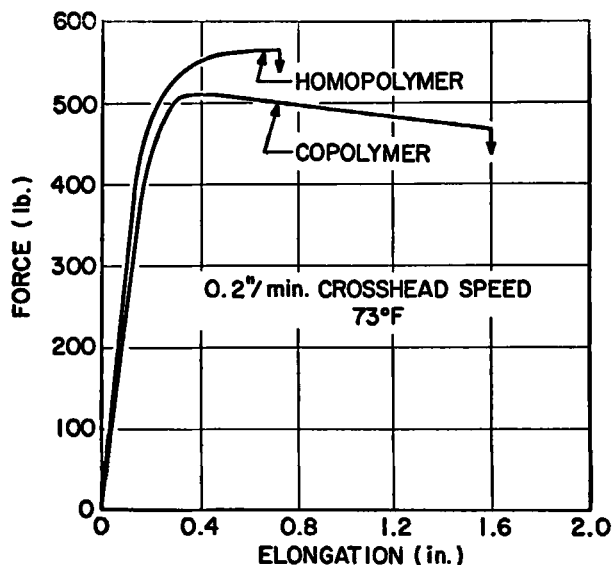


FIG. 3. Typical tensile curves.

(Fig. 3). Another important difference between end-capped trioxane homopolymer and trioxane copolymer is stability. Because the copolymer has oxyethylene units spread randomly along the chain, a scission thermally or acidolytically caused in a chain does not result in complete depolymerization. Both the homo-

polymer and copolymer have excellent solvent resistance. The copolymer and only certain end-capped (e.g., by etherification) homopolymers are stable in basic media. Both polymers are unstable in strongly acidic media.

CONCLUSION

Polymer formed from trioxane is structurally equivalent to anionically polymerized HCHO. Trioxane can be polymerized by a variety of Lewis and Brønsted acids. The nature of the gegenion is pertinent to the rate of polymerization and the molecular weight of the polymer produced. Transacetalization is responsible for random distributions of comonomer units along a polymer chain. Such units affect the position temperature at which the β transition occurs in dynamic mechanical testing, reduce tensile strength and modulus, increase ductility, and improve thermal stability.

APPENDIX

Experimental

Consumption of Ethylene Oxide during the Induction Period. To a heated 2-liter 3-necked round-bottomed flask was charged a solution composed of 980 g of freshly distilled trioxane and 20 g of ethylene oxide. The flask was fitted with a mechanical stirrer, thermometer, and drying tube, and then immersed in an oil bath maintained at 65°C. Once the system had attained thermal equilibrium, a 25-g sample was removed and quenched in 100 ml of glacial acetic acid. Next, a catalyst composed of 0.073 g of boron fluoride-di-*n*-butyletherate in 50 g of cyclohexane was added to the flask. Time was counted from this point. Additional samples were taken at various times during the induction period. The length of the induction period was from catalyst addition until the first appearance of solid polymer (turbidity). Ethylene oxide in the samples was determined by titrating with HBr in glacial acetic acid (0.25 *N*) to a methyl violet end point.

Preparation of Triphenylmethyl Antimony Hexachloride. Chlorotriphenylmethane (Matheson, Coleman and Bell) and antimony pentachloride (Baker & Adamson) were used for the catalyst

preparation. The procedure followed was that described by Holmes and Pettit (20).

Copolymerization of Trioxane and Tetrahydrofuran with Triphenylmethyl Antimony Hexachloride as Catalyst. To a 250-ml round-bottomed flask was charged 52.9 g of freshly distilled (over Na) tetrahydrofuran. Next, 51.4 g of distilled trioxane and 0.2475 g of triphenylmethyl antimony hexachloride (4.28×10^{-4} mole) were added to the flask. The flask was sealed and allowed to stand (with occasional stirring) at room temperature for 72 hr. At the end of this period the contents of the flask existed as a solid mass. After repeated extraction of the product with acetone the acetone-insoluble material was dried. Weight of the dried material was 55.6 g (m.p. 164 to 165°C). This melting point and 87% recovery of a material 160 to 161°C m.p. from a sealed-tube base hydrolysis (160°C, 59.9% methanol, 39.9% water, 0.2 wt-% triethylamine) are characteristic of a trioxane copolymer containing about 5% comonomer. The acetone-soluble material was isolated and dried (32.9 g); it was originally in the form of a viscous syrup, which crystallized (m.p. 36 to 37°C) after standing. The melting point of this material is characteristic of low-molecular-weight tetrahydrofuran homopolymer (21).

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