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### New Trioxane Copolymers

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## New Trioxane Copolymers

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### ABSTRACT

A review is given on two types of trioxane copolymers: trioxane/dioxolane copolymers and copolymers of trioxane with polar monomers. It has been possible to find reaction conditions that influence the transacetalization reaction and, hence, the molecular weight distribution and the sequence length of trioxane/dioxolane copolymers. Trioxane copolymers with varying dioxolane content show an unusual behavior with respect to density, specific volume, and melting point as a function of composition. This is possibly caused by the formation of at least four different crystal structures in such copolymers. The synthesis of polyoxymethylenes carrying reactive groups is possible by copolymerizing trioxane with substituted phenylglycidyl ethers. These copolymers can be subjected to further chemical modification leading to polyoxymethylenes with aldehyde, carboxy, and amino groups or derivatives thereof.

### INTRODUCTION

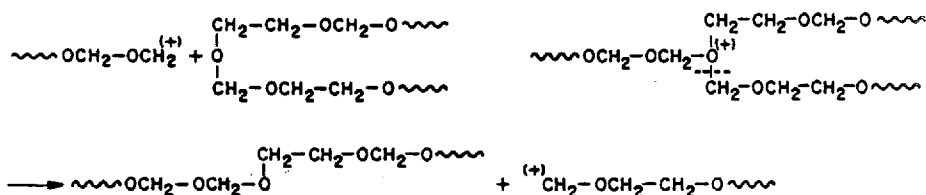
The ring-opening polymerization of trioxane is the most versatile route to high molecular weight polyoxymethylenes. In the past numerous papers dealing with the homopolymerization of trioxane [1, 2, 3] or with the copolymerization of trioxane with small amounts

of comonomers [ 1, 4, 5 ] have been published. The present paper summarizes new results on two types of copolymers: trioxane/dioxolane-copolymers and copolymers of trioxane with polar monomers.

### TRIOXANE/DIOXOLANE COPOLYMERS

The ring-opening polymerization of trioxane with cationic initiators is accompanied by several side reactions of the growing carbonium ions. One of these side reactions is the so-called transacetalization reaction [ 4 ], i.e., the reaction of the polymeric carbonium ions with oxygen atoms of the same or of another polymer molecule (intra-molecular and intermolecular transacetalization) ( Fig. 1 ).

#### 1. Intermolecular Transacetalization



#### 2. Intramolecular Transacetalization

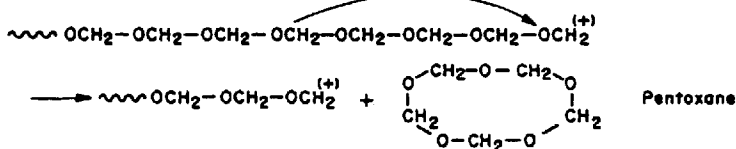


FIG. 1. Intramolecular and intermolecular transacetalization in trioxane copolymerizations.

The transacetalization reaction thus leads to a continuous cleaving and forming of acetal linkages [ this is comparable with side reactions of polycondensation processes ( transesterification, transamidation ) ] which finally results in copolymers with narrow molecular weight distribution and high chemical uniformity. In some cases it is interesting also to study the properties of copolymers with broad

molecular weight distribution and with sequence lengths of the comonomer larger than unit. We have, therefore, studied how the transacetalization reaction can be influenced [6]. It was found that the proportion of transacetalization depends largely on the type of initiator.

### Trioxane/Dioxolane Copolymers with Varying MW Distribution

Table 1 lists results on the influence of the initiator on the molecular weight distribution ( $M_w/M_n$  as obtained by gel permeation chromatography) of trioxane/dioxolane copolymers (50:50). It is obvious that  $\text{HClO}_4$  leads to broader molecular weight distribution.

TABLE 1. Influence of Different Initiators on the Molecular Weight Distribution of Trioxane/Dioxolane Copolymers (50:50). Gel Permeation Chromatography Analysis in THF at 45°C

Initiator	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w/M_n$
$\text{SnCl}_4$	13.0	8.6	1.51
	10.2	6.9	1.49
	8.0	5.3	1.52
$\text{BF}_3$	11.8	8.0	1.47
	9.6	6.3	1.53
	8.7	5.6	1.58
$\text{HClO}_4$	26.2	10.4	2.54
	21.6	7.8	2.76
	17.1	6.4	2.67

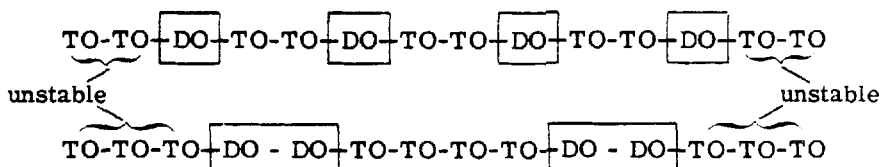
### Trioxane/Dioxolane Copolymers with Different Chemical Uniformity

Table 2 shows the influence of the initiator on the sequence length of the comonomer in trioxane/dioxolane copolymers (98:2). Two different data were taken as a measure of the sequence length: first, the alkali-unstable portion of the copolymer, i.e., the amount of alkali degradable  $\text{CH}_2\text{O}$ -units at both ends of the copolymer chains;

TABLE 2. Alkali-Unstable Portion and Crystalline Melting Point of TO/DO Copolymers (98:2) Obtained with Different Initiators

Initiator	Alkali-unstable portion (%)	Crystalline melting point (°C)
BF <sub>3</sub>	8	166.0
SnCl <sub>4</sub>	9	166.4
HClO <sub>4</sub>	17	171.8

and second, the crystalline melting point. The amount of degradable oxymethylene units increases—at constant comonomer content—with increasing sequence length as illustrated in the accompanying scheme where TO stands for CH<sub>2</sub>O units and DO stands for dioxolane units.



A very sensitive indication of sequence length distribution is the crystalline melting point ( $T_m$ ) of the copolymer. The higher the sequence length of the dioxolane units, the higher will be  $T_m$ .

Again, HClO<sub>4</sub> differs from the other initiators in that it leads to higher sequence length of the dioxolane units, i.e., to chemically less uniform copolymers. Similar results were also obtained with copolymers of higher dioxolane contents.

### Trioxane/Dioxolane Copolymers with Different Crystal Structures

Unexpected results were found when a series of trioxane/dioxolane copolymers with dioxolane contents from 12 to 95% were characterized by measuring their density, specific volume, and crystalline melting point [7]. At certain ranges of composition these copolymers show an unusual behavior as can be seen from Table 3 and Fig. 2.

TABLE 3. Dependence of Density, Specific Volume, and Crystalline Melting Point on the Composition of Trioxane/Dioxolane Copolymers

Dioxolane (wt-%)	Density at 20°C (g/cm <sup>3</sup> )	Specific volume at 20°C (cm <sup>3</sup> /g)	Melting point (°C)
12.7	1.3898	0.7195	154
21.4	1.3639	0.7332	143
30.0	1.3408	0.7458	135
43.8	1.3158	0.7600	100
46.0	1.2992	0.7697	?
52.4	1.2796	0.7815	54
63.0	1.2708	0.7869	48
64.9	1.2674	0.7890	34
72.0	1.2714	0.7865	32
79.0	1.2858	0.7777	37
85.0	1.2865	0.7773	40
90.0	1.2798	0.7814	43
95.0	1.2778	0.7826	44
100.0	1.2800	0.7812	62

Although the experiments are not yet completed, it can be envisaged that this unusual behavior possibly results from at least four different crystal structures which these copolymers—as a function of their composition—seem to be able to form.

#### COPOLYMERS OF TRIOXANE WITH POLAR MONOMERS

The introduction of functional groups into polyacetals is possible via 3 routes:

- (1) Reaction of the OH end groups with suitable reagents.
- (2) Addition of suitable chain-transfer agents during the polymerization of trioxane.
- (3) Copolymerization of trioxane with polar monomers.

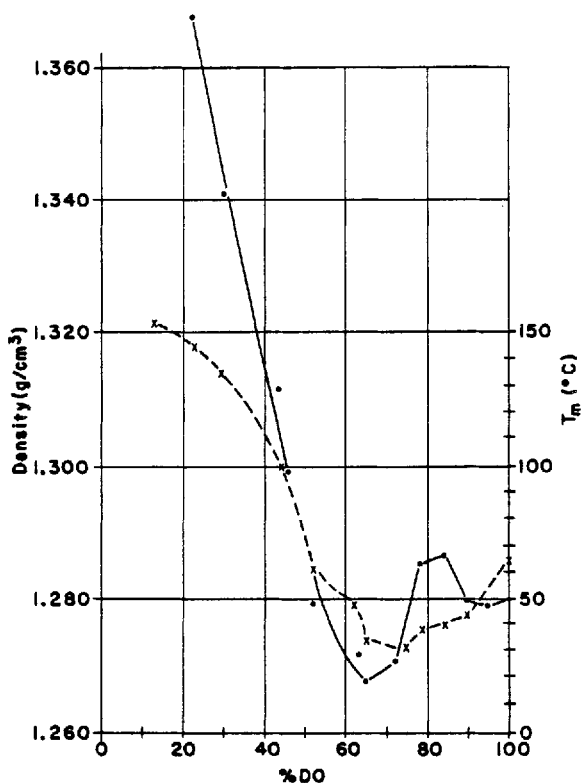


FIG. 2. Density (●) and crystalline melting point (×) as functions of composition in trioxane/dioxolane copolymers.

### Copolymerization of Trioxane with Substituted Phenylglycidylethers

Reaction (1) [1, 8, 9] and Reaction (2) [10] lead to polyacetals with functional end groups only. Instead, copolymerization of trioxane with monomers which contain another functional group besides a polymerizable group in the same molecule provides polyoxymethylenes with randomly distributed reactive sites along their main chain. It has been found [11] that substituted phenylglycidylethers are suitable comonomers. They are easily obtained in good yields according to the reaction scheme in Fig. 3 (top). Copolymerization of these monomers with trioxane gives polyoxymethylenes with randomly distributed reactive groups (Fig. 3, bottom).

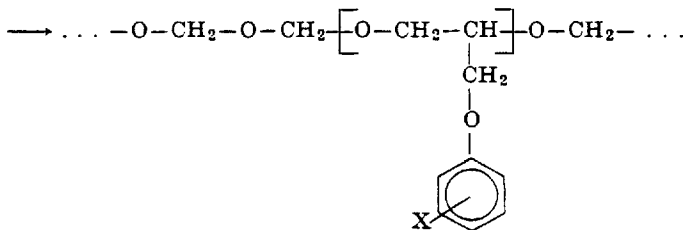
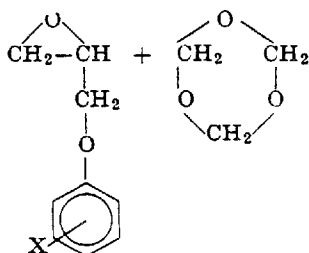
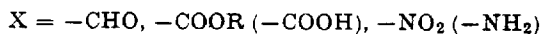
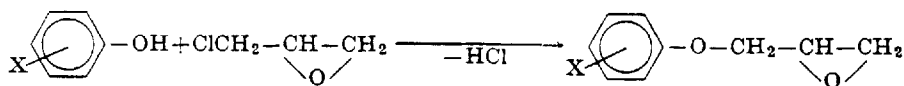


FIG. 3. Preparation of polyoxymethylenes with reactive groups via copolymerization.

In this way, polyoxymethylenes with aldehyde, ester, and nitro groups were obtained which could be reacted further with suitable reagents (see below). It was surprising that none of these reactive groups influenced the copolymerization noticeably; thus high-molecular weight and noncross-linked copolymers were obtained.

#### Reactions of Polyoxymethylenes Carrying Reactive Groups [11]

Most of the reactions described below were carried out heterogeneously, some of them were also carried out in solution or in the molten stage.



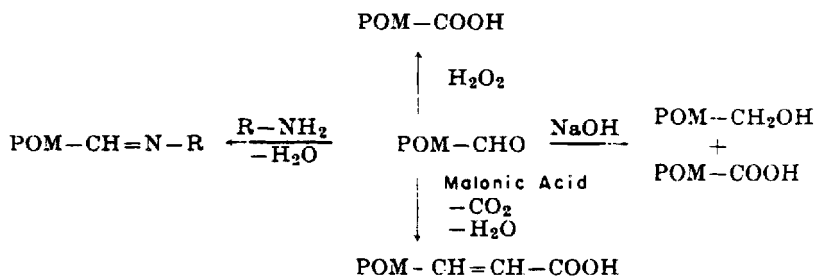
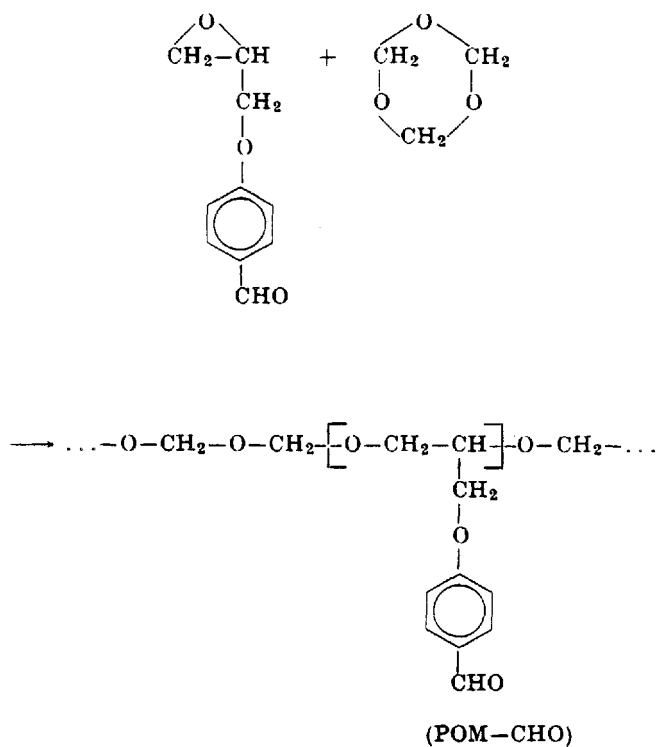
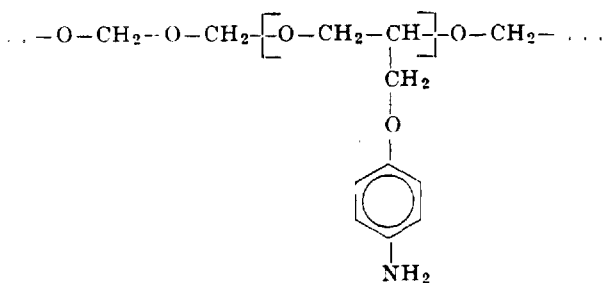
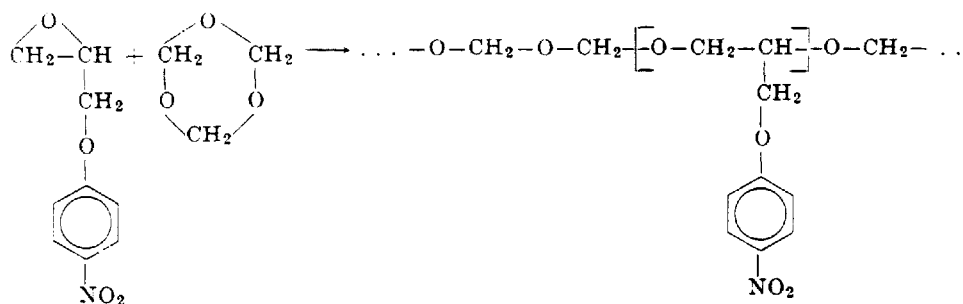


FIG. 4. Reactions of polyoxymethylenes containing free aldehyde groups.



(POM-NH<sub>2</sub>)

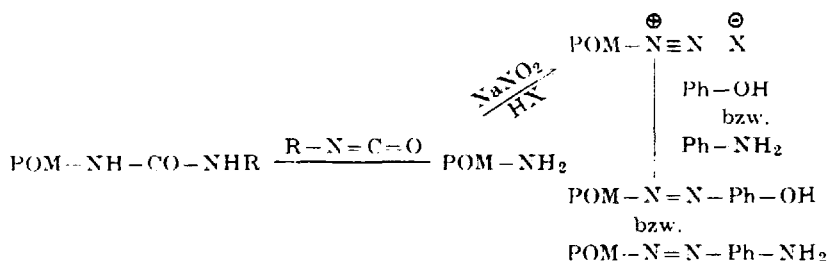


FIG. 5. Reactions of polyoxymethylenes containing free amino groups.

Reactions of Polyoxymethylenes with Free Aldehyde Groups

Polyoxymethylenes with free aldehyde groups (POM-CHO), obtained by copolymerizing trioxane with p-glycidoxybenzaldehyde, are

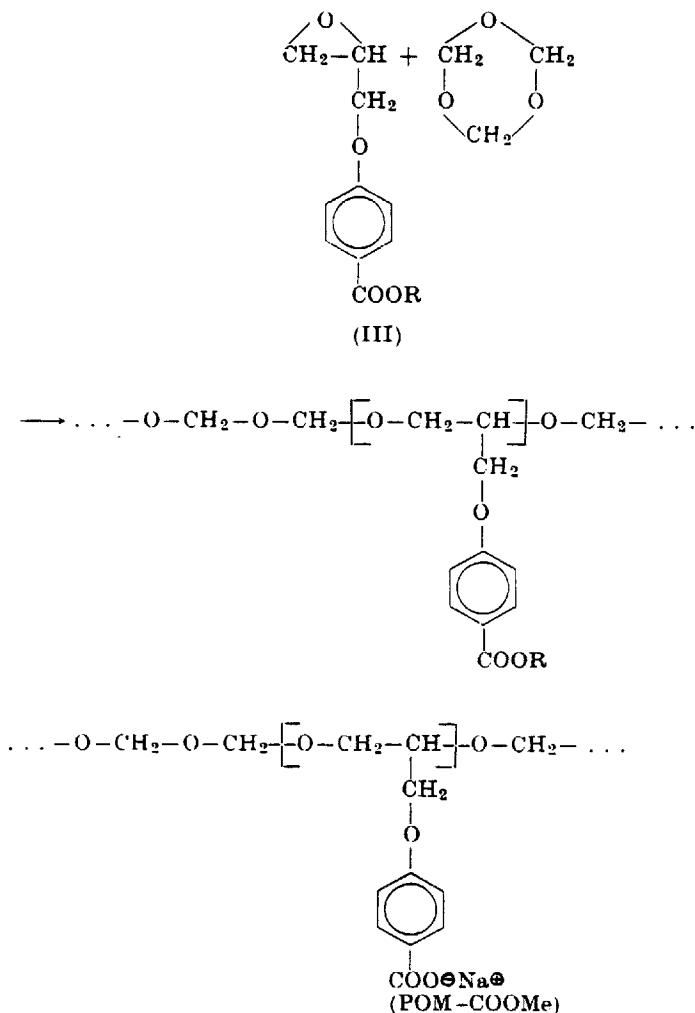


FIG. 6. Reactions of polyacetals containing free ester groups.

easily converted into various polymeric reaction products. Some examples are shown in the reaction scheme of Fig. 4.

#### Reactions of Polyoxymethylenes with Free Amino Groups

Polyoxymethylenes with free amino groups ( $\text{POM}-\text{NH}_2$ ) are obtained by copolymerizing trioxane with p-glycidoxynitrobenzene and then subsequently reducing the nitro groups containing copolymer with, for example, hydrazine hydrate in the presence of traces of Raney nickel. These copolymers are susceptible to all reactions of aromatic amines, e.g., to diazotization and coupling or to the reaction with isocyanates as shown in Fig. 5.

The diazotization and coupling with phenols or aromatic amines opens a route to polymeric dyestuffs. Graft copolymers or cross-linked polyoxymethylenes can be obtained by choosing proper isocyanates and reaction conditions.

#### Reactions of Polyoxymethylenes with Free Ester Groups

Polyoxymethylenes with ester groups are obtained by copolymerizing trioxane with p-glycidoxybenzoic acid esters. Alkali hydrolysis leads to polyoxymethylenes with free carboxyl groups (Fig. 6).

The introduction of even small amounts of carboxyl groups (0.01 mole %) increases the melt viscosity considerably [11]. At higher concentrations the crystallinity of polyoxymethylenes is drastically reduced and the opaque material is finally transformed to a transparent one [12].

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