

Degradation and Stabilization of Polyacetal Copolymers

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Synopsis

Acetal copolymers prepared from trioxane and ethylene oxide consist of polyoxymethylene segments with oxyethylene units distributed in the chain. These oxyethylene units profoundly affect the thermal and chemical behavior of the polymer. The presence of the oxyethylene units renders the copolymer amenable to thermal or base hydrolytic treatment which results in a final product with stable endgroups. The copolymers so obtained are significantly more stable, thermally and chemically, than acetylated polyoxymethylene homopolymer.

I. INTRODUCTION

Polyoxymethylene, terminated with hemiformal endgroups, is subject to degradation by several processes; i.e., stepwise thermal depolymerization from the chain ends, oxidative attack leading to chain scission and depolymerization, acidolytic cleavage of the acetal linkages of the polymer chain, and thermal chain scission at elevated temperatures (280–350°C).¹

Acetylation²⁻⁶ and methylation^{1,2,6-8} of the hemiformal chains ends of high polymers of polyoxymethylene, as means of stabilization against thermal depolymerization ("unzipping"), have been described in the older and more recent literature.

Stabilization against oxidative attack is a problem common to many polymers, and this mode of degradation in polyoxymethylene is retarded by the addition of known antioxidants.^{9,10}

Acidolytic degradation arises from the presence of acidic species originating from one of several sources: (1) acidic catalyst residues which may have been used in preparation of the polymer, (2) formic acid formed *in situ* when the trace quantities of formaldehyde generated in processing are oxidized,¹ and (3) acetic acid generated from acetate endgroups when a given chain, so stabilized, depolymerizes as a result of occasional oxidative or acidolytic chain scission.¹¹ The use of basic nitrogen-containing additives, such as aromatic amines, hydrazides, hydrazines,¹² polyamides,¹³ ureas,¹⁴ and amidines,¹⁵ which are capable of reacting with acidic species or with formaldehyde to prevent its oxidation to formic acid, have been described in the patent literature.

The subject of interest in this paper is the significant improvement of thermal and chemical stability which derives from the distribution of limited amounts of oxyethylene units in the polyoxymethylene chain. Methods of preparation and stabilization of these copolymers have been broadly described in the patent literature.¹⁶⁻¹⁸

II. EXPERIMENTAL

The polymers used in this study comprised: (a) polyoxymethylene; (b) trioxane-ethylene oxide copolymer with unstable chain-end segments; (c) acetylated polyoxymethylene; (d) commercial acetylated polyoxymethylene; (e) trioxane-ethylene oxide copolymer with stable endgroups.

The homopolymer (a) and copolymer (b) were prepared by cationic polymerization of trioxane, or trioxane and ethylene oxide, by the procedures described below. The polymers so prepared have unstable ends subject to thermal depolymerization with evolution of formaldehyde.

The acetylated polyoxymethylene (c) was prepared by treatment of homopolymer with acetic anhydride in the presence of sodium acetate catalyst as described below.

The commercial resin (d) was a polyacetal, which analyses indicated to be acetylated polyoxymethylene stabilized with 4,4'-butylidene bis(3-methyl-6-*tert*-butyl phenol) and a polyamide.

Trioxane-ethylene oxide copolymer (e) with stable end groups was obtained hydrolytically by a procedure described below.

Degradation rates for the above polymers, in the presence of additives which inhibit or minimize oxidative and acidolytic degradation, were studied. With the exception of the commercial resin (d), all polymers contained as additives 0.1% dicyandiamide and 0.5% 2,2'-methylene bis(4-methyl-6-*tert*-butyl phenol).

Routine comparison of thermal stability of polymers over extended periods of time and monitoring of changes effected by different additives was also carried out.

Two chemical resistance tests were employed to demonstrate further the differences in behavior between homopolymer and copolymer. These tests were resistance to degradation by finely divided metals compounded with the polymer and resistance to strong alkali.

A. Preparation of Polyoxymethylene

Materials. Trioxane (Celanese Corp.) was purified by distillation (in the presence of NaOH pellets) through a $\frac{3}{4} \times 18$ in. vacuum-jacketed column packed with glass helices, necessary precautions being taken to minimize exposure to air and moisture; trioxane b.p. 114.5°C./760 mm.

Other materials, used as received, were boron trifluoride di-*n*-butyl etherate (Allied Chem.), cyclohexane "pure grade" (Phillips Petroleum Co.), and tri-*n*-butylamine (General Laboratory Supply Co.).

Reactor. The reactor (Read Manufacturing Co., York, Pa.) was a 5-liter stainless-steel (316) jacketed vessel provided with counter-rotating sigma blades for stirring the reaction mixture.

Polymerization. Polymerization of 1500 g. of trioxane dissolved in 640 g. cyclohexane at 55°C. was initiated by addition of 0.30 ml. of boron trifluoride dibutyl etherate dissolved in 20 ml. cyclohexane. The peak reaction temperature was held to 60°C. by appropriate circulation of cooling water in the reactor jacket. One hour after initiation of polymerization, the powdery reaction product was discharged into 3 liters of acetone containing 5 ml. of tri-*n*-butylamine, and the mixture stirred in a Waring Blendor. The polymer was filtered, washed free of amine with acetone, and air-dried at 60°C.; the yield was 61%. The polymer had an inherent viscosity of 1.9–2.0 when measured in 98/2 *p*-chlorophenol/ α -pinene at 60°C.

B. Preparation of Trioxane–Ethylene Oxide Copolymer

Materials. Materials used were ethylene oxide (Eastman Kodak Co.), trioxane, boron trifluoride di-*n*-butyl etherate, cyclohexane, and tri-*n*-butylamine (same sources as above).

Reactor. The reactor used was the same as that used for preparation of polyoxymethylene.

Polymerization. Liquid ethylene oxide (75 g.) was injected with a cold syringe beneath the surface of molten (65°C.) trioxane (3000 g.) contained in the reactor. Polymerization was initiated by addition of 0.44 ml. boron trifluoride di-*n*-butyl etherate dissolved in 20 ml. cyclohexane. The peak reaction temperature was held to 96°C. by circulation of cold water in the reactor jacket. Forty minutes after initiation of polymerization, the powdery reaction product was discharged into 3 liters of acetone containing 5 ml. tri-*n*-butylamine and processed as the homopolymer described above; the yield was 90%, and inherent viscosity was 1.1–1.2.

C. Acetylation of Polyoxymethylene

A 100-g. portion of polymer, 800 ml. acetic anhydride (ACS analytical reagent grade), and 0.32 g. anhydrous sodium acetate were charged to a stirred stainless-steel autoclave. The reactor was purged with dry nitrogen and the polymer dissolved and acetylated by heating to 158–160°C. for 20 min. The reactor was cooled, and the precipitated polymer washed free of acetic anhydride by repeated washing in a Waring Blendor with acetone and water. The polymer was dried at 60–65°C.; recovery was 93%; inherent viscosity was 1.7.

D. Hydrolytic Stabilization of Trioxane–Ethylene Oxide Copolymer

A stirred stainless-steel autoclave was charged with 120 g. of copolymer, 600 ml. dimethylformamide, 590 ml. water, and 20 g. concentrated ammonium hydroxide (28% NH₃). The reactor was purged with nitrogen and

heated to 158°C. for 7 min. as the polymer dissolved. The charge was cooled and the precipitated polymer washed with water and acetone in a Waring Blendor until free of NH_4OH . The filtered product was air-dried at 60–65°C; the recovery was 80–85%; inherent viscosity was 1.1.

E. Measurement of Degradation Rates

Each unit of the apparatus consisted of a cylindrical brass chamber (2 in. high, $3\frac{1}{4}$ in. in diameter) with a stainless-steel screw cap capable of giving a vacuum-tight seal on a Teflon (polytetrafluoroethylene) gasket. The cap was provided with two valved inlets through which the desired atmosphere could be circulated into the chamber. In the present studies, preheated air (by circulation through coil in heating bath) was passed over the samples at 1 liter per minute. The chambers were heated by immersion in a constant-temperature silicone-oil bath.

The polymer specimen was in the form of a 7-g. disk, $2\frac{1}{8}$ in. in diameter, compression-molded at 190°C. for $\frac{1}{2}$ –1 min. under 1700 psi pressure. Under these conditions there was no significant loss of weight in the molding operation, and the specimens had the same geometry and surface. Weighed specimens, contained in aluminum dishes, were placed in the chambers and subjected to the desired temperature. Samples were successively removed at increasing time intervals, and weighed to determine amount of polymer volatilized. The results were plotted as per cent weight loss as a function of time or as log per cent of polymer remaining as a function of time. In each case, the best line drawn through the experimental points did not necessarily pass through the origin because of the time required for the polymer to reach the elevated temperature where decomposition occurs.

F. Routine Thermal Stability Test

The apparatus consisted of a forced draft oven containing a cylindrical aluminum block, 4 in. high and 14 in. in diameter, as a heat sink. The block was provided with six recesses, $\frac{1}{2}$ in. deep and $2\frac{1}{4}$ in. in diameter, to accommodate aluminum dishes containing polymer samples. . . A thermocouple inserted in the block was connected to a recorder-controller system capable of maintaining the block temperature to within $\pm 0.25^\circ\text{C}$. over the range 200–270°C.

A guided lid, providing 1 in. of space above the samples when resting on the block, was lifted by a pulley and cable arrangement as the oven door was opened and lowered as the door was closed. A $\frac{1}{8}$ in. hole drilled into the top surface of the block and out the side, provided a vent for degradation products to displace the air and escape. Thus, there was limited access of air above the sample; in this respect, the environment to which the polymer was subjected tends toward that prevailing in the barrel of a polymer-processing machine, such as an extruder or injection molding apparatus. In the polymer degradation test the samples were exposed to a constant sweep of air.

A polymer specimen (5 g.) was accurately weighed (to 0.2 mg.) in a disposable aluminum dish, and placed in the block recess. After 45 min., the sample was removed, cooled in a desiccator to room temperature, and weighed. The per cent weight loss, divided by 45 min., gave a K_{D230} value which is the average per cent weight loss per minute at 230°C. The coefficient of variation for values determined by this method was 4-7%.

This apparatus was also used to obtain comparative data between samples subjected to thermal exposure over extended periods of time by simply plotting weight loss suffered versus time at the given temperature.

G. Resistance to Degradation by Metals

Polymer was milled with 10% of the metal powder in the heated chamber of a Plastograph at 200°C. for 5-7 min. The sample was removed, cooled to room temperature, and subjected to the thermal stability test (K_{D230}) as described above. The Plastograph consists of a stainless steel chamber, jacketed for circulation of heating fluid; molten polymer is milled within the chamber by two counter-rotating sigma blades. The instrument is manufactured by C. W. Brabender Instruments, Inc. (South Hackensack, N. J.).

H. Resistance to Alkali

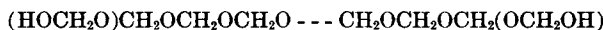
The polymer specimen (5-10 g.), in the form of a compression-molded disk, was immersed in a stirred 50% caustic solution under reflux at 140-145°C. After 1 hr. at this temperature, the specimen was removed, rinsed with water, and air-dried to constant weight at 60-65°C. The weight loss is a measure of susceptibility to alkaline degradation.

III. RESULTS AND DISCUSSION

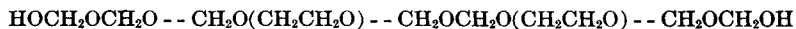
A. Effect of Comonomer on Degradation Rates

To demonstrate the effect of copolymerization with ethylene oxide on thermal degradation behavior, the five polymers referred to in the experimental section were examined. Their structures may be depicted as follows:

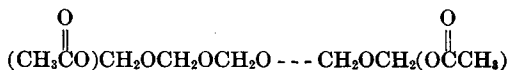
(a) Homopolymer with unstable hemiformal endgroups:



(b) Copolymer with unstable terminal oxymethylene ($-\text{CH}^2\text{O}-$)_z chains segments having hemiformal endgroups:



(c) and (d) Homopolymers with endgroups acetylated:



(e) Copolymer with stable endgroups obtained by the hydrolytic procedure:



There is some evidence that the endgroups of the trioxane-ethylene oxide copolymer (e), which has been stabilized by base hydrolysis, are hydroxyethoxy groups; i.e., $\text{R} = \text{HOCH}_2\text{CH}_2\text{O}-$. This is largely based on the fact that hemiacetals are subject to base hydrolysis, whereas hydroxyethoxy groups are not. Base hydrolysis of copolymer with unstable terminal oxymethylene chain segments having hemiformal endgroups (as prepared in section IIB) would be expected to depolymerize hydrolytically from the chain ends down to an oxyethylene unit, thereby terminating the chain with a hydroxyethoxy endgroup. Infrared absorption spectra for the homopolymer (a) and the hydrolytically treated copolymer (e) show absorptions for terminal hydroxyls at 2.91 and 2.85 μ , respectively.

The distribution of ethylene oxide in a copolymer and the analytical procedures employed to determine structure will be the subjects of a future publication. It will suffice to say here that the distribution of ethylene oxide in the polyoxymethylene chain is in the form of mono-, di-, and trimeric oxyethylene units. At the level of 0.5% ethylene oxide, the ratio of mono- to di- to trimeric units is about 92:7:1, at the 2% level the ratio is 77:19:4, while at the 6% level of ethylene oxide the ratio is about 57:29:14. These units appear to be randomly distributed in the polymer chain.

Each of the polymers (a, b, c, e), dry-blended with dicyandiamide and 2,2'-methylene bis(4-methyl-6-*tert*-butyl phenol), was compression-molded and its degradation rate determined at 230°C. according to the procedure given in the Experimental Section. The commercial resin (d), which already contained 4,4'-butylidene bis(3-methyl-6-*tert*-butyl phenol) and polyamide, was used without further addition of stabilizers. The antioxidant and nitrogen-containing compound were added to inhibit the oxidative and acidolytic attack to which all of the above polymers are subject. Then the differences in behavior observed between homopolymers and copolymers essentially derive from the presence of oxyethylene units in the copolymer structures.

The data obtained were plotted in two ways; i.e., per cent weight loss as a function of time (Fig. 1), and log per cent of polymer remaining as a function of time (Fig. 2). Figure 1 shows that the homopolymer with its unstable hemiformal ends rapidly depolymerizes with the greatest weight loss. The copolymer having unstable oxymethylene $(-\text{OCH}_2)_x$ terminal chain segments initially decomposes very rapidly, but after about 10% weight loss the degradation rate is greatly reduced. This is clearly demonstrated when the data are plotted in Figure 2 according to first-order kinetics. The homopolymer yields a degradation rate constant of $3.0 \times 10^{-2} \text{ min.}^{-1}$ (60–70% polymer depolymerized). The copolymer with its unstable oxymethylene terminal chain-segments decomposes at a high initial rate ($k = 1.2 \times 10^{-2} \text{ min.}^{-1}$), but then shows a sharp reduction to a specific rate constant of $4.3 \times 10^{-4} \text{ min.}^{-1}$. What is visualized, in the case of the copolymer, is a

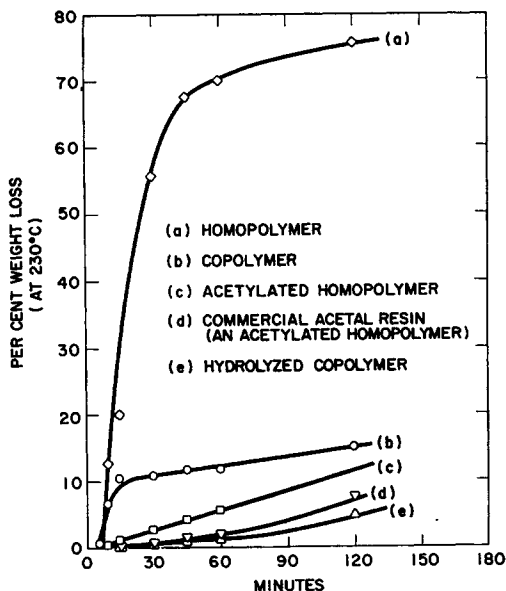


Fig. 1. Polymer weight loss at 230°C. as a function of time.

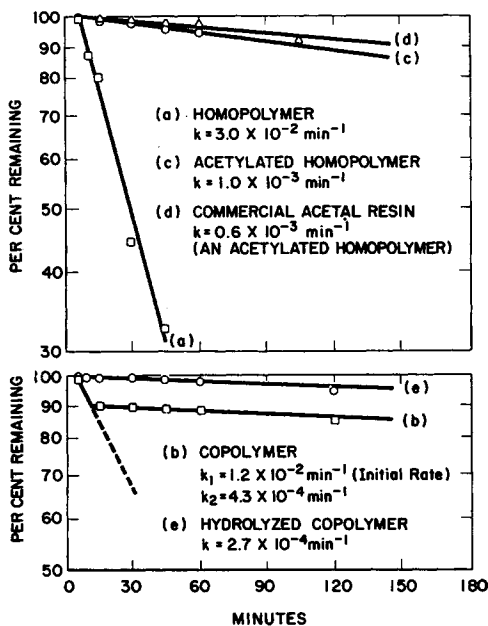


Fig. 2. Logarithmic plot of per cent polymer remaining at 230°C. as a function of time.

stepwise depolymerization originating from hemiformal endgroups, with formaldehyde being evolved until the depolymerization is interrupted by an oxyethylene ($-\text{OCH}_2\text{CH}_2-$) comonomer unit, the interruption corresponding to the reduction in degradation rate after 10% weight loss.

The acetylated homopolymers (*c* and *d*) and the copolymer which had been hydrolytically stabilized (*e*) exhibit low degradation rates without high initial depolymerization rates (Figs. 1 and 2). The specific rate constants for the acetylated homopolymers, however, are somewhat higher than that for the hydrolytically stabilized copolymer; i.e., $0.6\text{--}1.0 \times 10^{-3} \text{ min.}^{-1}$ compared to $2.7 \times 10^{-4} \text{ min.}^{-1}$. This may be related to the probability that an occasional chain scission caused by oxidative or acidolytic attacks on a given copolymer chain does not result in complete depolymerization of the chain, while a like scission occurring in the homopolymer would probably be followed by depolymerization of the entire oxymethylene chain with consequent greater weight loss. A further consequence of the decomposition of acetylated homopolymer, as suggested by Kern,¹¹ is the generation of acidic species from the acetate endgroups which may cause acidolytic chain scission. The differences in behavior between acetylated homopolymer and stabilized copolymer are further demonstrated in the sections which follow.

B. Comparative Thermal Stabilities of Homopolymer and Copolymer Acetal Resins

The homopolymer used was the commercial acetal resin, which analysis indicated to be acetylated polyoxymethylene stabilized with the additives 4,4'-butylidene bis(3-methyl-6-*tert*-butyl phenol) and a polyamide.

The copolymer was one prepared from trioxane and ethylene oxide as described in the Experimental Section, and the unstable oxymethylene ($-\text{CH}_2\text{O}-$)_{*x*} chain-end segments were removed by the hydrolytic procedure.

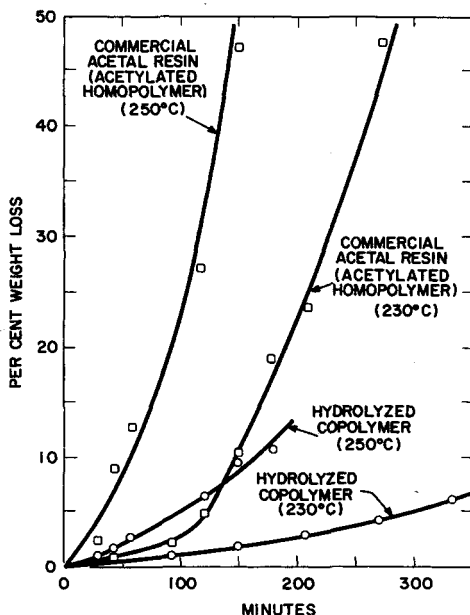


Fig. 3. Polymer weight loss at 230 and 250°C. under conditions of limited access of air.

The stabilizers, 0.1% dicyandiamide and 0.5% 2,2'-methylene bis(4-methyl-6-*tert*-butyl phenol), had been incorporated by dry-blending with the polymer and milling 5-7 min. in the Plastograph at 200°C.

The apparatus and procedures used to compare thermal stabilities for the extended periods of time were those described in the Experimental Section.

Reference to Figure 3 shows that, for the first 50-60 min. at 230°C., the weight losses for acetylated homopolymer and the copolymer do not differ greatly and essentially vary linearly with time; this linearity furnishes the basis for calculating the K_{D230} value (per cent loss per minute) referred to in Section IIF. Beyond 50-60 min. the test clearly indicates the differences in polymer stability; thus, the homopolymer curve turns sharply upward showing inferior stability when compared to the copolymer. The same behavior is shown at 250°C., and here the homopolymer curve diverges even sooner (about 25-30 min.).

C. Effect of Metals on Thermal Stability of Homopolymer and Copolymer

The copolymer and the commercial acetal resin (acetylated homopolymer) used in the comparisons were those described in the immediately preceding section. The stabilized polyacetal resins were compounded with 10% metal powder (325 mesh) as described in the Experimental Section, and the K_{D230} value as a measure of thermal stability was determined.

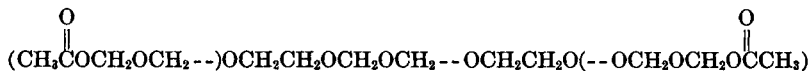
Examination of the data in Table I shows that all of the metals tested had a detrimental effect on the stability of the commercial acetal resin (acetylated homopolymer). This is believed to result from the instability of the acetate ester endgroups of the homopolymer, whereas the endgroups of the hydrolytically stabilized copolymer are insensitive. Support for this expla-

TABLE I
Effect of Metal Powders on Thermal Stability of Acetal Resins

Metal added	K_{D230} , % wt. loss/min.*	
	Commercial acetal resin (acetylated homopolymer)	Copolymer
None	0.016	0.017
Copper	0.17	0.014
Zinc	>1	0.010
Aluminum	0.026	0.012
Bronze	0.18	0.007
Lead	0.76	0.009
Antimony	0.35	0.016
Bismuth	0.086	0.009
Iron	0.43	0.008
Nickel	0.92	0.048
Stainless steel	0.35	0.024

* K_{D230} in all cases corrected for weight of metal added to resin; i.e., weight loss is based on resin weight.

nation lies in the fact that unhydrolyzed copolymer with acetylated oxymethylene chain-end segments:



when compounded with zinc powder at elevated temperatures (200–230°C.), loses only that portion of its weight represented by the terminal oxymethylene chain segments ($-\text{CH}_2\text{O}-$)_x, and is relatively stable thereafter. Since the copolymer used for the experiments summarized in Table I already had been freed of unstable chain-end segments in its preparation (hydrolytically stabilized), it was stable to further decomposition in the presence of metals.

D. Effect of Strong Alkali on Acetylated Homopolymer and Copolymer

A distinguishing feature of acetal copolymer stabilized by the hydrolytic procedure, when compared to acetylated homopolymer, is the resistance of the copolymer to degradation by strong alkali. This is simply demonstrated by exposure of the polymer sample to 50% caustic solution at 140–145°C. as described in the Experimental Section. When the stabilized copolymer and acetylated homopolymer samples cited above were so treated, the homopolymer lost 95% of its weight while the copolymer showed a weight loss of less than 0.1%. The poor stability of the acetylated homopolymer results from the hydrolysis of the acetate endgroups, followed by depolymerization. The copolymer with its stable endgroups is not subject to alkaline attack.

Contributions made to this paper by W. E. Heinz, G. J. Fisher, and co-workers are gratefully acknowledged.

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Résumé

Les copolymères d'acétals préparés à partir de trioxane et d'oxyde d'éthylène sont composés de segments de polyoxyméthylène et d'unités oxyéthyléniques distribuées dans la chaîne. Ces unités oxyéthyléniques affectent profondément le comportement thermique et chimique du copolymère. La présence d'unités oxyéthyléniques rend le copolymère sensible au traitement thermique ou au traitement hydrolytique sous l'influence de bases résultant de la formation d'un produit final avec des groupements terminaux stables. Les copolymères ainsi obtenus sont beaucoup plus stables, thermiquement et chimiquement, que le polyoxyméthylène acétylé homopolymère.

Zusammenfassung

Aus Trioxan und Äthylenoxyd dargestellte Acetalcopolymeren bestehen aus Polyoxymethylensegmenten mit über die Kette verteilten Oxyäthyleneinheiten. Diese Oxyäthyleneinheiten besitzen einen tiefgreifenden Einfluss auf das thermische und chemische Verhalten des Polymeren. Die Anwesenheit der Oxyäthyleneinheiten macht das Copolymeren einer thermischen oder basischen hydrolytischen Behandlung zugänglich, welche zu einem Endprodukt mit stabilen Endgruppen führt. Die so erhaltenen Copolymeren besitzen eine höhere thermische und chemische Stabilität als das acetylierte Polyoxymethylenhomopolymere.

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