Thermally Stable High Molecular Weight Polyoxymethylenes

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INTRODUCTION

Background

Formaldehyde has been encountered in a polymeric form by those who have studied its chemistry ever since its earliest preparation by Butlerov in 1859.[1] Typical polymers of formaldehyde, including the white solid he had observed, are low molecular weight substances which melt with rapid decomposition at about 150°C. and are readily soluble in dilute acids and bases. Being pulverulent, they possess none of the mechanical properties characteristic of load-bearing plastics of today. The structure of formaldehyde polymers remained obscure until the thorough investigations of Staudinger and his collaborators during the 1920's. At that time, it was established that the polymers are comprised of molecular chains of polyoxymethylene units.[2]

In the course of those investigations, Staudinger prepared polymers with molecular weights that exceeded the typical by a considerable degree. This he accomplished by allowing purified liquid formaldehyde, which boils at about −21°C., to polymerize in bulk at −80°C., with production of a tough, transparent or semitransparent solid reminiscent of the eucolloids of that day. Because of this resemblance he called the polymer eu-polyoxymethylene.

Polymers of lower molecular weight were obtained when he polymerized purified formaldehyde, which had been dissolved in an inert solvent, at a higher temperature. These he called "solution" polymers and noted that they were not film-forming. Thus, they differed significantly from the eu-polymers. Furthermore, it is important to note that they differ also in this respect from polymers prepared in inert media in these investigations.

Unfortunately for his purposes, eu-polyoxymethylene and the "solution" polymers were insoluble in cold solvents. Moreover, they decomposed when the solvents were heated so that he was not able to determine their true molecular weights. He did believe, however, the eu-polyoxymethylene was a very long, thread-like molecule, in keeping with the structure he had established for the lower molecular weight, typical polymers. In addition, he proposed that the molecular weights of "solution" polymers lay between that of eu-polyoxymethylene and those of the typical polymers. Investigations in these laboratories, wherein molecular weights have been measured, have confirmed that this is correct, as will be indicated later.

The fact that formaldehyde polymers are composed of threadlike molecules rather than of giant rings, an alternate possibility, requires that the ends be functional groups derived either by reaction with a foreign molecule or by rearrangement of the growing end. Since the endgroups were shown by Staudinger to be predominantly hydroxyl, formaldehyde polymers came to be called polyoxymethylene glycols. They have the general structure

$$HOCH_2O—(CH_2O)_n—CH_2OH$$

and differ from each other in their degree of polymerization.

Despite this structural similarity, it should be emphasized that the properties of eu-polyoxymethylene differ importantly from those of the typical, low molecular weight homologs as well as from the "solution" polymers. In the form of a thin film, it is tough and flexible. If drawn into filaments, it produces fibers which show considerable strength and even a limited degree of elasticity. However, like the lower molecular weight homologs, eu-polyoxymethylene is also thermally unstable. Gentle heating promotes depolymerization, and, at the melting point, thermal decomposition quickly results in complete embrittlement and, therefore, total loss of mechanical properties.

At the stage of development of polymer science in the 1920's, major attention was centered on polymer structures rather than properties. The useful properties of only one thermoplastic, cellulose nitrate, had been explored sufficiently to make it of interest beyond the laboratory. Polystyrene, acrylics, and certain other cellulosics were still the objects of early experimentation. The combinations of properties which would lead ultimately to their application on a large scale outside the laboratory still awaited discovery. Distinguished chiefly for its thermal instability in this file of laboratory curiosities was eu-polyoxymethylene. There it remained until the late 1930's.

Recent Developments

Investigations in these laboratories carried out at various times over the last 18 years have led to the discovery of ways to polymerize formaldehyde to a high molecular weight polymer having high thermal stability.[3] Furthermore, polymers of such high molecular weights and unusual thermal stabilities have been prepared that mechanical properties of bars, films, fibers, and other physical forms are fully exhibited. Qualitatively these properties are high modulus, high heat distortion temperature, excellent toughness, unusual solvent resistance, low power loss, and good retention of stiffness when wet. Quantitative information is presented in companion papers.[4,5]

POLYMERIZATION

From the work of Staudinger, of Trautz and Ufer,[6] and later of J. F. Walker[7] and of Carruthers and Norrish,[8] it is apparent that the polymerization of formaldehyde is initiated ionically. That this is true has been thoroughly confirmed by studies in these laboratories. The great facility with which formaldehyde is attacked by either nucleophilic or electrophilic agents carries over into polymerization, and one finds therefore a broad spectrum of active initiators. These are summarized in Table I. It should be noted that the list includes simple acids and bases, amines, Lewis acids, organometallic compounds, phosphines and related compounds of other elements in group VB of the periodic table, and even carbonyls such as those of iron, cobalt, and nickel.

Staudinger had noted that oxygen retards the formation of polymer in liquid formaldehyde at $-80°C$. His interpretation of this oxygen effect would seem to be in accord with the evidence for
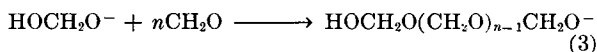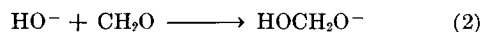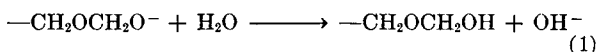
TABLE I
Polymerization Initiators

| Simple acids and bases[2] |
| Organic acids[8] |
| Lewis acids[2] |
| Amines[2,3,7] |
| Organometallic compounds[9] |
| Phosphines, arsines, stibines[10] |
| Carbonyls of iron, cobalt and nickel[11] |

ionic initiation presented above. He held that oxygen was an effective inhibitor because it occupied the active sites on the glass walls of the reaction vessel, thereby preventing the initiation of polymerization. Evidence that formaldehyde is subject to polymerization by free radical initiators is lacking.

In his mechanism for the polymerization of formaldehyde, Staudinger proposed that a chain reaction occurred whereby the growing chain rapidly added on formaldehyde units one after another. Growth of the chain stopped, he believed, when some foreign molecule interacted with the growing end, as, "otherwise, the thread molecules would grow to infinity." In these laboratories it has been confirmed that his viewpoint is essentially correct, but with one important modification: growth of the molecular chain does terminate when the growing end interacts with a foreign molecule, an impurity in the system; however the interaction of an ion with a neutral foreign molecule produces a new ion which, in turn, acts to initiate a new molecular chain. Thus, the kinetic chain is continued and one initiator molecule produces a large number of polymer molecules.[12]

Chain transfer with a water molecule during polymerization may be depicted by the reactions:

$$-CH_2OCH_2O^- + H_2O \longrightarrow -CH_2OCH_2OH + OH^- \quad (1)$$

$$HO^- + CH_2O \longrightarrow HOCH_2O^- \quad (2)$$

$$HOCH_2O^- + nCH_2O \longrightarrow HOCH_2O(CH_2O)_{n-1}CH_2O^- \quad (3)$$

In step (1), the growing chain, which has been initiated by nucleophilic attack on formaldehyde followed by addition of monomer units, reacts with water to complete the growth of the molecular chain and liberate a hydroxyl ion. Step (2) depicts initiation of a new chain, and step (3) shows addition of monomer to yield a new polymer chain. Thus, it can be seen that the molecular weight of the polymer will depend upon the number and kind of chain-transfer agents present in the polymerization system.

A typical polymerization as carried out in these laboratories would be as follows. Formaldehyde monomer suitable for polymerization is prepared from alkali-precipitated formaldehyde low polymer which has been carefully washed with distilled water and dried for several hours in a vacuum oven at about 80°C. The dried polymer is thermally decomposed by being heated to 150–160°C. Monomeric formaldehyde which evolves is passed through several, say four, traps cooled to −15°C. In this manner some prepolymerization takes place in the traps, thereby removing certain undesirable impurities from the monomer stream. The substantially anhydrous monomer so obtained is introduced into the polymerization vessel over the surface of a rapidly stirred inert liquid medium containing the initiator. The medium, for example, heptane, is thoroughly dried and is placed in a clean, dry polymerization vessel. In order to insure that the polymerization system is particularly dry, about 10% of the inert medium is topped off just prior to introducing the monomer. Initiator, which may be triphenylphosphine, is present to the extent of about 20 ppm based on the medium. Diphenylamine, which helps to stabilize the polymer after isolation, may be added at a concentration of about 100 ppm. Polymerization is continued until the medium contains about 20% solids. The flow of monomer is terminated, the polymer is isolated by filtration, washed first with fresh heptane and then with pure acetone, and dried in a vacuum oven at 80°C.

THERMAL STABILITY

Two tests that were useful in determining the thermal stability of formaldehyde polymers are shown in Table II. These are the k test, k being the approximate first-order reaction rate constant for thermal degradation measured at 222°C., and the "degree of toughness" test, a heat-aging test.
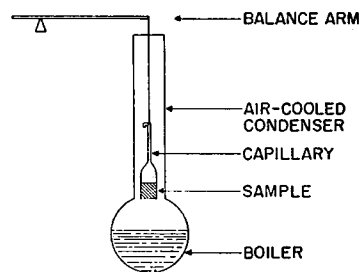

Fig. 1. Apparatus for k test.[13]

to the atmosphere through a capillary tip, the bulb being suspended from the arm of a sensitive balance into a vapor bath. Methyl salicylate is used as the refluxing liquid so that the temperature of the polymer is held close to 222°C. By following the loss in weight of the polymer sample, the rate of thermal decomposition can be determined. This is because decomposition is mainly a first-order reaction and hence a plot of the log of the weight per cent undecomposed versus time gives a straight line from which the rate constant k is determined.

In the degree of toughness test, a compression-molded film, 3–7 mils in thickness, is aged at 105°C. for 7 days. After this time, the film is creased through 180° along a line. It is then folded back along this same line through 360° to complete one cycle. The number of creasing cycles which the film can withstand before it breaks is referred to as the "degree of toughness." This is a relatively simple, but very effective test. Molecular weights of the polymers may be measured in dimethylformamide as described in a companion paper.[14]

Comparisons by the thermal stability tests show the polymers prepared in these investigations to be more stable than those obtained by procedures in the literature. Results are summarized in Table III. This difference in thermal stability has been attributed speculatively to the presence or absence of weak links in the polymer chains.[3]

TABLE II
Thermal Stability Tests[3]

1. k Test: Measure reaction rate constant for thermal decomposition at 222°C.
2. "Degree of Toughness" Test: Determine toughness of film of polymer after oven-aging at 105°C. for 7 days.

Apparatus for the k test is shown schematically in Figure 1 and is patterned after the technique used by Naylor and Anderson[13] for other polymers. In the k test, polymer is heated in a glass bulb open

TABLE III
Comparative Thermal Stabilities

Polymer	η_{inh}	k_{222} °C., %/min.	Degree of toughness
Bulk, −80°C.[a]	0.90	5.8	0
"Solution"[a]	1.2	4.9	0
Example 9, ref. 3	1.7	0.67	>100
Example 11, ref. 3	1.4	0.83	>100
Example 21, ref. 3	1.2	0.42	>100

[a] S. H. Jenkins, Jr., private communication.

A somewhat simpler, and perhaps more plausible explanation may be one based on the higher molecular weight of the recent polymers, the rapid polymerization, and the highly purified polymerization system. If it is assumed that decomposition occurs chiefly by unraveling from the chain ends, it is clear that polymers of the highest molecular weight should be the most stable. They have the lowest concentration of chain ends from which to lose formaldehyde. Therefore, both k and degree of toughness would appear to depend in part upon the molecular weight of the polymer.

The molecular weight of the polymer was stated earlier to be determined by the concentration of chain-transfer agents in the polymerization system. Thus, the absolute purity of the monomeric formaldehyde and the polymerization medium is important to molecular weight. So, also, is the mode of polymerization. It is important that the monomer be polymerized rapidly. A high concentration of formaldehyde in the polymerization system promotes side reactions which can give rise to formation of active chain-transfer agents. Thus, a highly purified sample of formaldehyde may undergo self-contamination if polymerization is not rapid and may thereby produce a lower molecular weight polymer than would normally be expected.

A second variable that may affect thermal stability is catalyzed depolymerization. Initiators that are effective in promoting polymerization can also effectively promote depolymerization. Hence residual initiator, particularly if it is one of the stronger acids or bases will hasten thermal decomposition to an appreciable degree. This means that a polymer that already is borderline in molecular weight may fail to pass one or both of the above thermal tests because of contamination by the catalyst. Therefore, it would appear that borderline molecular weight and catalyzed depolymerization afford a possible, but not necessarily complete explanation for the failure of polymers prepared in solution by procedures in the literature to exhibit good thermal stability.

The thermal instability of polymers prepared in bulk at $-80°C.$ must be explained on a different basis. Since these polymers are of relatively high molecular weight and since they are not likely to retain appreciable amounts of initiator residue, they would be expected to possess good thermal stability. Unfortunately, speculation over the reasons for their lack of thermal stability has produced no very convincing arguments up to this time. The fact remains, however, that we have never been able to make a bulk polymer which had an acceptable thermal stability. Additional study may be expected to explain this behavior.
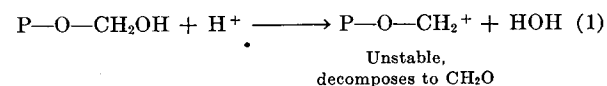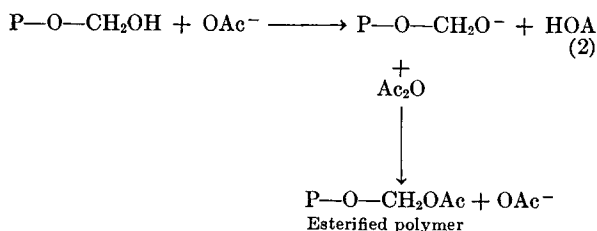
POST STABILIZATION

Despite the superior degree of thermal stability to be found in the polymers prepared in these investigations, it was evident that a further improvement could result in a fuller realization of their potential physical and chemical properties.

Staudinger had shown that the diacetates of the very low molecular weight polyoxymethylenes, containing up to 20 or so oxymethylene units, are very much more thermally stable than the corresponding polyoxymethylene glycols. However, diacetates containing about 50 or more oxymethylene units proved to be thermally unstable. Truly high molecular weight polyoxymethylene glycols, containing a 1000 or more oxymethylene units, were not converted to their corresponding high molecular weight esters. This important step has been accomplished in the course of these investigations.

Details of the esterification are to be found in the patent literature.[15] While they will not be discussed here, several points of interest will be reviewed. For example, it has been found that a variety of anhydrides—aliphatic or aromatic—may be used. Hence, esterification need not be restricted to the use of a particular anhydride. The reaction is catalyzed by amines and the soluble salts of the alkali metals. The yield from the esterification step is inversely proportional to the concentration of acid which is present as an impurity in the anhydride. For example, as the level of acetic acid in the acetic anhydride used for esterification is raised from 1% to 10%, the yield of esterified polymer falls from 98% to 84%. And, finally, the reaction temperature will depend somewhat upon the particular anhydride and catalyst used. While temperatures up to 200°C. have been found to be operable, temperatures as low as 130°C. also are useful. Also, it is not necessary for the polymer to be soluble in the esterification medium.

The esterification reaction is believed to proceed in the following manner.

$$P—O—CH_2OH + H^+ \longrightarrow P—O—CH_2^+ + HOH \quad (1)$$

<div align="center">Unstable,
decomposes to CH_2O</div>

$$P—O—CH_2OH + OAc^- \longrightarrow P—O—CH_2O^- + HOA$$
(2)

$$+$$
$$Ac_2O$$

$$\downarrow$$

$$P—O—CH_2OAc + OAc^-$$
Esterified polymer

Acetic anhydride is used here as the esterification agent and sodium acetate as the catalyst, acetate anion being the true catalyst. It is suggested in reaction (1) that loss of polymer is caused by attack of H^+ at the hydroxyl end. Concentration of H^+ is dependent upon the level of acetic acid in the
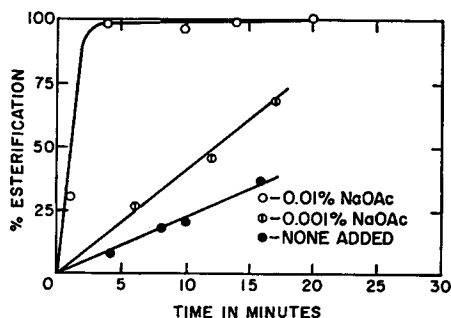

Fig. 2. Esterification vs. catalyst concentration.

system. The resulting cation is unstable and rapidly decomposes by an unzipping reaction to liberate formaldehyde. On the other hand, attack by the acetate anion on the chain end produces a new anion, which then attacks the anhydride, resulting in esterification and regeneration of the acid anion. It is quite possible that these reactions are concerted.

In Figure 2 the effect of a base catalyst upon the rate of esterification is shown. Sodium acetate is used as the catalyst in acetic anhydride. The reaction temperature is 139°C., the boiling point of acetic anhydride. It will be noted that the reaction is essentially complete in 5 minutes with a catalyst concentration of only 0.01% sodium acetate based upon anhydride. The rate falls sharply with a tenfold decrease in catalyst concentration and is very appreciably lower with no added catalyst.

Physical and chemical properties of esterified polyoxymethylene are described in companion papers.[4,5] Molecular structure and fine structure are treated in other companion papers.[14,16] We propose that the generic term "acetal resin" be used to describe high polymers that are composed of repeating oxymethylene units.

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Synopsis

In this, the first of a series of five papers, the historical development of formaldehyde polymers, beginning with the work of Butlerov and continuing through the investigations of Staudinger and his collaborators, is reviewed. Recent studies in these laboratories have led to thermally stable high polymers of formaldehyde. Initiators and the role of impurities in the polymerization are described. An explanation is offered to account for differences in thermal stabilities between old and new polymers. Esterification, by which further increases in thermal stability are achieved, is described. It is proposed that the generic term "acetal resin" be used to describe high polymers that are composed of repeating oxymethylene units.

Résumé

Dans la première d'une série de cinq publications on donne une revue du développement historique des polymères du formaldéhyde. Cette revue débute par les travaux de Butlerov et se poursuit par les recherches de Staudinger et ses collaborateurs. Des travaux récents dans ces laboratoires ont conduit à des hauts polymères du formaldéhyde thermiquement stables. Les initiateurs et le rôle des impuretés dans la polymérisation ont été decrits. On propose une explication qui rend compte des différences de stabilité thermique entre les anciens et les nouveaux polymères. On décrit l'estérification qui est à l'origine d'une accroissement

supplémentaire de la stabilité thermique. Le terme générique "résine acétal" est proposé pour les hauts polymères composés d'unités oxyméthyléniques successives.

Zusammenfassung

In der vorliegenden Arbeit, der ersten aus einer Reihe von fünf Mitteilungen, wird ein Uberblick über die historische Entwicklung auf dem Gebiet der Formaldehydpolymeren, beginnend mit den Arbeiten von Butlerow und fortgesetzt durch die Untersuchungen von Staudinger und seinen Mitarbeitern, gegeben. Neue Versuche in unseren Laboratorien haben zu thermisch stabilen, hochmolekularen Formaldehydpolymeren geführt. Sowohl Starter, als auch die Rolle von Verunreinigungen bei der Polymerisation werden beschrieben. Eine Erklärung für die Unterschiede in der thermischen Stabilität zwischen den alten und den neuen Polymeren wird gegeben. Es wird eine Veresterung beschrieben, durch welche eine weitere Zunahme der thermischen Stabilität erreicht wird. Die Gattungsbezeichnung "Acetalharz" wird für Hochpolymere, die aus sich wiederholenden Oxymethyleneinheiten aufgebaut sind, vorgeschlagen.