

Investigation of Thermal Oxidation and Photooxidation of Acetal Plastics by Infrared Spectroscopy

P. G. KELLEHER and L. B. JASSIE, *Bell Telephone Laboratories,
Incorporated, Murray Hill, New Jersey*

Synopsis

Infrared spectroscopy was used to study the thermal oxidation, accelerated and natural photooxidation of acetal homopolymer and copolymer. Chain scission is the predominant reaction, as revealed by changes observed in the hydroxyl, carbonyl, and methylene absorption regions of the infrared spectra. Photolysis accelerates the degradation of both plastics. Reaction mechanisms are presented to explain the behavior of these materials under oxidative conditions.

INTRODUCTION

The thermal oxidation of unmodified polyoxymethylene homopolymer and polyoxymethylene with esterified end groups has been investigated by Kern and Cherdron.¹ Alishoev and others² have studied the thermal oxidation of esterified polyoxymethylene and its inhibition by added stabilizers. Copolymers of trioxane with oxacyclic compounds which form carbon to carbon bonds in the chain have been found to be thermally stable.³ However, no work on the photooxidation of these materials has been reported to date. The purpose of this study is to determine the mechanism of photolysis of acetal plastics by using infrared spectroscopy and to show the relationship of this mechanism to that of thermal oxidation.

EXPERIMENTAL

Spectra were obtained in the range of 2.5–15 μ by means of a Perkin-Elmer model 21 spectrometer on 1.5 mil films of commercial homopolymer and copolymer compression-molded for 30 sec. at 182–188°C. and 1000 psi. The films were exposed to 60°C., 125°C,* ultraviolet light from an S-1 sunlamp (ASTM D620), and outdoors at a 45° angle facing south from December 9, 1963 to July 2, 1964.

* These samples were extracted 16 hr. in boiling toluene.

RESULTS AND DISCUSSION

Homopolymer

Samples of homopolymer exposed at 60°C. for 1000 hr. showed no measurable change in the infrared spectrum. At 125°C., however, a significant change was observed in the carbonyl region as a result of ther-

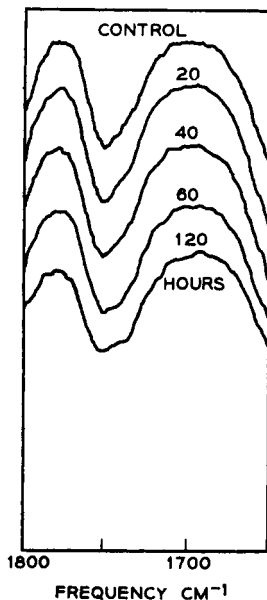


Fig. 1. Development of carbonyl absorption in extracted polyoxymethylene homopolymer exposed at 125°C.

mal oxidation. The homopolymer has an inherent carbonyl at 1750 cm.^{-1} due to the ester endgroups.⁴ As thermal oxidation proceeds, an aldehyde carbonyl band⁵ develops at 1733–1735 cm.^{-1} similar to that found by Igarashi⁶ (Fig. 1), while the ester endgroup carbonyl absorption remains essentially constant. We find that the deterioration caused by accelerated photolysis with an S-1 lamp is essentially the same as that caused by thermal oxidation, except that photolysis accelerates the reaction. Since the S-1 environment involves a temperature of 60°C., a comparison may be made of the 60°C. thermal oxidation data with the S-1 photooxidation results. The absence of carbonyl development in the former contrasts markedly with the increased carbonyl observed at 1733–1737 cm.^{-1} (Fig. 2) and shows the accelerating effect of ultraviolet light. This behavior is also shown by weight loss data (Fig. 3). Mass spectrometric analysis (Table I) provides additional verification.

The infrared spectra of samples exposed outdoors over a 5-month period show the same changes as those observed in the accelerated test with the

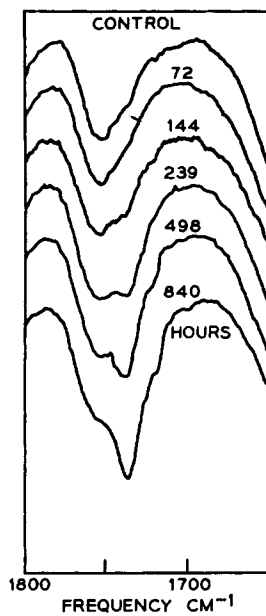


Fig. 2. Development of carbonyl absorption in polyoxymethylene homopolymer exposed to S-1 lamp.

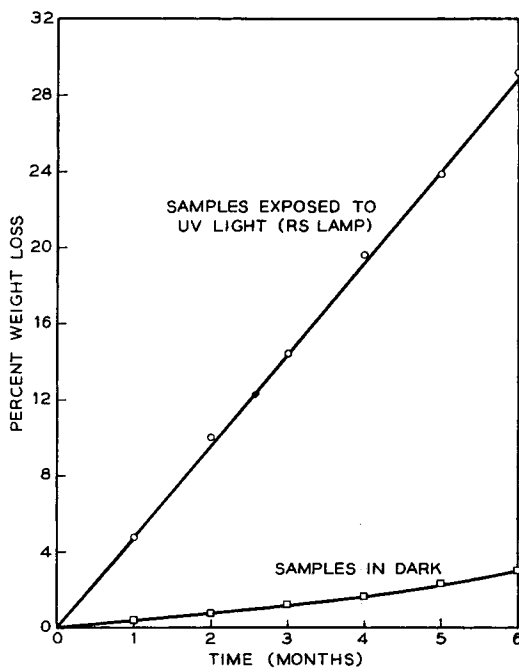


Fig. 3. Weight loss of polyoxymethylene homopolymer at 82°C.

TABLE I
Analysis of the Atmosphere above Polyoxymethylene Homopolymer Sealed in Air^a

Conditions		
Temperature, °C.	82	82
Atmosphere	Air	Air
Time	1 week	1 week
Environment	Dark	UV Light ^b
Constituents		
Nitrogen, %	78	42
Oxygen, %	20	<0.02
Argon, %	0.9	0.5
Hydrogen, %	0.01	25
Carbon monoxide, %	<0.8	28
Carbon dioxide, %	0.5	2.7
Methyl formate, %	0.01	1.6
Higher formates, %	0.01	0.05

^a Mass spectrometric analysis by Gollob Analytical Service, Inc.

^b Type RS sunlamp.

use of the S-1 lamp (Fig. 4). No changes were observed in the hydroxyl region under these thermal and photooxidative conditions.

The results of thermal oxidation at 125°C. in air correlate well with the mechanism of Kern and Cherdron¹ that in oxygen, degradation of esterified polyoxymethylene starts at some point along the chain and not at the chain end. That the chain ends are not involved in the degradation is supported by the observation that no change occurs in the intensity of the carbonyl

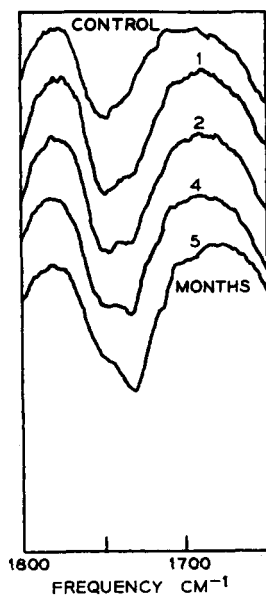
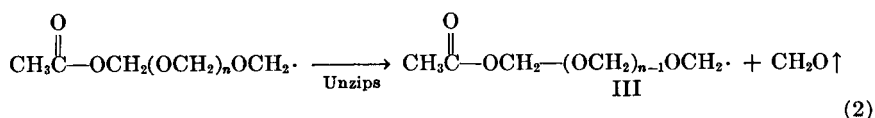
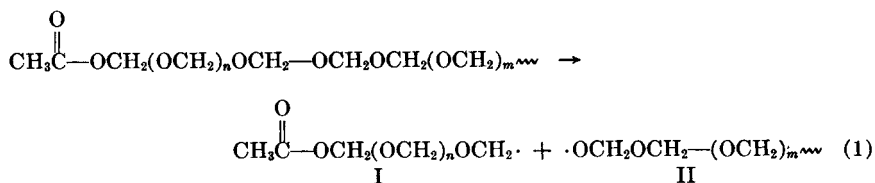


Fig. 4. Development of carbonyl absorption in polyoxymethylene homopolymer exposed outdoors.

bands at 1750 cm^{-1} due to ester endgroups. Once initiated, degradation proceeds by splitting off of monomeric formaldehyde until the degradation of the chain is complete.¹



Carbonyl formation is a likely fate of the products of main-chain scission. The fact that we observe substantial increases in $\text{C}=\text{O}$ absorption lends additional evidence for the formation of fairly long chain relatively stable (hence detectable by infrared spectroscopy) intermediates⁶ in the manner shown in eq. (3):

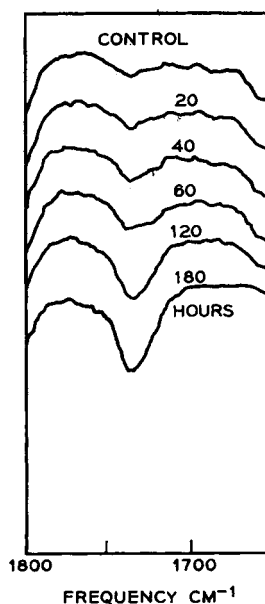
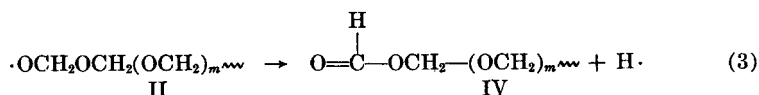


Fig. 5. Development of carbonyl absorption in extracted polyoxymethylene copolymer exposed at 125°C .

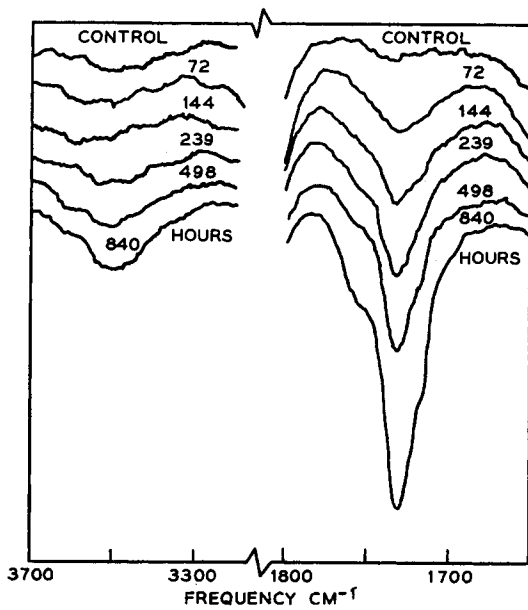


Fig. 6. Changes in the infrared absorption spectrum of polyoxymethylene copolymer exposed to S-1 lamp.

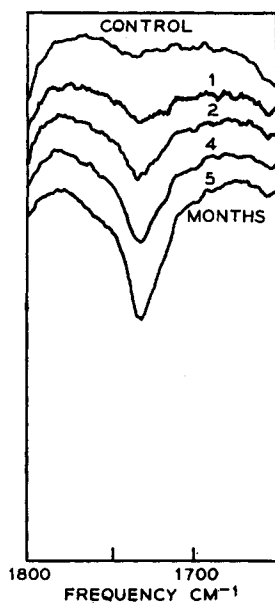
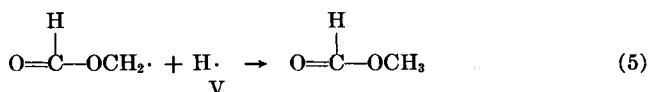
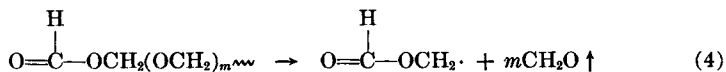


Fig. 7. Development of carbonyl absorption in polyoxymethylene copolymer exposed outdoors.

As the number of chain fragments increases, they too will be subject to attack, with scission possibly occurring along the chain with subsequent unzipping to produce formaldehyde. The continuing degradation of IV can lead to the formation of endproducts such as the methyl formate found by mass spectrometric analysis in the way shown in eqs. (4) and (5):

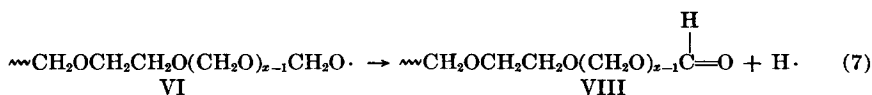
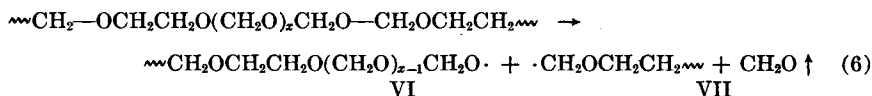


The oxidation of these materials most likely proceeds through a peroxide-hydroperoxide free-radical mechanism. These steps have been omitted, however, since such intermediates have never been observed experimentally.

Copolymer

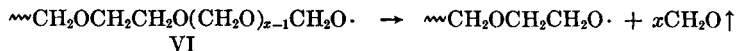
Thermal oxidation of the copolymer at 125°C. produces an aldehyde absorption at 1733–1735 cm.⁻¹ similar to that observed in the homopolymer (Fig. 5). However, there is a difference in the OH region. In these films, the small OH absorption present initially disappears when heated at 125°C. and never reappears. Apparently oxidation causes a slight amount of degradation proceeding from the unesterified chain end.

Under the S-1 lamp conditions, the same carbonyl absorption as in the homopolymer occurs in the 1733–1737 cm.⁻¹ region. The major difference is in the progressive development of the OH absorption band near 3500 cm.⁻¹ (Fig. 6). The results of outdoor exposure are the same as those for the S-1 lamp environment (Fig. 7). The outdoor sample showed no OH absorption because the specimen was physically damaged by weathering before any change was apparent. The presence of a similar carbonyl band in the 1733–1737 cm.⁻¹ region in the spectrum of the copolymer under thermal, photooxidative, and natural oxidative conditions suggests that main chain scission occurs in much the same fashion as in the homopolymer to produce similar products [eqs. (6) and (7)].

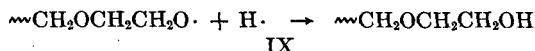


Intermediate VIII would be similar to the stable long-chain intermediates of the homopolymer, and the same type of unzipping reaction would occur, with splitting off of monomeric formaldehyde.

That the oxidation mechanism of the copolymer differs from that of the homopolymer is revealed by changes in the OH region. In order for the increased OH to be observed in the infrared spectrum it must be present on the ends of fairly long chain fragments, as the volatile low molecular weight homologs would not be seen. One possible route to formation of the OH groups in the copolymer is the degradation of the intermediate VI, as shown in eq. (8).



Recombination with a hydrogen radical produces IX,



at which point the reaction terminates.³ It would seem, therefore, that the quantity of additional OH endgroups formed is directly related to the concentration of ethylene oxide (or other comonomer) units in the chain. In this particular instance the net change is rather small, suggesting that very few comonomer units are present.

That main-chain scission is the mechanism of oxidation in the copolymer is not proved conclusively by the changes observed in the carbonyl and hydroxyl regions of the infrared spectra. The copolymer has unprotected OH endgroups where unzipping could begin and apparently a slight amount of oxidation does occur in this way. However, there are additional changes in the 1275–1300 cm^{-1} region which can be interpreted as evidence of chain scission and lend support to the proposed mechanism. In the spectra of both materials, there are two bands in this region, one at 1295 cm^{-1} , the other at 1283 cm^{-1} . The former has been ascribed to $-\text{CH}_2-$ twisting and the latter to a $\text{C}-\text{O}-\text{C}$ overtone vibration.⁷ In the copolymer, the two bands are of nearly equal intensity, whereas the 1295 cm^{-1} band in the homopolymer is more pronounced. During thermal and photooxidation, the methylene absorption increases in intensity with respect to the 1283 cm^{-1} band, which remains relatively unchanged, as illustrate in Figure 8.

The reason for the increased absorption as degradation advances is that the methylene group giving rise to the vibration occurs nearer a chain end, where its intensity may be enhanced. This behavior is attributed to main chain scission where each break in the chain produces two more methylene groups closer to a chain end. Unzipping of the chain could not account for an increase in $-\text{CH}_2-$ group absorption.

In the carbonyl region we find that the thermal and photooxidation damage produced artificially in the laboratory is the same as that occurring in natural sunlight. A similar change, along with the definite appearance of hydroxyl groups, was observed by Pascale and Salovey⁸ when they subjected the same materials to γ -irradiation. Apparently the oxidative changes, indicated by the formation of $\text{C}=\text{O}$, are not dependent on the source of irradiation, since these acetal plastics, when exposed to heat

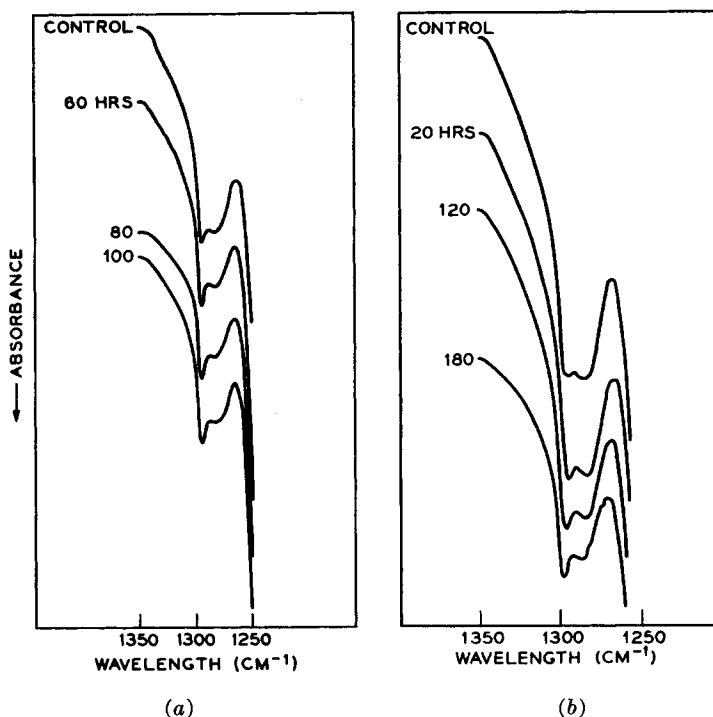


Fig. 8. Changes in the 1295 cm.^{-1} $\text{—CH}_2\text{—}$ absorption in polyoxymethylene at 125°C : (a) homopolymer; (b) copolymer.

(125°C), artificial ultraviolet light, natural sunlight, or γ -irradiation, all show an aldehyde carbonyl absorption at $1733\text{--}1737\text{ cm.}^{-1}$

CONCLUSIONS

Irrespective of the type of oxidative conditions, commercial polyoxymethylene homopolymer and copolymer exhibit the same distinct change in the carbonyl region of their infrared spectra. While photolysis accelerates the oxidation reaction in both materials, an increase in the OH absorption region is noted only in the copolymer under accelerated photooxidative conditions. The infrared spectroscopic changes produced by both thermal and photooxidation are consistent with the theory that oxidative degradation of these materials starts along the chain without significant involvement of the chain ends. This infrared evidence indicates that on oxidation, chain scission is the predominant reaction. In the polyoxymethylene homopolymer unzipping occurs, whereas in the copolymer the reaction terminates at the comonomer unit.

The authors are grateful to D. L. Wood for many helpful discussions.

References

1. Kern, W., and H. Cherdron, *Makromol. Chem.*, **40**, 101 (1960).
2. Alishoev, V. R., M. B. Neiman, B. M. Kovarskaia, and V. V. Gurlianova, *Vysokomolekul. Soedin.*, **5**, 644 (1963).
3. Kern, W., H. Cherdron, and V. Jaacks, *Angew. Chem.*, **73**, 177 (1961).
4. Koch, T. A., and P. E. Lindvig, *J. Appl. Polymer Sci.*, **1**, 164 (1959).
5. Bellamy, L. J., *Infra-Red Spectra of Complex Molecules*, Wiley, New York, 1958, p. 133.
6. Igarashi, S., I. Mita, and H. Kambe, *Bull. Chem. Soc. Japan*, **37**, 1160 (1964).
7. Novak, A., and E. Whalley, *Trans. Faraday Soc.*, **55**, 1484 (1959).
8. Pascale, J. V., and R. Salovey, private communication.

Résumé

On a utilisé la spectroscopie infrarouge pour étudier l'oxydation thermique, la photooxydation accélérée et naturelle de l'acétal homopolymère et copolymère. La scission de chaîne est la réaction prédominante, cela se révèle par les changements observés dans les régions d'absorption de l'hydroxyle, du carbonyle et du méthylène dans le spectre infrarouge. La photolyse accélère la dégradation des deux plastiques. On présente des mécanismes de réactions pour expliquer le comportement de ces produits dans des conditions oxydantes.

Zusammenfassung

Eine infrarotspektroskopische Untersuchung der thermischen Oxydation sowie der beschleunigten und natürlichen Photooxydation von Acetalhomo- und-Copolymeren wurde durchgeführt. Wie die beobachteten Änderungen im Hydroxyl, Carbonyl- und Methylenabsorptionsbereich des Infrarotspektrums zeigen, ist die Kettenspaltung die vorherrschende Reaktion. Die Photolyse beschleunigt den Abbau beider Polymerer. Reaktionsmechanismen zur Erklärung des Verhaltens dieser Stoffe unter oxydativen Bedingungen werden angegeben.

Received February 23, 1965