

¹H-NMR Investigation of the Thermooxidation Degradation of Poly(oxymethylene) Copolymers

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ABSTRACT: The thermooxidative degradation of poly(oxymethylene) copolymer (CPOM-Y) powder was studied in air in 150°C. The effect of the sequence distribution of degraded poly(oxymethylene) (POM) samples on the thermal decomposition behavior was investigated with ¹H-NMR and gas chromatography/mass spectrometry. The results showed that the degradation process of CPOM-Y could be divided into three stages with a gradually increasing degradation rate. The change in the sequence molar fractions agreed with the fact that the ethylene oxide (EO) units had higher thermal stability, and the degradation of POM

was due to the decomposition of formal units. At the beginning, CPOM-Y tended to split off formaldehyde, starting at the chain ends, some of which were not ended by EO units. In stage 2, the thermooxidation of POM occurred in the amorphous phase. In stage 3, no obvious rules for the changes in the sequence contents were obtained from NMR results, and this indicated further random chain scission and unzipping occurring heavily in the crystalline bulk. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 577–583, 2004

Key words: NMR; polyethers; thermal properties

INTRODUCTION

Poly(oxymethylene) (POM) copolymer resins are strong, hard, highly crystalline thermoplastics. They are true engineering plastics with a unique balance of mechanical, thermal, chemical, and electrical properties. They behave in a predictable, reproducible manner under loads and in known environments and have for many years turned in high levels of performance in demanding long-term applications. Their use is growing steadily in the automobile and electronics industries.

Commercial POM copolymers are typically produced through the cationic copolymerization of trioxane and 0.1–15 mol % of a cyclic ether, such as ethylene oxide (EO), dioxolane, or 1,3,5-trioxepane.^{1,2} Acetal copolymers consist of POM segments with oxyethylene units distributed in the chain. These oxyethylene units profoundly affect the thermal and chemical behavior of the copolymer. The presence of the oxyethylene units renders the copolymer amenable to thermal or base hydrolytic treatment, which results in a final product with stable end groups. The properties of POM copolymers depend on the

comonomer composition and also on the sequence distribution of the constituent comonomers, which can range from alternating to random to blocky. Various investigators have presented two methods for determining the comonomer content: gas chromatography^{3,4} and NMR spectroscopy.^{5–7} Concerning the comonomer content, both methods are satisfactory, except when very exact values are required. However, the sequence length is obtainable only by NMR. The aforementioned publications are concentrated on the process and mechanism of POM copolymerization with stabilized and unstabilized end groups and are based on NMR spectroscopy studies.^{8–10}

Many scientists have concentrated on the thermal degradation and oxidation of POM. Grassie and Rocher¹¹ investigated the mechanism of POM degradation with IR spectroscopy, oxygen-uptake and weight-loss measurements, viscosity measurements in solution, and molecular weight determination; these were analyzed over the course of thermooxidative degradation. A detailed study of the behavior of this material at elevated temperatures was performed by Amano et al.,¹² who studied samples heated in paraffin-oil Woods metal. Amano et al. reported that the twin orientation was removed via heating at 185°C. Evidence of prior melting of the twin material was provided by small-angle X-ray and electron microscopy observations of the presence of lamellae after heating. Colson and coworkers^{13,14} observed the behavior of individual fibers of POM upon heating, using an electron microscope, and they found that twin

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crystals melted at a lower temperature than crystals that were entirely of the main orientation. Mucha^{15,16} reported the thermogravimetric decomposition of the POM homopolymer in the molten state in nitrogen and in an air atmosphere for comparison. The presence of small amounts of oxygen led to oxidative chain scission and mainly to the formation of formic acid, which escaped; this led to the observed weight losses of the samples. He presented the results of thermogravimetric kinetic studies of POM thermooxidation in the solid state, and he discussed the effects of the degree of crystallinity and morphological structure of the polymer on the rate of weight loss. The thermal degradation behavior of γ -irradiated POM was investigated by Hasegawa et al.¹⁷ They also described the effect of radiation on the thermal stability of POM in films. However, until now, there have been few reports on the effect of the sequence distribution on the thermal degradation behavior of POM copolymers, especially in the solid state or crystallizing state. The degradation behavior of POM in its end use should be considered.

In this article, we present the results of thermogravimetric, gas chromatography/mass spectrometry (GC-MS), and ¹H-NMR studies of POM copolymer thermooxidation in the solid state in an air atmosphere, and we discuss the effects of the sequence distribution and contents of oxymethylene and oxyethylene units of the POM copolymer on the thermal stability and thermal degradation mechanism.

EXPERIMENTAL

Materials

The POM copolymer (CPOM-Y), prepared with 1,3-dioxolane and 1,3,5-trioxane, was supplied by Yunnan Yuntianhua Co. (Shuifu, China) with a melt index of 9.4 g/10 min. The weight-average molecular weight was 101,840.

Thermooxidation degradation of CPOM-Y

The studies of thermooxidative degradation in air were conducted on CPOM-Y powder without thermal stability agents. CPOM-Y powder was heated in an oven at 150°C; some was taken out for weighing and analysis at different times. In the following discussion, these degraded samples are called CPOM-Y1, CPOM-Y2, CPOM-Y3, and so forth, the labels indicating that they were degraded for 60 min, 480 min, 600 min, and so forth.

NMR and gas chromatography

¹H-NMR spectra of 4% solutions of CPOM-Y and degraded samples in *p*-chlorophenol were recorded at

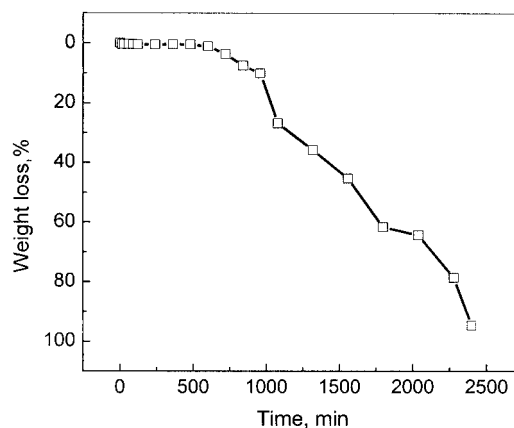


Figure 1 Weight loss of CPOM-Y versus time at 150°C.

85°C with an Inova 400 spectrometer (America Varian Co., California) working at 400 MHz; 128 scans were accumulated at a repetition rate of 10 s to produce the spectra. Tetramethylsilane was used as the internal standard.

Gas chromatograms and mass spectra were recorded on an HP 5890A gas chromatograph and a 5972 MS instrument (Hewlett-Packard Co., Palo Alto, CA) at a column [HP-5MS; low bleed (5%)–diphenyl (95%)–dimethylsiloxane] temperature of 80°C with helium as the carrier gas. The analyzed samples were pyrolyzed with an SGE pyrojector (SGE Pty., Ltd., Melbourne, Australia) at 320°C for 15 min and then at 520°C for 75 min.

RESULTS AND DISCUSSION

Thermooxidation degradation of CPOM-Y

An isothermal weight-loss curve of CPOM-Y in air at 150°C is shown in Figure 1. At this temperature, CPOM-Y is in the crystallizing state and near the molten state. Although no antioxidants are added, CPOM-Y is relatively stable at first. The bulk of the sample weight loss is observed after nearly 1000 min. Figure 2 presents the natural logarithm of the remaining weight versus time. Obviously, the decomposition reaction in air is not following first-order kinetics, and the degradation rate is not constant over the whole isothermal decomposition process. Very little weight loss of CPOM-Y can be observed at the beginning of the decomposition process, which may be called stage 1. The highest weight loss before 1000 min (stage 2) is around 10%. After 1000 min (stage 3), a faster degradation rate is observed, and more than 85% of the weight of CPOM-Y is lost from 1000 to 2500 min. During the different stages, plots of the natural logarithm of the retained weight versus time (Fig. 3) are linear; they may not be perfect and indicate complicated influence factors. The rate constants for each

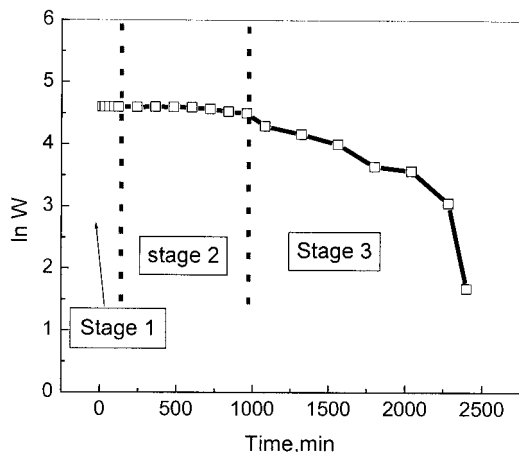


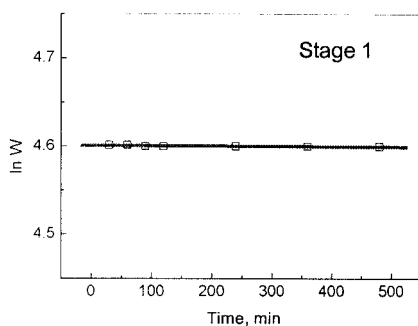
Figure 2 Natural logarithm of the retained weight (ln W) of CPOM-Y versus time.

stage, derived from regression analyses, are summarized in Table I. The results show that the decomposition process accelerates greatly after aging for 500 min.

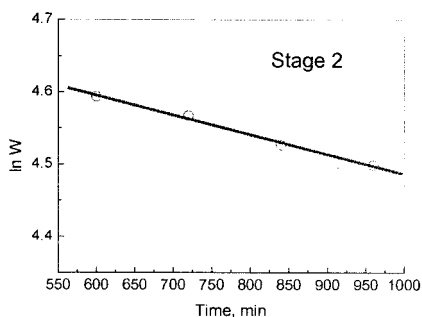
TABLE I
Rate Constant at Different Stages of the Degradation of CPOM-Y in Air at 150°C

	Degradation time (min)	Total weight loss (%)	Rate Constant (min ⁻¹)
Stage 1	0-500	0.6	2.93907×10^{-6}
Stage 2	500-1000	10.2	2.71914×10^{-4}
Stage 3	> 1000	89.2	9.87727×10^{-4}

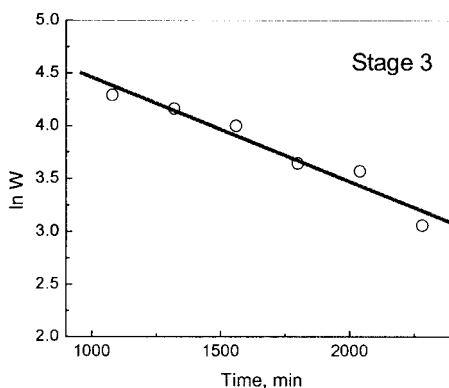
Pyrolyzed CPOM-Y was identified by gas chromatography and mass spectrometry. At lower temperatures (<320°C), no signal was tested by gas chromatography within hours. With an increase in the pyrolysis temperature from 320 to 520°C, three peaks appeared in a chromatogram (Fig. 4). The analytical results for the three parts of the pyrolyzed species are summarized in Table II. At first, the pyrolyzed species are mainly formaldehyde. Later, thermal degradation yields numerous volatile species, such as formaldehyde, acetaldehyde, EO, propane, ethane, and carbon dioxide.



(a)



(b)



(c)

Figure 3 Natural logarithm of the retained weight (ln W) of CPOM-Y versus time at (a) stage 1, (b) stage 2, and (c) stage 3.

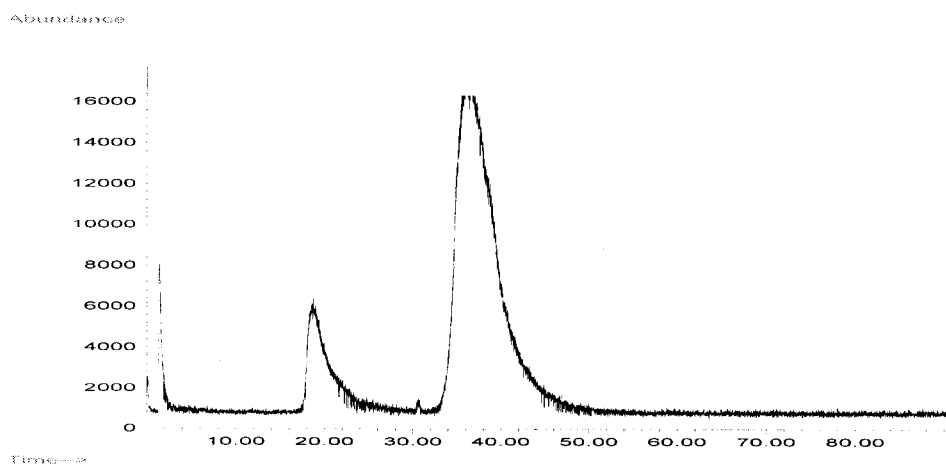


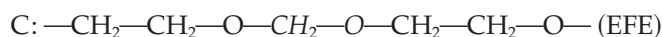
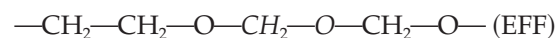
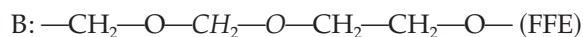
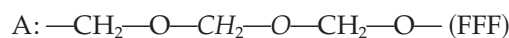
Figure 4 Chromatogram of CPOM-Y pyrolyzed at 320–520°C.

Only a single peak at 1.4 min was obtained if the pyrolyzed temperature was unchanged at 320°C. After the temperature increased to 520°C, two other peaks were obtained. Thus, the most unstable part of CPOM-Y existed, the ion peak intensity of which was about 3%. The ion intensity of the most stable part was about 84%. In comparison with the weight-loss process, the decomposition process of CPOM-Y appar-

ently can be divided into three stages, even under different degradation conditions. It is further indicated that CPOM-Y is composed of three parts with different thermal stabilities.

¹H-NMR results of degraded CPOM-Y

The poly(oxymethylene) copolymer (CPOM-Y) is composed of formaldehyde units ($-\text{OCH}_2-$, or F) and EO units ($-\text{OCH}_2\text{CH}_2-$, or E). The possible triad sequences are



Peak	Time (min)	Assignment	Area (%)
1	1.4	Formaldehyde	3.1
2	18.6–25.5	Formaldehyde Propane Acetaldehyde EO	12.5
3	30.6–45.0	Carbon dioxide Formaldehyde Acetaldehyde EO Ethane	84.4

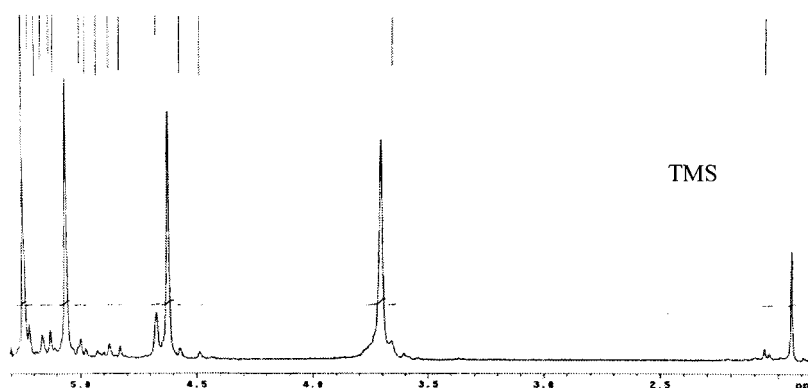
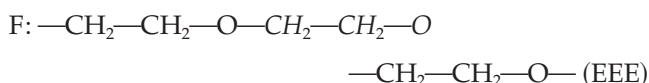
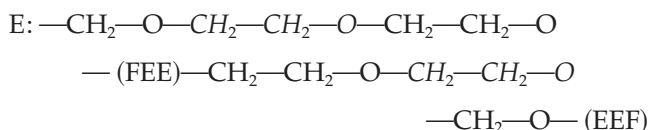


Figure 5 Typical ¹H-NMR spectrum of CPOM-Y.

TABLE III
Assignment and Molar Fractions of the Peaks of CPOM-Y due to Methylene Oxide and EO Units

Unit	Triad sequence	Chemical shift (ppm)	Molar fraction R (%)
—CH ₂ —O—	FFF (F)	5.20	65.3
—CH ₂ —O—	FFE (F)	4.63	27.0
—CH ₂ —O—	EFE (F)	4.50	3.5
—CH ₂ —CH ₂ —O	FEF (E)	3.73	4.2



The ¹H-NMR spectrum of CPOM-Y is shown in Figure 5. Some assignment results are presented in Table III. The spectrum shows that EO is primarily mono units (FEF) because of a single peak at 3.73 ppm. The resonance peaks occurring at 5.20, 4.63, and 4.50 ppm can be assigned to trimer (FFF), dimer (FFE/EFF), and mono (EFE) methylene oxide units, respectively.^{18,19} The small peaks around the main peaks are spinning sidebands and solvent peaks.

The molar fractions of the corresponding sequences (R) are given by the following relations:

$$R_{FFF} = KA \quad (1)$$

$$R_{FFE} + R_{EFF} = 2R_{FFE} = 2R_{EFF} = KB \quad (2)$$

$$R_{EFE} = KC \quad (3)$$

$$R_{FEF} = KD/2 \quad (4)$$

where A , B , C , and D are the corresponding peak areas. K is a normalization constant:

$$K(A + B + C + D/2) = 1 \quad (5)$$

The calculated R values are also shown in Table III. The number-average lengths of F- and E-successive sequences (L_F and L_E , respectively) can be calculated with the following relations:

$$L_F = R_F / (R_{EFE} + R_{FFE}) \quad (6)$$

$$L_E = R_E / (R_{FEF} + 1/2R_{FEE}) \quad (7)$$

L_F and L_E of CPOM-Y are 5.64 and 1.0, respectively.

The changes in the microstructure of the CPOM-Y n samples corresponding to different degradation times were studied with ¹H-NMR. All the ¹H-NMR spectra have four single peaks around 5.20, 4.63, 4.50, and 3.73 ppm, which correspond to sequences FFF, FFE/EFF, EFE, and FEF. The NMR analysis results for CPOM-Y at different decomposition times are summarized in Table IV. The molar fractions of the corresponding sequences (formaldehyde units and EO units) and the number-average lengths of F-successive sequences are listed. Because almost all the EO is present as FEF units with a single peak at 3.70 ppm in all the NMR spectra obtained, L_E is about 1.0.

The NMR results (Table IV) show that, at different degradation stages, there are obviously different structural changes in decomposition samples due to dissimilar degradation mechanisms. However, some common rules can be observed during the whole decomposition process. The molar fractions of EO units (R_E) of all the degraded samples (CPOM-Y n) are

TABLE IV
¹H-NMR Results of CPOM-Y and Degraded CPOM-Y n

Sample	Degradation time (min)	Weight loss (%)	Δ loss (%)	R_{FFF} (mol %)	$2R_{FFE}$ (mol %)	R_{EFE} (mol %)	R_F (mol %)	R_E (mol %)	L_F	
CPOM-Y	0	0		65.3	27.0	3.5	95.8	4.2	5.6	
Stage 1	CPOM-Y1	60	0.38	0.38	70.9	20.8	2.3	94.0	6.1	7.4
	CPOM-Y2	480	0.54	0.16	60.5	26.3	1.3	88.1	11.9	6.1
Stage 2	CPOM-Y3	600	1.15	0.61	55.3	28.0	1.2	84.4	15.6	5.6
	CPOM-Y4	750	4.44	1.04	78.5	15.4	1.4	95.3	4.7	10.5
	CPOM-Y5	840	7.57	3.13	74.7	16.9	3.5	95.2	4.9	8.0
	CPOM-Y6	960	10.12	2.55	68.6	20.5	2.6	91.7	8.3	7.1
Stage 3	CPOM-Y7	1080	26.81	16.69	78.8	14.1	1.8	94.7	5.3	10.6
	CPOM-Y8	1320	35.73	18.92	80.9	8.5	1.1	90.5	9.5	16.9
	CPOM-Y9	1560	45.31	9.58	66.8	23.7	1.5	91.9	8.1	6.9
	CPOM-Y10	1800	61.72	16.41	65.5	24.3	1.2	91.0	9.0	6.8
	CPOM-Y11	2280	78.68	16.96	72.5	19.1	2.5	94.2	5.8	7.8
	CPOM-Y12	2400	94.64	15.96	78.2	15.4	1.9	95.5	4.5	9.9

$$\Delta\text{loss} = \text{weight loss} [(CPOM-Y_n) - (CPOM-Y_{n-1})].$$

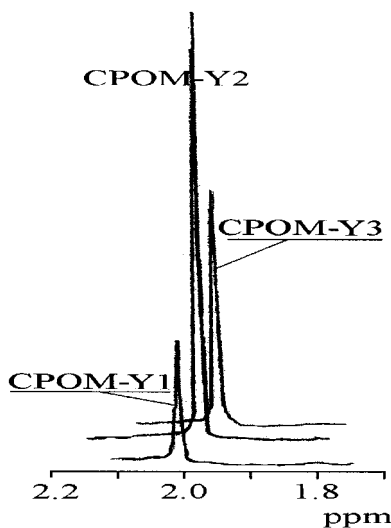
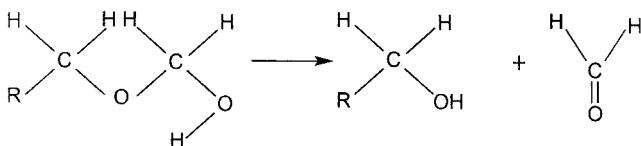


Figure 6 $^1\text{H-NMR}$ spectra of the OH end group.

higher than those of the original sample (CPOM-Y), whereas the molar fractions of formal units (R_F) of CPOM- Y_n are less than those of CPOM-Y. This result is in agreement with the fact that EO units have higher thermal stability and that the degradation of POM is due to the decomposition of formal units. The data listed in Table IV show that the L_F values of CPOM- Y_n are higher than those of CPOM-Y. This indicates that thermooxidation degradation of CPOM first happens on the irregular formal segments, including end groups and short segments. The longer regular F sequences are stable because they may be in the crystalline region.

As shown in Table IV, at the beginning of the isothermal decomposition process (stage 1, 0–500 min), R_F decreases, whereas R_E rises a lot. According to the previous results of GC-MS, during the first stage, the pyrolyzed species are mainly formaldehyde. In light of the small weight loss, these results suggest that CPOM tends to split off formaldehyde, starting at the chain ends, some of which are not ended by EO units. This unzipping reaction would not proceed with the C—C—O units. This depolymerization mechanism is believed to be related to the mobile hydrogen of the hydroxyl group on the chain ends:

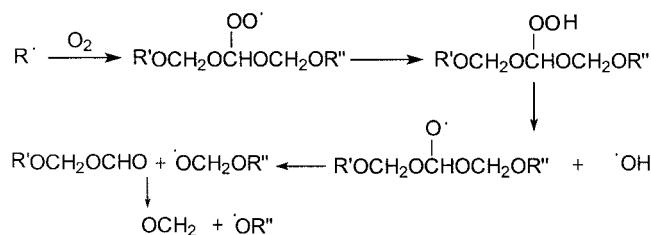


In the spectrum of the original CPOM-Y sample, the peak of hydroxy groups at 2.078 ppm is not obvious. However, in the NMR spectra of CPOM-Y1, CPOM-Y2, and CPOM-Y3, there are obvious strong peaks of OH groups in the region of 1.9–2.1 ppm (Fig. 6). The chemical shifts and relative contents of the OH groups

are shown in Table V. When the degradation process begins, the OH peak shifts to lower ppm values, and the relative content of OH is high. However, this peak gradually disappears in stage 2. This may indicate that the OH peak is related to H_2O and O_2 for the dried samples kept in humid air at the beginning of the degradation experiments. H_2O and O_2 react with CPOM to form radicals $\text{R}\cdot$ and $\text{OH}\cdot$ or react with formaldehyde degraded to create formic acid and carbonyl groups.

After more than 500 min, the degradation becomes effective in the presence of oxygen and at 150°C . Δloss (see Table IV) increases obviously, and the degradation rate is rapid at stage 2. In comparison with stage 1, R_E drops greatly, whereas R_{FFF} , R_F , and L_F are higher. Lower molar contents related to E units, including R_E , R_{FFE} , and R_{EFE} , are obtained. It seems that some of the EO units are lost during this stage. Because the introduction of EO units to the POM chain results in an irregularity of the acetal chain and a lower degree of crystallinity, most EO units and irregularity segments stay in the amorphous phase, in which further decomposition may occur. Because the crystalline phase is mainly composed of regular FFF units, L_F of the retained samples is relatively high. It has been reported that the thermooxidation of POM is initiated in the amorphous part, and this has been proved by our NMR results.

In stage 2, thermooxidation degradation yields numerous different volatile fragments, such as formaldehyde, acetaldehyde, EO, propane, ethane, and carbon dioxide. This may indicate that decomposition occurs in the amorphous part by random chain scission. First, a polymer hydroperoxide is formed by the oxygen action, and this leads to subsequent cleavage of the chain. The oxidative degradation mechanism is as follows:



However, the crystalline degree of CPOM-Y is about 67.8%. From the beginning of degradation to stage 2,

TABLE V
 $^1\text{H-NMR}$ Results for the OH End Group

Sample	ppm	Relative content ^a
CPOM-Y	2.078	0.002
CPOM-Y1	2.052	0.040
CPOM-Y2	1.974	0.125
CPOM-Y3	1.943	0.061

^a Molar fraction ratio [$R_{\text{OH}}/(R_F + R_E)$].

the total weight loss is nearly 17%. Thus, some amorphous part may be an interfacial region, and the surface of the crystal has not been removed.

When the thermooxidation of CPOM- Y_n continues more than 1000 min (stage 3), the bulk of the sample weight loss (>80%) is observed. It has been suggested that the decomposition rate may become reduced after the removal of the amorphous part of the polymer.¹⁵ We have observed that the degradation rate accelerates and the degree of crystallinity reaches a value of 67.9%, which is similar to the original degree. As shown in Table IV, no obvious rule of sequence content changes has been obtained from the NMR results. This means that further random chain scission follows after the amorphous phase to the surface of the crystal, and then chain scission and unzipping occur heavily in the crystalline bulk under thermooxidation and acid. The samples were heated at high temperatures for a long time in the presence of oxygen, and great amounts of formic acid and hydroperoxide radicals were produced in the previous stage; this could have led to the accelerating degradation rate and a great deal of oxidative chain scission. Because of these complicated effects, no clear rules of structural changes have been obtained, and decomposition may occur randomly.

CONCLUSIONS

The decomposition reaction of CPOM at 150°C in air does not follow first-order kinetics, and the degradation rate is not constant over the whole isothermal decomposition process. However, the degradation process of CPOM- Y apparently can be divided into three stages.

During the different stages, the decomposition reactions follow first-order kinetics. Gradually accelerated rates of thermooxidation of CPOM in the solid state have been obtained.

At the beginning of thermooxidation degradation (stage 1), CPOM- Y tends to split off formaldehyde,

starting at the chain ends, some of which are not ended by EO units. Degraded samples have many OH end groups or OH· radicals and formic acid. In stage 2, the thermooxidation of POM occurs in the amorphous part because R_E drops greatly, and R_{FFF} and R_F are high in comparison with the data for stage 1. In stage 3, the bulk of the sample weight loss and an accelerated degradation rate can be observed. No obvious rules for changes in the sequence contents have been obtained from the NMR results, and this indicates further random chain scission and unzipping occurring heavily in the crystalline bulk.

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