*Thermogravimetric Analysis of Polyoxymethylene**

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Several studies[1,2] of the thermal decomposition of polyoxymethylene in the bulk state have been made; in them the weight loss of the polymer has been measured during its degradation at a constant temperature in the 100~350°C range. Recently, Dudina and his co-workers[3-7] have also extensively studied the thermal and thermo-oxidative degradation of polyoxymethylene. However, there has been little attempt to make a thermogravimetric analysis (TGA) of polyoxymethylene. In this technique the temperature of the polymer is elevated at a constant rate until the sample decomposes completely; then the general character of the thermal degradation process and the thermal stability of the polymeric materials can be determined.

The data presented in this paper are based largely on the thermogravimetric analysis of polyoxymethylene, acetylated polyoxymethylene and commercial Delrin resin, both in air and in nitrogen. The derivative thermogravimetric analysis (DTGA) curves of the three samples show two peaks in each case. In order to clarify the above observations, the effect of the concentration of oxygen on the DTGA curve was also investigated. From the TGA in a vacuum, some knowledge of the volatility of pyrolysates and their thermal decomposition character in a very low concentration of oxygen has been obtained.

It has been found that the first stage is due to the chain depolymerization as well as to the oxidative decomposition and that the second stage is to be attributed to the random degradation of a stable fragment formed during first-stage decomposition. Moreover, an increase of carbonyls in the polyoxymethylene as a result of the degradation has been confirmed by the infrared absorption method.

Experimental

Materials.—The polyoxymethylene ($[\eta]=1.6$ g./

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** Central Research Laboratories, Toyo Rayon Company, Ltd., Sonoyama, Otsu, Shiga.

1) C. E. Schweitzer, R. N. MacDonald and J. O. Punderson, *J. Appl. Polymer Sci.*, 1, 158 (1959).

2) W. Kern and H. Cherdron, *Makromol. Chem.*, 40, 101 (1960).

3) L. A. Dudina and N. S. Enikolopyan, *Vysokomolek. Soed.*, 5, 861 (1963).

4) L. A. Dudina and N. S. Enikolopyan, ibid., 5, 986 (1963).

5) L. A. Dudina and N. S. Enikolopyan, ibid., 5, 1135 (1963).

6) L. A. Dudina, L. V. Karmilova and N. S. Enikolopyan, ibid., 5, 1160 (1963).

7) L. A. Dudina, L. A. Agayants, L. V. Karmilova and N. S. Enikolopyan, ibid., 5, 1245 (1963).

100 ml. in *p*-chlorophenol at 60°C) used in this work was supplied by the Toyo Rayon Co., Ltd. It was free from additives. The acetylation of polyoxymethylene was carried out using acetic anhydride and sodium acetate at 139°C.[1] Commercial Delrin 5000X was also used without further purification.

Apparatus. — The automatic recording thermobalance[8] used in this work consists of a tungsten spring balance and a linear variable differential transformer to detect the elongation of the spring. The temperature of the furnace regulated by a program controller.

Procedure. — A weighed quantity of polymer (eigher 100 mg. or 10 mg.) was placed in a glass crucible with a diameter of 12 mm. and a depth of 10 mm. The weight loss of the polymer was recorded against the time using the automatic recording thermobalance while the sample was heated at the rate of about 1°C/min. or, in some cases, at 0.5°C/min., from room temperature to about 350°C in various concentrations of oxygen. The DTGA curves were obtained by the graphical differentiation of the weight loss versus the temperature curves.

The isothermal decomposition of polyoxymethylene was conducted in nitrogen at temperatures ranging from 200 to 240°C and in air at 177~225°C.

The infrared spectra were recorded with a Shimadzu IR-2A spectrophotometer. The sample, decomposed partially during the thermogravimetric measurements, was used after having been rapidly cooled to room temperature. The infrared analysis was carried out by using potassium bromide pellets.

Results

Thermogravimetric Analysis in Nitrogen and in Air.—The TGA curves of polyoxymethylene, acetylated polyoxymethylene and Delrin using a sample of 100 mg. in nitrogen are shown in Fig. 1. All of these polymers show two peaks in each DTGA curve. Polyoxymethylene alone shows a large peak at 200°C, whereas the others exhibit no large weight loss in this temperature. The temperature at which the sample decomposes completely becomes higher in the order of polyoxymethylene, acetylated polyoxymethylene and Delrin.

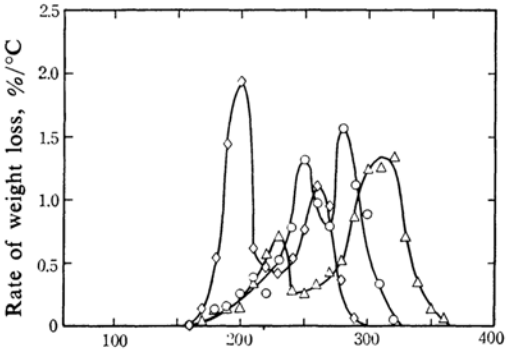

Fig. 1. Thermogravimetric analysis curves for polyoxymethylene (POM), acetylated polyoxymethylene (POMAc) and Delrin in nitrogen atmosphere.
◇ POM, ○ POMAc, △ Delrin 5000X

The DTGA curves of these polymers using a sample of 100 mg. in air are shown in Fig. 2. In each curve of these polymers, two peaks were observed, as in nitrogen. However, both polyoxymethylene and acetylated polyoxymethylene showed a large weight loss over the range from 150 to 200°C. In the case of oxidative decomposition, the completely decomposing temperature is the highest for Delrin and the lowest for polyoxymethylene.

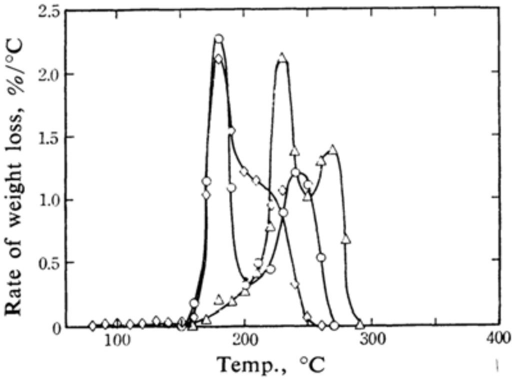

Fig. 2. Thermogravimetric analysis curves for polyoxymethylene (POM), acetylated polyoxymethylene (POMAc) and Delrin in air.
◇ POM, ○ POMAc, △ Delrin 5000X

Isothermal Decomposition of Polyoxymethylene in Nitrogen and in Air.—The thermal decomposition of polyoxymethylene was isothermally studied at temperatures in the 200~240°C range. The plot of the logarithm of the weight loss of the sample against the time in nitrogen is shown in Fig. 3. A deviation of the reaction rate from the first-order law was observed. The decomposition seems to occur in two stages.

The plot of the logarithm of the weight loss of the sample against the time at various temperatures in air is shown in Fig. 4. In this case, no simple straight line was observed; accordingly, the oxidative decomposition is more complex than the thermal decomposition in a nitrogen atmospher (cf. Fig. 3).

Effect of the Concentration of Atmospheric Oxygen on Thermal Decomposition. — As has been mentioned above, the thermal decomposition of polyoxymethylene is significantly affected by the concentration of oxygen.

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[8] H. Kambe and S. Igarashi, *Rept. Aeronaut. Res. Inst., Univ. Tokyo*, **28**, 145 (1963).

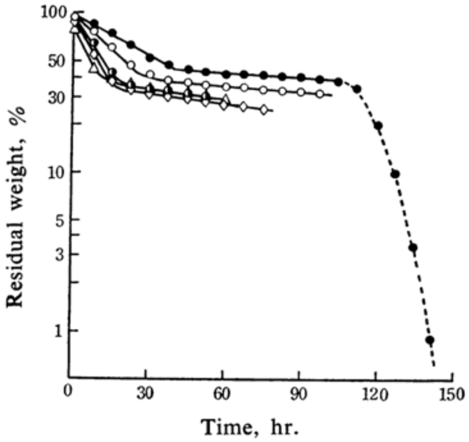

Fig. 3. Thermal decomposition of polyoxymethylene in nitrogen at various temperatures. Broken line; at 300°C
● 200°C, ○ 210°C, ◑ 220°C
◇ 230°C, △ 240°C

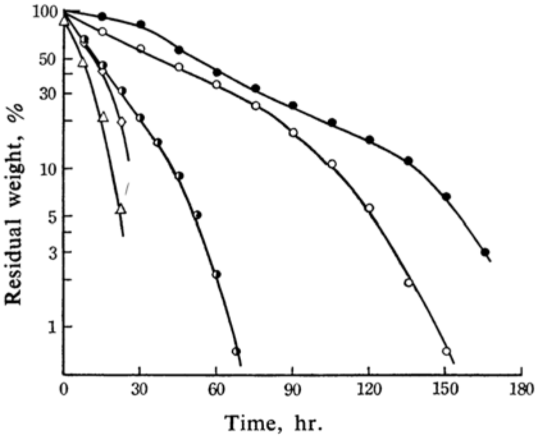

Fig. 4. Thermal decomposition of polyoxymethylene in air at various temperatures.
● 177°C, ○ 185°C, ◑ 200°C
◇ 215°C, △ 225°C

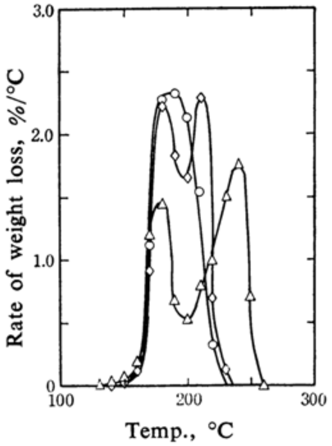

Fig. 5. Thermal decomposition of polyoxymethylene in various concentrations of oxygen.
(△) 0.24 mol. %; (◇) 5.6 mol. %;
(○) 21.0 mol. %

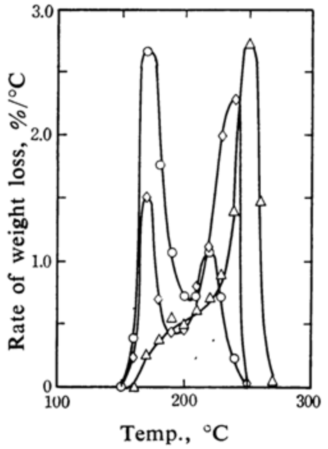

Fig. 6. Thermal decomposition of acetylated polyoxymethylene in various concentrations of oxygen.
(△) 0.24 mol. %; (◇) 5.6 mol. %;
(○) 21.0 mol. %

Therefore, TGA measurements were performed in various concentrations of oxygen. The typical curves for the decomposition of polyoxymethylene shown in Fig. 5 indicate a significant difference between the DTGA curves. The weight loss at the first stage, from 150 to about 200°C, increases with the concentration of oxygen. The weight of the sample used in these measurements was about 10 mg. From Figs. 2 and 5, the weight loss at the first stage for experiments using a sample of 10 mg. may be seen to have been greater than for measurements using a sample of 100 mg. in air (i.e., 21.0 mol. % of oxygen). This will be discussed furthere below.

The DTGA curves for the decomposition of acetylated polyoxymethylene are shown in Fig. 6. The weight loss at the first stage, from 150 to about 200°C, increases with the concentration of oxygen. The weight losses at the first stage in the decomposition for polyoxymethylene and its acetylated sample calculated from Figs. 5 and 6 are plotted against the concentration of oxygen in mole per cent in Fig. 7. The weight loss of the first peak for both samples increases clearly with the concentration of oxygen, and the weight loss for polyoxymethylene is greater than that for acetylated polyoxymethylene.

The effects of the concentration of oxygen on the thermal decomposition of polyoxymethylene and acetylated polyoxymethylene are listed in Table I.

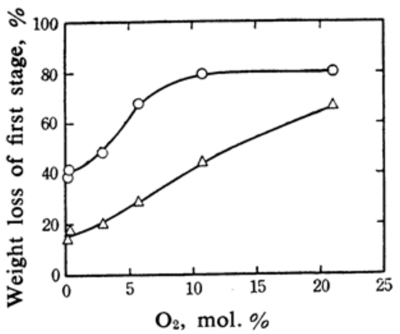

Fig. 7. Effect of the concentration of oxygen on the first stage of thermal decomposition of polyoxymethylene (POM) and acetylated polyoxymethylene (POMAc).
(○) POM, (△) POMAc

TABLE I. EFFECT OF THE CONCENTRATION OF OXYGEN ON THE FIRST STAGE OF THERMAL DECOMPOSITION

Oxygen in the atmosphere	Polyoxymethylene		Acetylated polymer	
	Wt. loss at the 1st stage	Temp. range	Wt. loss at the 1st stage	Temp. range
mol. %	%	°C	%	°C
21.0[a]	80.8	130～200	66.6	150～200
10.8	79.5	130～200	44.7	150～190
5.6	67.8	130～200	28.8	150～190
2.9	47.9	130～200	20.1	150～200
0.24[b]	41.9	130～200	17.5	150～200

a) In air.
b) In nitrogen.

Thermogravimetric Analysis in a Vacuum.—We consider that the effect of oxygen on the decomposition of polyoxymethylene can be eliminated by carrying out the thermogravimetric measurements in a vacuum. The DTGA curves of polyoxymethylene and acetylated polyoxymethylene in a vacuum are shown in Fig. 8. Polyoxymethylene shows a sharp peak at about 180°C and a second peak over the range from 200 to 330°C. For polyoxymethylene, there is no significant difference between the curve obtained at 1°C/min. and that at 0.5°C/min.

Acetylated polyoxymethylene shows two peaks in the DTGA curves; the former is in the region from 150 to 200°C, and the latter, from 200 to 340°C. Moreover, the first peak is smaller than the second one.

The TGA results obtained in the several atmospheres are summarized in Table II.

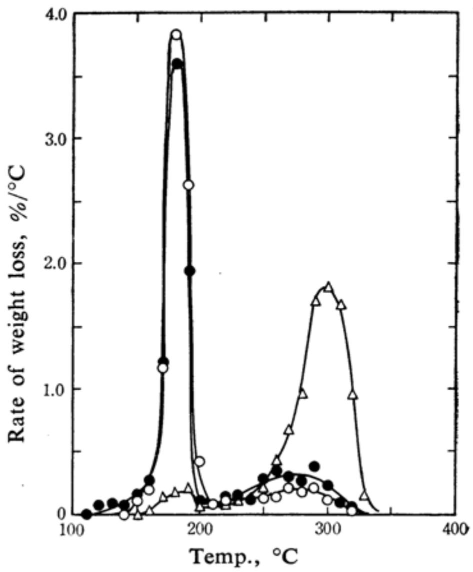

Fig. 8. Thermogravimetric analysis curves for polyoxymethylene (POM) and acetylated polyoxymethylene (POMAc) in a vacuum at different heating rates.
○ POM 1°C/min., ● POM 0.5°C/min.
△ POMAc 1°C/min.

TABLE II. THERMOGRAVIMETRIC ANALYSIS OF POLYOXYMETHYLENE AND ACETYLATED POLYOXYMETHYLENE

	Wt. loss		Temp. range	Energy of activation[a]	Residue
	at the 1st stage	at the 2nd stage			
	%	%	°C	kcal./mol.	%
Polyoxymethylene					
In air[b]	80.8		130～200	40	0
		19.2	200～230		
In N_2[c]	41.9		130～200	45	0
		58.1	200～260	43	
In vacuum	84.7		140～210	57	0
		15.1	210～320	18	
Acetylated polyoxymethylene					
In air[b]	66.6		150～200		6
		27.4	200～250		
In N_2[c]	17.5		150～200	28	3
		79.5	200～280	37	
In vacuum	6.9		150～210		4
		89.1	210～340	31	

a) Values estimated from the DTGA curves by assuming that the reaction is of the first order.
b) 21.0 mol. % of oxygen, sample weight used is 10 mg.
c) 0.24 mol. % of oxygen, sample weight used is 10 mg.

Infrared Analysis of Partially-Degraded Polyoxymethylene.—Infrared analysis was carried out for polyoxymethylene heated from room temperature to a desired maximum temperature. A great change in the infrared spectra because of carbonyl groups is observed at the absorption of the 1740 cm^{-} band. The ratio

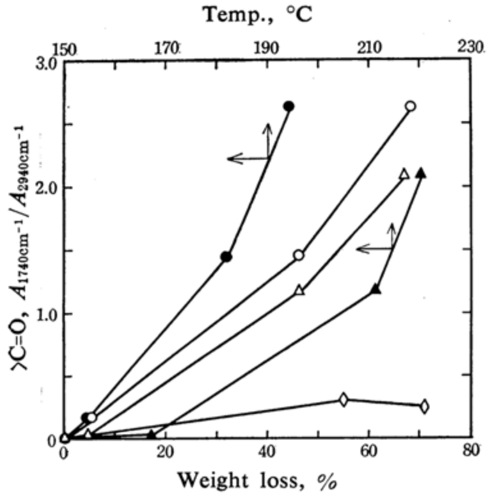

Fig. 9. The increase of carbonyls in polyoxymethylene with the decomposition in the different atmospheres.
○ in air, △ in N_2, ◇ in vacuum

TABLE III. INFRARED ANALYSIS OF DEGRADED POLYOXYMETHYLENE

Atmosphere	Wt. loss %	Relative absorbance $A_{1740\mathrm{cm}^{-1}}/A_{2940\mathrm{cm}^{-1}}$	Maximum temp. °C
Air	0	0	
	5	0.17	154
	46	1.45	182
	68	2.63	194
Nitrogen	4	0.04	167
	46	1.18	211
	67	2.09	220
Vacuum	55	0.308	230[a]
	71	0.260	250[a]

a) Isothermal decomposition.

of the absorbance at the 1740 cm^{-1} band to that at the 2940 cm^{-1} band is plotted against the weight loss and also against the maximum heated temperature in air and in nitrogen in Fig. 9. The results obtained by infrared analysis are listed in Table III.

Discussion

Thermal Decomposition Character.—Dainton, Ivin and Walmsley,[9] Schweitzer and MacDonald,[1] and Kern and Cherdron,[2] found that the thermal degradation of polyoxymethylene is of the chain-depolymerization type, involving the successive release of formaldehyde from a hydroxyl end group, and that the oxidative degradation may occur at random along the chain. Recent investigation[3] has revealed that the isothermal decomposition of polyoxymethylene occurs in two stages.

As is shown in the DTGA curves in Figs. 1 and 2, polyoxymethylene, acetylated polyoxymethylene and Delrin undergo thermal and oxidative degradation in two stages. The results in Fig. 1 clearly show that the polyoxymethylene with an acetyl end group is thermally more stable than the original polymer with a hydroxyl end group; the weight loss of the former in the 200°C region is smaller than that of the latter. Although polyoxymethylene is stabilized by the acetylation of the hydroxyl end group, the stabilization of the chain ends has a minor effect on the oxidative decomposition, as may be seen in Fig. 2. This means that, in air, the chain scission due to oxidation occurs at random points along the chain. Since the decomposition of polyoxymethylene in the 200°C region occurs also in nitrogen, it may be deduced that its oxidative decomposition in this stage occurs as a combination of random degradation and chain depolymerization. Delrin shows a good thermal stability at temperatures in the above-mentioned region. This may be attributed to the effects of a stabilization of the end group and of an antioxidant added to the polymer upon decomposition.

The two steps of degradation observed by TGA are confirmed by the isothermal decomposition, as is shown in Fig. 3. Each peak in the DTGA curve may correspond to two straight lines in the isothermal decomposition, which is a reaction of the first order. The isothermal decomposition character of polyoxymethylene in air illustrated in Fig. 4 is similar to that reported by Kern.[2]

The effect of the concentration of oxygen on the DTGA curve is shown in Figs. 5 and 6 for polyoxymethylene and acetylated polyoxymethylene, respectively. The weight losses of the first stage in the 200°C region increases with the concentration of oxygen, as Fig. 7 shows. This indicates that the oxidative decomposition occurs more easily as the concentration of oxygen increases. Acetylated polyoxymethylene undergoes the oxidative decomposition entirely, but polyoxymethylene decomposes preferentially at the chain ends in addition to the decomposition which occurs as a result of the random attack of oxygen. This may be a reason why the weight loss of polyoxymethylene is larger than that of acetylated polyoxymethylene.

The thermogravimetric measurements were conducted in a vacuum at 10^{-2} mmHg. The results in Fig. 8 reveal clearly that the

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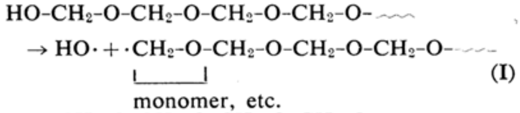
[9] F. S. Dainton, K. J. Ivin and D. A. G. Walmsley, *Trans. Faraday Soc.*, 55, 61 (1959).

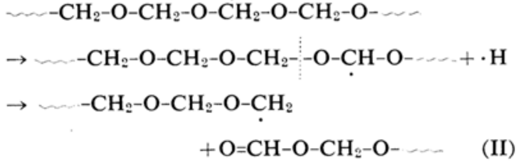
degradation occurs in two stages in such a low concentration of oxygen. The fraction of the weight loss in the first stage of polyoxymethylene is larger than that obtained in nitrogen at atmospheric pressure (see Table II). The rate of the vaporization of the degradation products from polyoxymethylene will depend on the pressure of the atmosphere. There is no significant difference between the curves obtained at different heating rates, as Fig. 8 shows. Accordingly, it is interesting that the thermal decomposition polyoxymethylene did not all occur in one stage. It is deduced that the second stage of weight loss corresponds to the decomposition of the stable fragments formed during the first stage of degradation. The scission of the main chain of the acetylated polyoxymethylene molecule occurs mainly over the range from 200 to 340°C. The small peak below 200°C is probably to be attributed to the thermal decomposition of an unacetylated polyoxymethylene.

The Mechanism of Decomposition. — The results in Fig. 9 and in Table III show that the carbonyl groups are formed during the decomposition of polyoxymethylene in each atmosphere and that its amount increases with the degree of degradation. The carbonyls are formed even in a vacuum. Since the oxygen remaining in a vacuum had no influence on the DTGA curve, it may be supposed that this formation is due to the interchange of the ether linkage into the carbonyl group (see step II below).

The following mechanism for the thermal decomposition of polyoxymethylene in the absence of oxygen is proposed:



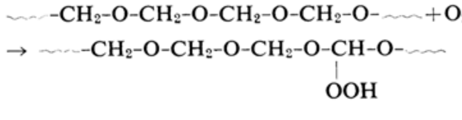
$$\mathrm{HO{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}}\sim\sim$$
$$\rightarrow \mathrm{HO\cdot + \cdot \underbrace{CH_2{-}O{-}CH_2}_{monomer,\ etc.}{-}O{-}CH_2{-}O{-}CH_2{-}O{-}}\sim\sim \qquad \mathrm{(I)}$$



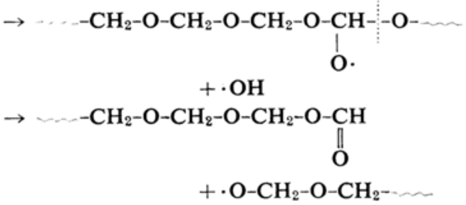
$$\sim\sim\mathrm{{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}}\sim\sim$$
$$\rightarrow \sim\sim\mathrm{{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}\,\vdots\,{-}O{-}\underset{\cdot}{C}H{-}O{-}}\sim\sim + \cdot\mathrm{H}$$
$$\rightarrow \sim\sim\mathrm{{-}CH_2{-}O{-}CH_2{-}O{-}\underset{\cdot}{C}H_2}$$
$$+\mathrm{O{=}CH{-}O{-}CH_2{-}O{-}}\sim\sim \qquad \mathrm{(II)}$$

In the light of the above mechanism, it may be deduced that a stable fragment with carbonyl groups at the chain ends decomposes in the second stage in the DTGA curve of polyoxymethylene in a vacuum.

In the presence of oxygen, the following scheme is well known:



$$\sim\sim\mathrm{{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}}\sim\sim + \mathrm{O_2}$$
$$\rightarrow \sim\sim\mathrm{{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}\underset{\displaystyle OOH}{\underset{|}{C}H}{-}O{-}}\sim\sim$$



$$\rightarrow \sim\sim\mathrm{{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}\underset{\displaystyle O\cdot}{\underset{|}{C}H}{-}\,\vdots\,{-}O{-}}\sim\sim$$
$$+\cdot\mathrm{OH}$$
$$\rightarrow \sim\sim\mathrm{{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}H}}$$
$$+\cdot\mathrm{O{-}CH_2{-}O{-}CH_2{-}}\sim\sim$$

The fact that the quantity of carbonyl groups formed in the decomposition in air is larger than that in nitrogen, as has been mentioned already, reflects the above mechanism for the oxidative degradation of polyoxymethylene.

Effect of Sample Size on the Thermogravimetric Analysis Curve.—It may be seen from Figs. 5 and 6 that the temperature of the second stage is altered to a lower temperature with an increase in the concentration of oxygen. Moreover, it should be noticed that the feature of the DTGA curve is dependent on the weight of the sample used for measuring. For instance, by comparing the curve for polyoxymethylene using a sample of 100 mg. in air (see Fig. 2) with that for polyoxymethylene using sample of 10 mg. in air (i. e., 21.0 mol. % of oxygen in Fig. 5), it is confirmed that the DTGA curve for the oxidative decomposition is greatly affected by the weight of the sample used. A similar effect for the oxidative decomposition of polyethylene has been reported in a previous paper.[10]

Summary

The character of the thermal decomposition of polyoxymethylene, acetylated polyoxymethylene and Delrin in air and in nitrogen has been studied by thermogravimetric analysis. Two peaks have been observed in each atmosphere in the derivative thermogravimetric analysis curves for these samples.

It has been confirmed that the feature of doublet peaks is related to the concentration of oxygen during the decomposition and, thus, that the first stage is due to the chain depolymerization as well as to the oxidative decomposition, and that the second stage is to be attributed to the random degradation of a stable fragment formed during the first stage decomposition.

An increase of carbonyl groups in the polymer molecule with the degradation was confirmed by infrared spectroscopy.

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[10] S. Igarashi and H. Kambe, This Bulletin, 37, 176 (1964).