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EVOLVED GAS ANALYSIS OF POLY(METHYL METHACRYLATE) *

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ABSTRACT

The thermal decomposition of various types of poly(methyl methacrylate) under vacuum was investigated by evolved gas analysis with a mass spectrometer. Though the volatilized product is mainly methyl methacrylate due to unzipping, four steps of volatilization were observed, and decompositions depend on the molecular weight and the polymerization process. The mechanisms of these four steps are elucidated by comparison of the amount of the volatilized product found at each step with the molecular weight and the polymerization process. The first step is a depolymerization initiated at the weak bond of copolymerized oxygen, and the second and third steps consist of depolymerization initiated at the chain ends, which occur due to disproportionation in propagating radical termination during polymerization. The fourth and final step is a depolymerization initiated by random scission in the main chain.

INTRODUCTION

Many reports have been published hitherto on the thermal decomposition of poly(methyl methacrylate) (PMMA), because it is one of the typical depolymerization processes of high polymers producing monomers by unzipping [1–22]. However, there are large discrepancies among the reported kinetic mechanisms and parameters, such as the number of degradation steps and the activation energy. By evolved gas analysis (EGA) with a mass spectrometer, the present authors observed four steps of decomposition, though the product is methyl methacrylate in all steps, and thus, the four steps are all depolymerizations producing the monomer. By comparison of the amount of the volatilized monomer with the molecular weight and the polymerization process it was elucidated that the four steps of depolymeriza-

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* Dedicated to Professor Syûzô Seki in honor of his contribution to calorimetry and thermal analysis.

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tion are different from each other in their initiation mechanisms. The reason for the above-mentioned discrepancy is ignorance of the four-step depolymerization of PMMA, so that the reporters did not assign the process they were observing to one of the four steps. Different depolymerizations were often compared with each other.

Although the four steps more or less overlap with each other, separately observed steps were kinetically analyzed by the method for the kinetic analysis of thermoanalytical data proposed by one of the present authors (T.O.) [23]. These results are also reported in this paper.

EXPERIMENTAL

The samples used in this research are listed in Table 1, where the initiators, the polymerization atmospheres and the molecular weights are shown. These seven samples are also different in the polymerization processes. Sample No. 2 is obtained by polymerizing 100 ml of methyl methacrylate in 400 ml of benzene with 5 g of the initiator benzoyl peroxide at 80 °C for 7 min. The conversion is ~ 10% and the polymeric sample was obtained by precipitation with a mixture of acetone and methanol. After obtaining sample No. 2, water was added to the filtrate and the gel precipitate was dried on a water bath to prepare sample No. 1, so that the molecular weight of sample No. 1 is thought to be smaller than that of sample No. 2.

Sample No. 3 was also obtained by polymerizing the 20% solution of the monomer in benzene with benzoyl peroxide at 70 °C for 20 min to a conversion of ~ 10% and by precipitating it in a mixture of acetone and methanol.

TABLE 1

Polymerization process and molecular weight of samples

Sample No.	Polymerization process		Molecular weight
	Catalyst	Atmosphere	
1	benzoyl peroxide	flow of nitrogen	–
2	benzoyl peroxide	flow of nitrogen	30000
3	benzoyl peroxide	flow of nitrogen	52000
4	benzoyl peroxide	flow of nitrogen	159000
5	– [a]	– [a]	396000
6	azoisobutylonitrile	sealed with nitrogen	666000
7	benzaldehyde anion (living polymerization)	under vacuum	3900000

[a] Commercial product.

Sample Nos. 4–7 were kindly supplied by Prof. Itaru Mita of the University of Tokyo. Sample No. 4 was polymerized with excess benzoyl peroxide to obtain a relatively low molecular weight sample. Sample No. 5 was obtained by precipitation of methylethyl ketone solution of a commericial product (Acrylicone AC) by methanol. Sample No. 6 was obtained by polymerizing the monomer with 0.2% of azoisobutylonitrile at 60°C to $> 90\%$ conversion in a sealed glass tube and by precipitating it in a mixture of chloroform and methanol. Sample No. 7 was polymerized by living polymerization with benzaldehyde anion at -78°C under vacuum and precipitated in methanol.

The molecular weights of sample Nos. 2–6 were estimated by measuring the viscosity of the acetone solution at 20°C and applying the following equation [24]:

$$[\eta] = 3.90 \times 10^{-3} M^{0.76} \tag{1}$$

where $[\eta]$ and M are the intrinsic viscosity and the molecular weight, respectively. The molecular weight of sample No. 7 was estimated by measuring the viscosity of the chloroform solution at 25°C and by applying the equation [25]:

$$[\eta] = 4.80 \times 10^{-3} M^{0.80} \tag{2}$$

The apparatus used for evolved gas analysis was described in our previous papers [15,26]. The sample was heated at a heating rate of 1, 2, 5 or 10°C min^{-1} under a pressure of $< 10^{-5}$ Torr. The volatilized products were directly introduced into the ionization region of the mass spectrometer as a molecular beam. They were then ionized with a pulsed electron beam and analyzed. The mass spectrum was observed at an appropriate interval and the ion current at m/e 100 was continuously recorded. To reduce fragmentation caused by electron bombardment and to detect the volatilized products as parent ions, the energy of the electron beam was lowered to 20 eV.

RESULTS AND DISCUSSION

At the beginning of thermal decomposition many peaks appeared in the mass spectrum, an example of which is shown in Fig. 1. However, this mass spectrum is exactly equal to that of the monomer, methyl methacrylate, and the large peaks at m/e 41, 69 and 100 are, respectively, assigned to $CH_3C{=}CH_2^+$, $CH_3C{=}CH_2CO^+$ and the parent ion [15]. The mass spectra obtained were essentially unchanged during the thermal decomposition, and the relative intensities of these three ion currents were also unchanged, so that it can be concluded that the product of the decomposition is the monomer and the decomposition mechanism is depolymerization. Typical EGA curves, which are the continuous records of the ion current, are shown

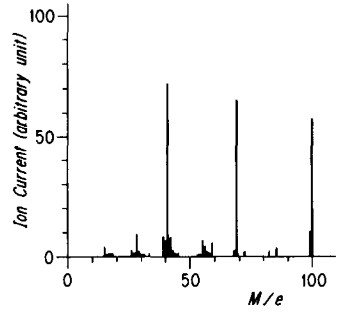


Fig. 1. Typical example of mass spectrum (sample No. 7, 2°C min^{-1}, 296°C).

in Fig. 2 for *m/e* 100 from sample Nos. 2 and 3. Four steps in the thermal decomposition were clearly observed for sample No. 3. Similar results were observed for sample Nos. 1–5, but for sample No. 6 three large peaks were detected with a very small first step, and for sample No. 7 only a one-step depolymerization was observed in the same temperature range as that of the fourth step of the other samples.

Because the area of the four peaks, such as in Fig. 2, is proportional to the amount of the monomer volatilized, the peak areas are measured and the percentages of each peak area to the total sum are listed in Table 2. As is seen in the table, there may be some dependence of the percentage of the fourth peak on the molecular weight, and the second and third peaks appear to be inversely dependent on the molecular weight, though these values may contain some error due to insufficient separation of overlapped peaks. On the other hand, the first peak areas of sample Nos. 6 and 7 are very small or undetectable. Sample No. 6 was polymerized in a sealed glass tube filled with nitrogen and sample No. 7 was polymerized under vacuum, whereas the first peak areas of samples 3–5 are roughly equal to each other, and samples 1–4 were polymerized in a flow of nitrogen. From these facts, the first step

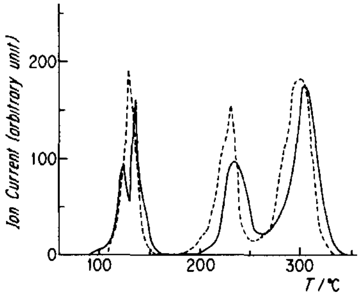


Fig. 2. Typical EGA curves: (— — —) sample No. 2; (———) sample No. 3, 2°C min^{-1}, *m/e* 100.

TABLE 2

Relative ratio of peak areas

Sample No.	Percentage			
	peak I	peak II	peak III	peak IV
1	40.3 [a]		21.3	38.4
2	22.9 [a]		30.0	47.1
3	11.4	15.3	23.0	50.3
4	12.9	5.3	6.3	75.6
5	14.8	5.3	9.5	70.5
6	1.4	0.8	18.8	79.0
7	0	0	0	100.0

[a] Peaks I and II cannot be separated.

of the decomposition seems to be initiated at the weak link of copolymerized oxygen from the polymerization atmosphere [2], and the second and third steps can be attributed to depolymerization initiated at the chain ends, while the fourth and last step can be inferred to be initiated at random in the main chain.

In order to substantiate these inferences, the ratio of the second, third or fourth peak area to the sum of these three peak areas, R, is plotted against the reciprocal molecular weight in Fig. 3. As is clearly seen, the second and third peak areas are both roughly proportional to the reciprocal molecular weight, which is proportional to the number of chain ends, and the initiation mechanism is ascertained to be that at the chain ends.

On the other hand, the fourth and last peak area is on a reverse line crossing the ordinate, i.e., infinite molecular weight at the 100% point, and the initiation is inferred to occur at random points in the main chain. By extrapolation, this line crosses the abscissa at a molecular weight of 23000, and this value seems to correspond to the sum of the average overall kinetic chain lengths in the second and third depolymerizations and the sum is estimated to be 230, though much error may be included in this figure due to

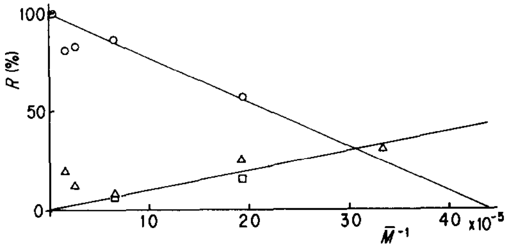


Fig. 3. Dependence of relative peak areas of decomposition steps upon reciprocal molecular weight. (□) Second step; (△) third step; (○) fourth step.

the long extrapolation. From the ratio of the fourth depolymerization for sample No. 2 in Table 2, the sum of the kinetic chain lengths in the first, second and third depolymerizations is estimated to be 160, which is in fairly good agreement with the above value.

In conclusion, the following mechanisms can be induced from these considerations:

(1) The first step of the decomposition is a depolymerization initiated at the weak links of copolymerized oxygen.

(2) These weak links are located randomly in the main chain.

(3) The termination of the first depolymerization does not produce any unstable chain ends which initiate the following depolymerization.

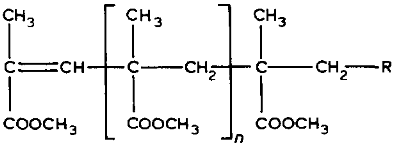
(4) The probability that the molecular chain ends initiating the second and third depolymerizations are lost in the first depolymerization is roughly independent on the molecular weight, so that the kinetic chain length of the first depolymerization is not as long as, but rather much shorter than, the polymerization degree of the initial polymer molecules.

(5) The second and third depolymerizations are initiated at the chain ends, so that there are two types of chain ends which can initiate depolymerization.

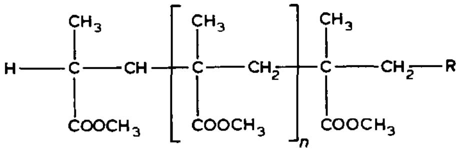
(6) The termination of the second and third depolymerizations does not produce any unstable chain ends which initiate further depolymerization.

(7) The fourth and last depolymerization is initiated by chain scission at random points in the main chain.

The next problem to be solved is to assign the type of chain ends which initiate the second and third depolymerizations. Gordon [27] reported that the chain ends of benzoyl-peroxide-initiated poly(methyl methacrylate) are as follows:



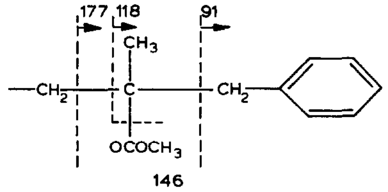
$$\mathrm{C(CH_3)(COOCH_3){=}CH{-}[C(CH_3)(COOCH_3){-}CH_2]_n{-}C(CH_3)(COOCH_3){-}CH_2{-}R}$$

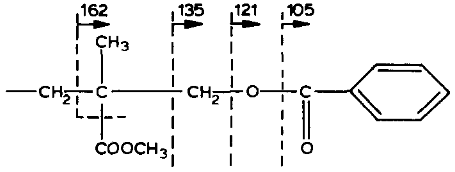


$$\mathrm{H{-}C(CH_3)(COOCH_3){-}CH{-}[C(CH_3)(COOCH_3){-}CH_2]_n{-}C(CH_3)(COOCH_3){-}CH_2{-}R}$$

where R is phenyl or phenyl carboxy radical. The double-bond chain end, produced by disproportionation, is thought to be the most unstable [5].

Because sample No. 1, of the lowest molecular weight, has the most chain ends of all the samples, the mass spectra of the volatilized products from sample No. 1 were examined in detail, and the ions of *m/e* 91, 118 and 177, which are considered to be produced from the phenyl chain end, as is shown below, are observed over the whole decomposition temperature range, while the ions of *m/e* 105, 135 and 162, which seem to be produced from the phenyl carboxy chain end, are similarly observed.





The temperature dependence of the ion currents at *m/e* 91 and 105 is shown in Fig. 4. The volatilization rate is almost identical to that of the monomer and the ion is observed even in the fourth and last step of the decomposition, though the rate in the first and second steps is somewhat smaller than that of the monomer, presumably due to a low diffusion constant and low vapor pressure of the products. From these facts it can be concluded that the phenyl and phenyl carboxy chain ends do not initiate depolymerization.

Thus, the second and third depolymerizations are initiated at the other chain ends made by the disproportionation. Considering the thermal stabilities of the chain ends [5], the chain end with the double bond seems to initiate the second depolymerization, and the other saturated chain end seems to initiate the third depolymerization. However, clear evidence, such

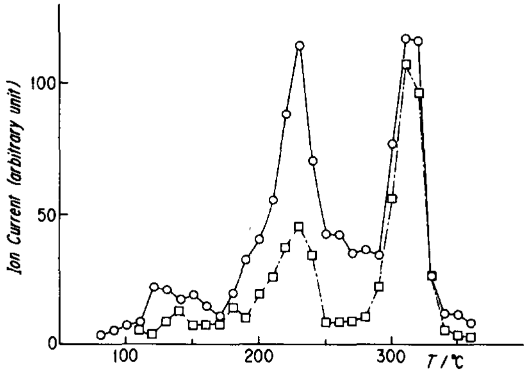


Fig. 4. EGA curve of chain end radicals. (□——□) *m/e* 91; (○——○) *m/e* 105, 2°C min^{-1}.

as ions originating from these chain ends cannot be obtained because of the similarity of these chain ends to the monomer.

From points (3) and (6) above, it is also inferred that depolymerization does not seem to terminate with disproportionation, but mainly on recombination of the unzipping radical ends, because the recombination does not produce unstable chain ends, like those with double bonds produced by disproportionation. If the termination was exclusively via disproportionation, the fourth depolymerization would not occur, because the residue would also be depolymerized due to the unstable chain ends produced by the disproportionation. However, it cannot be completely denied that the termination proceeds partly by disproportionation. If the termination is exclusively via recombination, the peak area ratios of the second and third steps would be equal to each other. Otherwise, the ratio of the third step becomes larger than that of the second step, because the saturated chain ends produced by the disproportionation due to termination of the second depolymerization initiate the third step, together with both the saturated and unsaturated chain ends produced in the third depolymerization, while only the unsaturated chain ends initiate the depolymerization in the second step. The results shown in Table 2 suggest the possibility that the termination proceeds partly via disproportionation.

The thermal decomposition of PMMA has been investigated by many workers and it was pointed out that it occurs via multiple processes (e.g., ref. 5). The discrepancy in the postulated mechanism, as well as in the estimated kinetic parameters [8,11], has also been pointed out. However, the cause for this discrepancy has not yet been made thoroughly clear. As is seen above, it was eventually clarified that the cause is a four-step depolymerization; these depolymerizations were hitherto not observed thoroughly or separately from each other.

For the separation, isothermal observation in a relatively high temperature range is not appropriate, and thermoanalytical observation is preferable to isothermal observation. Thermal analyses, such as thermogravimetry (TG), evolved gas detection (EGD) and differential scanning calorimetry (DSC), have also been applied to the depolymerization of PMMA. For instance, Wilson and Hamaker found two steps by TG and observed three steps by EGA [14]. Similarly, Sazanov et al. [16], Hirata et al. [21] and Goh and Lee [22] observed a two-step depolymerization in their DTG and TG curves. On the other hand, McNeill obtained EGD curves for various types of PMMA by one variety of EGD, i.e., so-called thermal volatilization analysis [12,13], and he found three steps in the depolymerization. The resolution in the EGD curves is not as high as that in the EGA curves by the present authors. This difference is presumably due to the difference in the detection of the volatilized products; in McNeill's EGD apparatus there is a long tube between the sample container and the Pirani gauge detector, and in the present authors' EGA apparatus the volatilized products are directly

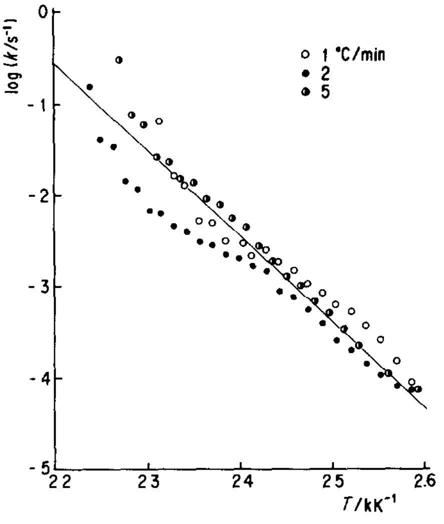


Fig. 5. Arrhenius plot of rate constants of first depolymerization on the assumption of a 1.5 order of reaction. Heating rates are indicated in the figure.

introduced as a molecular beam into the ionization region for analysis. This direct introduction gives a high resolution, and with this apparatus the dependence of the amount of product on the molecular weight and the polymerizing process can be clearly observed.

Furthermore, it has been revealed from the results obtained so far that EGA with a mass spectrometer, in which the volatilized products are directly introduced into the ionization region as a molecular beam, is a powerful tool for characterization of PMMA. A high-sensitivity EGD, in which the volatilized products are detected in a similar manner, also seems to be a useful tool for the same purpose.

Kinetic information can also be obtained from the temperature dependence of the ion currents, because the ion current is proportional to the

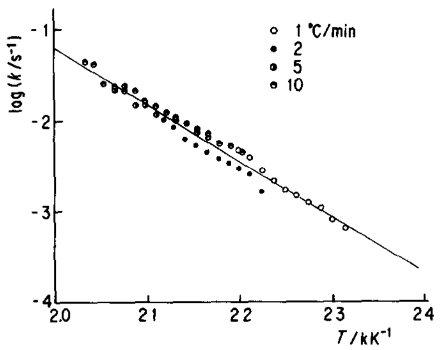


Fig. 6. Arrhenius plot of rate constants of second depolymerization on the assumption of a first-order reaction. Heating rates are indicated in the figure.

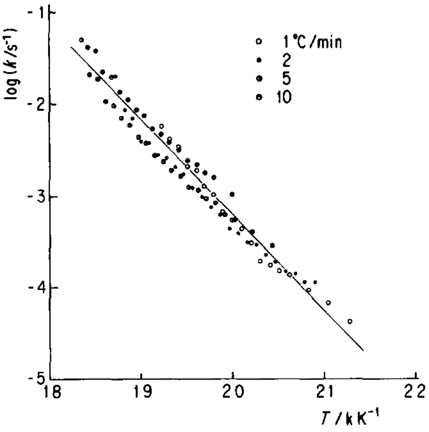


Fig. 7. Arrhenius plot of rate constants of third depolymerization on the assumption of a first-order reaction. Heating rates are indicated in the figure.

volatilization rate. The simple depolymerization of the very high molecular weight sample No. 7 has already been analyzed kinetically and is reported elsewhere [15]. Although the kinetic analysis of the other samples is somewhat difficult and complicated by overlapping of adjacent peaks in the EGA curves, the same method, proposed by one of the present authors (T.O.) [23], was applied to sample No. 4, because the separation of the EGA peaks for this sample is just sufficient for the kinetic analysis.

First, the activation energy was estimated by plotting the logarithms of the heating rate against the reciprocal absolute temperature at the peak, but this value is an approximate one, because the peak tends to shift slightly to a different point due to the overlapping of the peaks. With the estimated activation energy, the reduced time and rate were calculated, and the

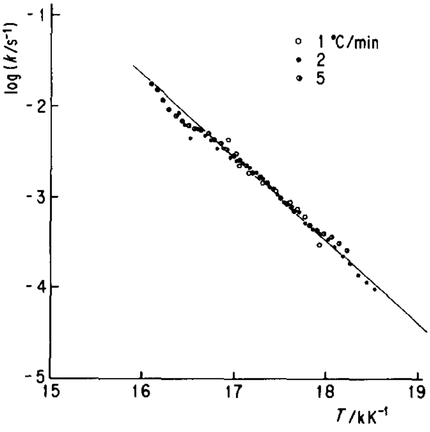


Fig. 8. Arrhenius plot of rate constants of fourth depolymerization on the assumption of a first-order reaction. Heating rates are indicated in the figure.

TABLE 3

Kinetic parameters of four depolymerizations of sample No. 4

	Order of reaction	ΔE (kJ mol^{-1})	log A (s^{-1})
Step 1	1.5	182	20.4
Step 2	1	118	11.3
Step 3	1	207	18.4
Step 4	1	172	12.8

mechanism was elucidated with these values [15,23]. Because the results thus obtained may contain some error due to the roughly estimated activation energy, the rate constants were estimated by using the relative reaction rate, i.e., the ion current, and the conversion obtained by integration of the current along the EGA curves, on the assumption of the mechanism obtained above [15,23]. The Arrhenius plots of the obtained rate constants are reproduced in Figs. 5–8. Except for the first depolymerization, a first-order reaction was assumed and it was found to be the real mechanism, because linear plots were obtained with a small scattering of the points. On the other hand, the best-fitted mechanism for the first depolymerization gives an order of reaction of 1.5 and the best Arrhenius plot of the rate constants was obtained on the assumption of this reaction order. However, it is not so good as the others, and rather large scattering was observed. For the first depolymerization of sample No. 5, the same procedure for kinetic analysis was applied, and the best-fitted plot is a similarly scattered Arrhenius plot obtained on the assumption of a 1.5 order of reaction. It cannot be denied completely that the kinetic parameters and mechanism obtained for the first depolymerization may not be real; the cause of such large scattering of the plot as in Fig. 5 is not clear at present. The results of the analysis are also summarized in Table 3. The disagreement between the kinetic parameters for the fourth depolymerization in Table 3 and the parameters in our previous paper seems to be caused by the overlapping of the EGA peaks; the previous parameters are considered to be better.

Before significant comparison can be made between the kinetic analyses reported in the literature, the depolymerization and initiation observed by the reporters must be identified exactly. However, the four steps of depolymerization had not been clearly elucidated until now, and an exact and significant comparison is difficult to make at present.

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