

# Depolymerization of Fluoroalkyl Methacrylate Polymers as Studied with Thermogravimetry

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## Synopsis

Thermal behaviors of a few kinds of poly(fluoroalkyl methacrylate) prepared by  $\gamma$ - or UV-ray polymerization were investigated by using thermogravimetric measurements with the intermittent analysis of the gaseous products. The degradation of fluoroalkyl methacrylate polymers, monomeric units of which were  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2(\text{CF}_2\text{CF}_2)_n\text{H}$ ,  $n = 1, 2,$  and  $3,$  proceeded according to the depolymerization mechanism reproducing the pristine monomer exclusively, but the thermogram in inert atmosphere showed the features of a two-step reaction. Two species of polymer differing in the heat stability were supposed to exist in the polymeric substance produced by  $\gamma$ - or UV-ray irradiation, and the fraction of polymer having lower heat stability increased with the increasing length of the fluoroalkyl ester group. In air, however, the thermogram of poly(fluoroalkyl methacrylate) showed no such a stepwise weight decrease as was observed in inert atmosphere with the elevating temperature, and the temperatures at which the depolymerization was introduced shifted to a much higher region. The results were ascribed to the reaction of initiating polymer radicals produced on polymer having lower stability with oxygen to form hydroperoxide, which once stabilized the polymer radicals and obstructed the initiation of the unzipping reaction till higher temperature.

## INTRODUCTION

It has well been recognized that thermal degradation of most of alkyl methacrylate polymers could be interpreted by the depolymerization mechanism. We have studied the radiation and photopolymerization of a few fluoroalkyl methacrylates which have the following monomeric structures,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2(\text{CF}_2\text{CF}_2)_n\text{H}$ , where  $n = 1, 2,$  and  $3,$  and noticed that the polymers of these esters exhibited the excellent heat stability in air rather than in an inert atmosphere, and the apparent aspect of depolymerization differed considerably depending on the atmosphere.

The present article deals with the thermogravimetric analysis of these polymers along with the continuous determination of the evolved substances with gas chromatography and comparison of the results with those on poly(methyl methacrylate).

## EXPERIMENTAL

**Materials.** The polymers of 1,1, $\omega$ -trihydroperfluoroalkyl methacrylate (FMA) of the general formula:  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2(\text{CF}_2\text{CF}_2)_n\text{H}$ , where  $n = 1$  (FMA<sub>1</sub>),  $n = 2$  (FMA<sub>2</sub>), and  $n = 3$  (FMA<sub>3</sub>), were prepared by  $\gamma$ -ray polymerization or ultraviolet-ray polymerization without a sensitizer as was described previously.<sup>1</sup> Those methods of polymerization were adopted to avoid a possible alteration in stability owing to the kind of chain ends. The

polymers were purified by reprecipitating into methanol-water (80:20 by volume) mixture followed by drying under vacuum. The condition of polymerization is described on each sample in the respective figures.

**Thermogravimetric Measurements.** Thermogravimetry (TGA) accompanied with derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were performed on about 10–20 mg of polymer placed in the platinum dish against the aluminum oxide as a control in the stream of helium or in air. In some of the thermogravimetric measurements with the temperature elevation at a constant rate, the gaseous products were transferred into the automatic sampler by the stream of helium and analyzed intermittently by gas chromatograph. The experimental conditions including sampling intervals and so forth are shown in the respective figures. The apparatus used for measurements was Rigaku-Denki differential thermobalance with Auto Gas Sampler.

## RESULTS

### Depolymerization in Inert Atmosphere

Figure 1 shows the typical thermal decomposition of FMA polymers vs. temperature relationship obtained from TGA at constant temperature elevation. It can be seen that in the stream of helium FMA polymers showed the stepwise decrease in weight with the increasing temperature. The fraction which decomposed in the former stage looked to increase with the increasing length of the fluoroalkyl group. Such a two-step decomposition of FMA polymers was more clearly demonstrated when the composition of the evolved gas mixture was examined, and the quantity of the regenerated monomer was measured at a constant interval during the temperature elevation.

The results of such measurements are shown in Figures 2 and 3, in which the relative amounts of the regenerated monomer were plotted against temperature together with the integral fraction of decomposed polymers.

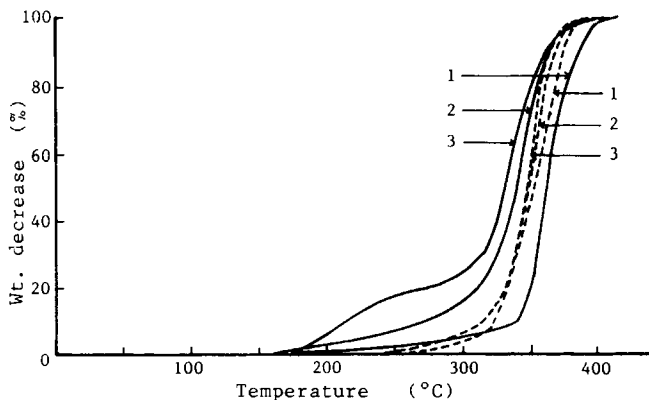


Fig. 1. Thermal decomposition of FMA polymers in helium and in air: rate of temperature elevation, 5°C/min; (—) in the stream of He (50 mL/min); (- - -) in air; (1) polyFMA<sub>1</sub>; (2) polyFMA<sub>2</sub>; (3) polyFMA<sub>3</sub>. For sample preparation see Figure 5.

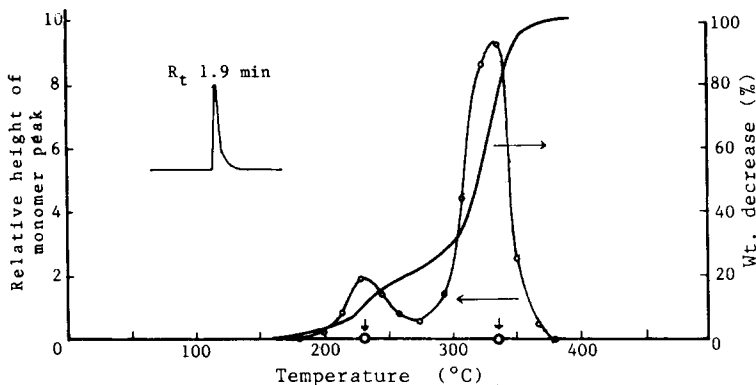


Fig. 2. Amount of regenerated monomer at respective temperatures during the thermogravimetry of polyFMA<sub>2</sub> in helium: rate of temperature elevation, 2.5°C/min; gas chromatography, PEG 6000, 1 m column at 150°C; measuring interval, 6 min by 10 s sampling; flow-rate of He, 50 mL/min; (○) on the abscissa show the temperature at which the DTG curve reached maxima.

Typical gas chromatographic peaks of the products are also shown in each figure. No other decomposition products than respective monomers were detected throughout the temperature range studied, in spite of the complicated change in rate of decomposition. There were two maxima in the quantity of evolved monomer, at 230°C and 330–340°C on both polymers, which coincided with the two maxima in the rate of weight decrease of polymer obtained by DTG. The rates attained a clear minimum around 270°C, which was followed by the resumption of the monomer regeneration. Concerning these temperatures there was not much difference between those of polyFMA<sub>2</sub> and those of polyFMA<sub>3</sub>. The fraction of lower heat stability polymer, however, was larger in polyFMA<sub>3</sub> than in polyFMA<sub>2</sub>, as is shown by the ratio of the maximum peak height of regenerated monomer in Figures 2 and 3.

The two-step depolymerization was also exemplified by the measurements at fixed temperatures. Figure 4(a) shows the weight decrease when the

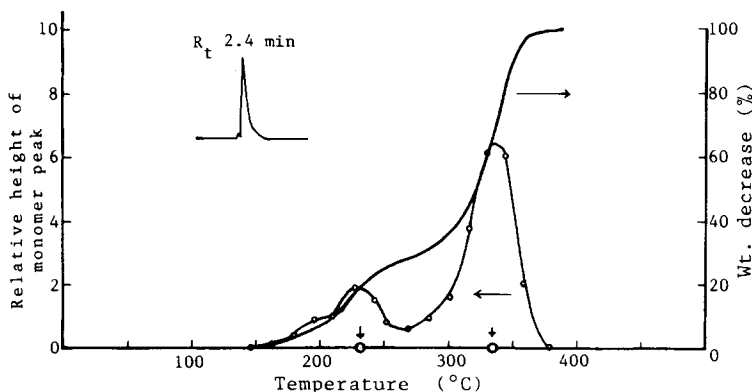


Fig. 3. Amount of regenerated monomer at respective temperatures during the thermogravimetry of polyFMA<sub>3</sub> in helium: rate of temperature elevation, 2.5°C/min; gas chromatography, the same as Figure 2.

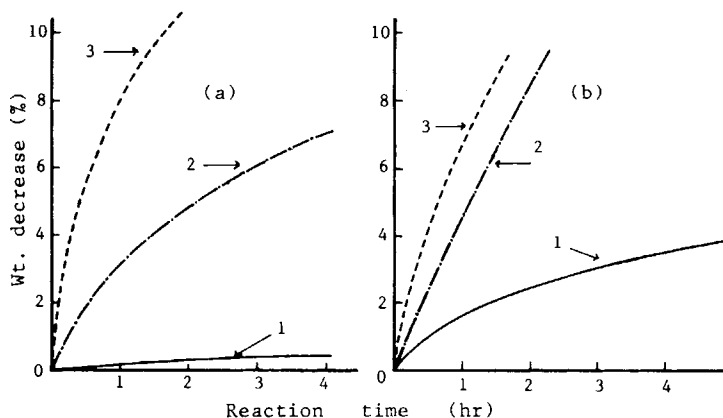


Fig. 4. Depolymerization of FMA polymers at fixed temperatures in helium: (a) 210°C; (b) 262°C. Preliminarily, the polymer samples were kept at 210°C for several hours [see (a) for the observed results] and then brought to 262°C. He 100 mL/min.; (1) polyFMA<sub>1</sub>; (2) polyFMA<sub>2</sub>; (3) polyFMA<sub>3</sub>.

polymer was kept at 210°C for several hours in a stream of helium; after that the remaining polymers were brought to 262°C rapidly and kept a while at this temperature, the results of which are shown in Figure 4(b). It can be seen that the rate of depolymerization of polyFMA<sub>3</sub> at 262°C was lower than that at 210°C. Probably the most of the fraction depolymerizable at lower temperature was consumed during the previous heating at 210°C and more stable one decomposed at 262°C with a lower rate. Such a remarkable fact was not observed in the other FMA polymers in Figure 4, but the difference in rates at both temperatures did not seem to be large compared with those observed on other polymers of depolymerizable nature.

The FMA polymers on which the decomposition measurements were carried out were found to have such polymerization degree distributions as shown in Figure 5. The adopted samples of polyFMA<sub>1</sub> and polyFMA<sub>2</sub> showed the presence of broad but obviously single peak, whereas that of polyFMA<sub>3</sub> had two peaks in distribution curve. Such a fact, however, may not be the

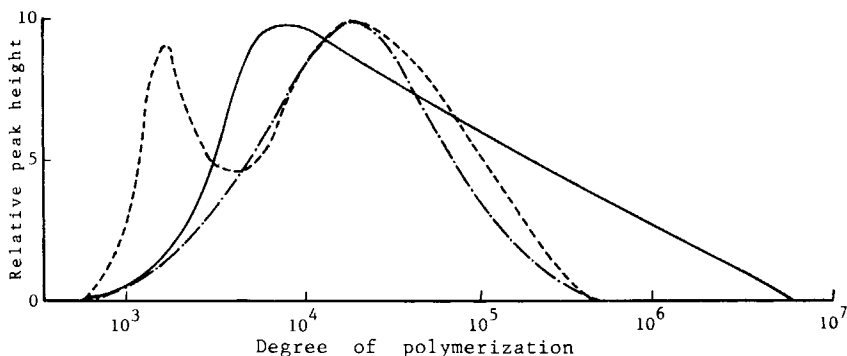


Fig. 5. Polymerization degree distribution of FMA polymers determined by gel permeation chromatography: column, Shodex 80MS; solvent, DMF; temperature, 70°C: (—) polyFMA<sub>1</sub> prepared by  $\gamma$ -ray bulk polymerization at a dose rate of  $4 \times 10^4$  R/h, 0°C, 6 h; (- · -) polyFMA<sub>2</sub> by  $\gamma$ -rays at  $4 \times 10^4$  R/h, 0°C, 6 h; (- - -) polyFMA<sub>3</sub> by  $\gamma$ -rays at  $4 \times 10^4$  R/h, -78°C, 17 h.

main reason for two-step depolymerization, because the latter was observed on polyFMA<sub>1</sub> and also on polyFMA<sub>2</sub>, which had only one peak in distribution curve respectively.

Figure 6 shows the result of the same experiment as above on polyMMA prepared by  $\gamma$ -ray bulk polymerization at 25°C. The presence of the fraction depolymerizable at lower temperature was not so apparent either from TGA curve or gaseous product analysis, contrary to FMA polymers.

Figure 7 shows the effect of changing the rate of temperature elevation on overall thermogram of polyFMA<sub>2</sub>. With the increasing rate of temperature elevation the first step of thermogram seemed to merge into the second step, which suggested that the two reactions should occur independently of each other rather than conflicting with each other.<sup>2</sup>

For the depolymerization reaction, the following equation is generally accepted to describe the kinetic feature:

$$-dh/dt = kh^n$$

where  $h$  pertains to the unreacted active weight fraction and  $n$  to the order of the process. The apparent specific rate constant  $k$  can be written as the Arrhenius equation,  $k = Ae^{-E_a/RT}$ , where  $E_a$  represents the overall activation energy of depolymerization. Several depolymerizable polymers have been known to give rise to rate curves which are linear over much of the volatilization range, as required by the first-order rate equation.<sup>3</sup> Therefore, the overall apparent activation energy of depolymerization can be obtained from the slope of  $\log(-dh/dt) - n \log h$  against  $1/T$  plot.<sup>4</sup> Figure 8 is such plots for TGA curves obtained in helium atmosphere on polyFMA<sub>2</sub> and polyFMA<sub>3</sub>, where  $n = 1$  was assumed *a priori* for calculation. It can be seen from Figure 8 that a big gap existed between two stages of reaction in respective curves, where the rate of monomer regeneration reached minimum. The results were summarized in Table I with those in air, which will

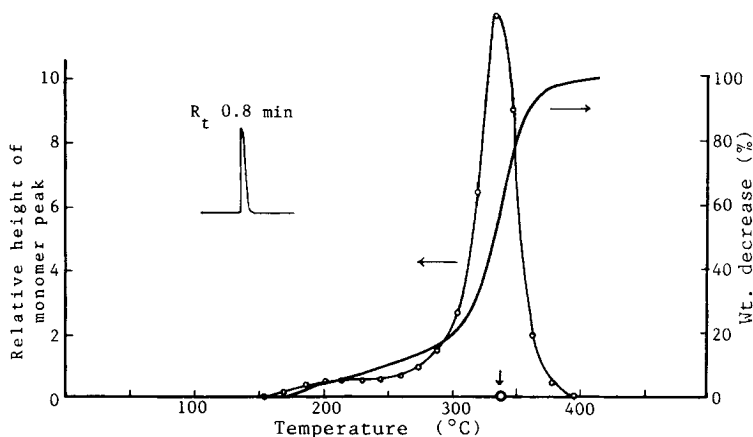


Fig. 6. Amount of regenerated monomer at respective temperatures during the thermogravimetry of polyMMA in helium: rate of temperature elevation, 2.5°C/min; gas chromatography, the same as Figure 2.

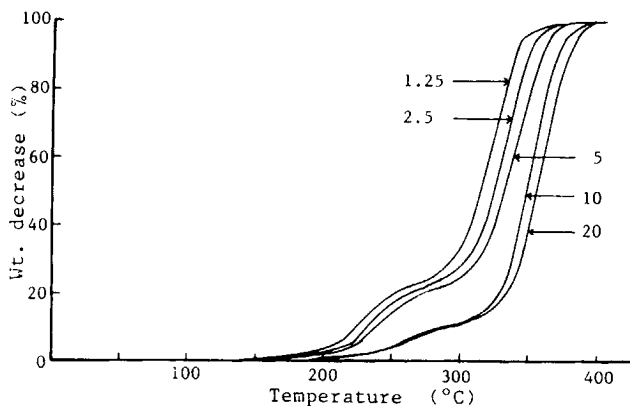


Fig. 7. Effect of changing the rate of temperature elevation on the thermogram of polyFMA<sub>2</sub> in the stream of helium, 100 mL/min. Numbers in the figure represent the rates of temperature elevation by °C/min.

be mentioned later.  $E_a$  of the second step in helium seemed to be not so different from that in air in every polymer. [The calculation of  $E_a$  from the following approximated equation was also performed<sup>3</sup>:  $E_a = (dh/dt) \cdot RT^2 / 2.3 h \log h - 2RT$ . The results, however, were less decisive than those by the graphical method cited above.]

### Depolymerization in the Presence of Air

The TGA curves of FMA polymers measured in the presence of air were also shown in Figure 1 by broken lines. The most distinguishable feature of the thermograms in air when compared with those in helium atmosphere seemed to be that the depolymerization at low temperature was not ob-

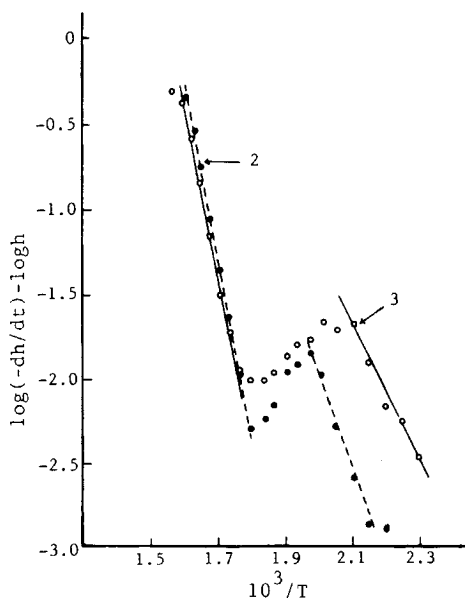


Fig. 8. Arrhenius plots of the rate of depolymerization: (2) polyFMA<sub>2</sub>; (3) polyFMA<sub>3</sub>.

TABLE I  
Overall Activation Energies of Depolymerization in Helium and in Air<sup>a</sup>

Polymer	In He (kcal/mol)		In air (kcal/mol)
	First step	Second step	
PolyFMA <sub>1</sub>	16	61	48
PolyFMA <sub>2</sub>	23	51	73
PolyFMA <sub>3</sub>	19	45	58
PolyMMA	—	41	54

<sup>a</sup> Rate of temperature elevation, 5°C/min.

servable any more and the two-stepwise reaction was almost merged imperceptibly into a single step. The depolymerization in air proceeded with a similar way to the latter step of that in helium. Apparently the FMA polymers were more stable in air than in helium and kept undegraded till higher temperature. The depolymerization, however, proceeded a little exothermically in air. Alteration of the rate of temperature elevation did not bring about the distinguishable change to the thermogram, as is seen in Figure 9.

The stabilization of depolymerizable polymer in air was also certified by the experiment at a constant temperature, the result of which is shown in Figure 10. It shows the weight decrease of FMA polymers at 210°C and 262°C. By comparing with Figure 4, it can be known that the reaction at 210°C was completely nullified by the existence of air, and the difference among the rates of depolymerization of FMA polymers diminished.

The obtained  $E_a$  was summarized in Table I; the values seemed to be not so different from  $E_a$  of the second step in helium on every polymer.

As for the possible different profile of the thermogram brought by the change of polymerization condition, TGA measurements were carried out on FMA<sub>2</sub> polymers prepared by  $\gamma$ -ray and ultraviolet-ray irradiation at various temperature. The results were much the same concerning the range of decomposition temperature and the overall activation energy of depolymerization.

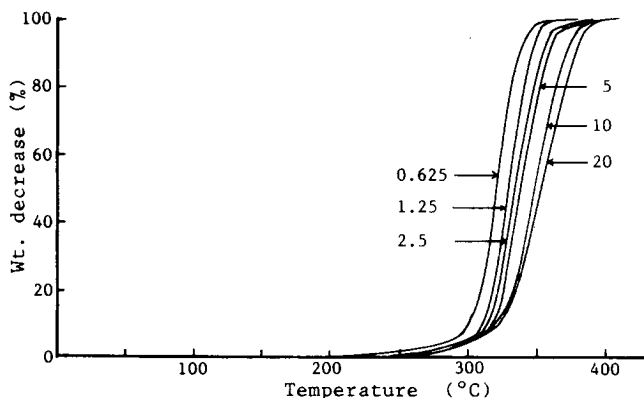


Fig. 9. Effect of changing the rate of temperature elevation on the thermogram of polyFMA<sub>2</sub> in air: numbers in the figure represent the rate of temperature elevation by °C/min.

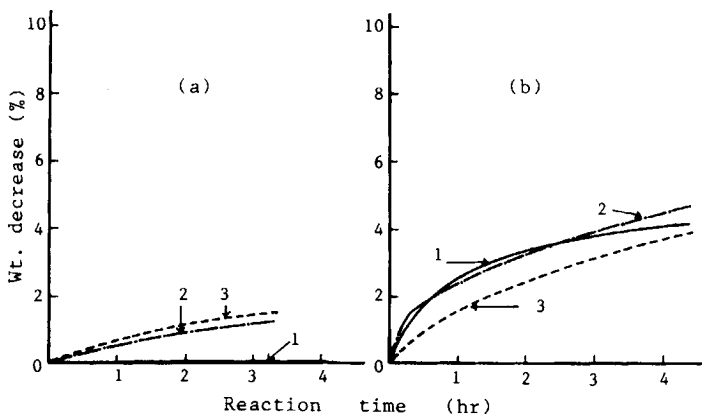
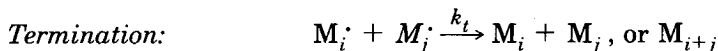


Fig. 10. Depolymerization of FMA polymers at fixed temperatures in air: (a) 210°C; (b) 262°C. Preliminarily, the polymer samples were kept at 210°C for several hours [see (a) for the observed results] and then brought to 262°C: (1) polyFMA<sub>1</sub>; (2) polyFMA<sub>2</sub>; (3) polyFMA<sub>3</sub>.

## DISCUSSION

When FMA polymers were subjected to thermal degradation, the products from them were exclusively their monomers irrespective of the reacting atmosphere, and the thermograms could be recognized as the result of the depolymerization reaction. As far as gas chromatographic evidence was concerned, there occurred no ester decomposition. The results seem to be natural because there is no  $\beta$ -H in fluoroalkyl group studied.

The mechanism of typical depolymerization reaction may be interpreted by the following equations:



where  $n$  is the chain length of the starting polymer and  $M_i$ ,  $M_j$ , etc., or  $M_i \cdot$ ,  $M_j \cdot$ , etc., denote respectively the "dead" polymer molecules or long-chain radicals, in which  $i$ ,  $j$ , etc., represent the length of monomer units. It has been shown that the initiation process takes place at the chain ends in the thermal depolymerization of polyMMA.<sup>5</sup> Since there are no tertiary hydrogen atoms in the polymer molecules, the transfer reaction may not be important in this system.

The fact that FMA polymers degraded via two-step process in inert atmosphere suggests to us the existence of two kinds of polymer mixed in one preparation, which had the same monomeric composition but differed with each other only in respect of thermal stability, because the degradation product was the same, pure monomer, throughout the temperature range studied. Although there are no additional data on the presence of two kinds of polymer and on the structural difference between them at present, except GPC data already shown in Figure 5, it is probable that the polymer mol-



ecules possessing the terminal unsaturation were more vulnerable, thus initiated unzipping at lower temperature. On polyMMA the unsaturated chain terminal structures formed in the termination by disproportionation during polymerization have been known to behave more unstably owing to the possible formation of the stable allylic-type radicals by their scission.<sup>6-8</sup> The same sort of cause would be valid and more eminent for polyFMA depolymerization.

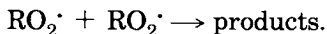
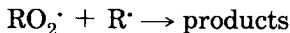
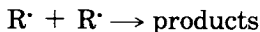
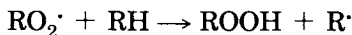
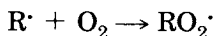
The overall activation energy of depolymerization,  $E_a$ , is given by the following equation from the above simplified mechanism of radical depolymerization:

$$E_a = E_d + 0.5E_i - 0.5E_t$$

where  $E_p$ ,  $E_d$ , and  $E_t$  pertain to the activation energies of terminal initiation, depropagation, and termination. The fact that the  $E_a$  values for the former step were smaller than those of the secondary step, as is seen in Table I, may reflect the difference of  $E_t$  between both steps. In the previous report,<sup>1</sup> we have obtained 1.0 kcal/mol for the overall activation energy for polymerization of FMA<sub>3</sub> induced by  $\gamma$ -ray or UV-ray irradiation, which corresponded roughly to  $E_p - 0.5E_t$ , where  $E_p$  is the activation energy for propagation which is equal to  $E_d - \Delta H$  ( $\Delta H$  represents the heat of polymerization). Assuming  $\Delta H = 13$  kcal/mol of MMA<sup>9</sup> is much the same for FMA for instance,  $E_t$  of 10 and 61 kcal/mol were obtained for each step. These value may be bigger than they are because we ignored the effect of viscosity of media on the diffusion of radicals.

In air, the thermogram showed such remarkable differences from that in helium in every case that the temperature where the depolymerization was introduced shifted to much higher region, and that the fraction having lower stability against heat disappeared completely from the thermogram.

The oxygen in air was supposed to react with the initiating radicals by the well-established hydroperoxidation mechanism as follows:



Thus oxygen seemed to play once a role of inhibiting the progress of unzipping reaction by changing radicals to polymer molecules. The radicals would be produced at lower temperature, but oxidized to hydroperoxide which obstruct the progress of depolymerization at this temperature. Moreover, the fact that the overall activation energy of depolymerization in helium (latter step) was much the same with those in air would mean that the stabilizing effect of oxygen is valid only for the decomposition of the

unsaturated chain ends and not for the decomposition of the saturated ends. The results may be natural if we compare the dissociation energy of hydroperoxide, ca. 54 kcal/mol, with that of carbon-carbon bond of polyMMA, 53.5 kcal/mol.

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