

Depolymerization of Poly(fluoroalkyl methacrylate-co-methyl methacrylate) as Studied with Thermogravimetry

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Synopsis

Thermal behaviors of a few kinds of poly (fluoroalkyl methacrylate-co-methyl methacrylate) prepared by γ -ray copolymerization were investigated by using thermogravimetric measurements together with the intermittent analysis of the gaseous products. The thermal degradation of copolymers composed of one of fluoroalkyl methacrylates of the following 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 methyl methacrylate proceeded according to the depolymerization mechanism reproducing the pristine component comonomers exclusively, but their thermograms in inert atmosphere showed the feature of a two-step reaction. In air, however, thermograms of copolymers did not show such a stepwise decrease in weight with the elevating temperature, and temperatures at which depolymerization was introduced shifted to a much higher region. The overall aspects of depolymerization of copolymers seemed to be much similar to that of fluoroalkyl methacrylate homopolymer previously reported, and the retardation of depolymerization by air was considered to be due mainly to the stabilization of once-formed polymer radicals by oxygen.

INTRODUCTION

In the previous paper on the thermogravimetry of fluoroalkyl methacrylate homopolymers,¹ we reported that those polymers depolymerized by a two step process in inert atmosphere, while a steady depolymerization was observed in air, which took place at much higher temperature. Thus, we were impressed by the effect of air for the apparent stabilization of polymer against thermal treatment.

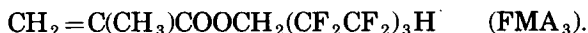
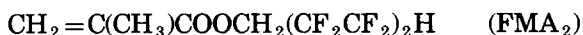
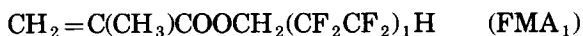
The copolymerization of one of those fluoroalkyl methacrylate monomers with methyl methacrylate has been carried out as a next stage of our study, because the homopolymers of the previous study, fluoroalkyl methacrylates, were too soft to be used as plastics and were considered to be better used as copolymers from the economical point of view as well.

We have carried out the thermogravimetric study on these copolymers, because the changes in thermal behavior brought about by the incorporation of a comonomer seemed to afford us some informations on the structural and chemical feature of copolymers. In particular, the effect of air on their depolymerization was expected to afford an important clue to our purpose. This report describes the results obtained by thermogravimetry accompanied with the intermittent analysis of the composition of gaseous products on the poly(fluoroalkyl methacrylate-co-methyl methacrylate).

EXPERIMENTAL

Preparation of Copolymer

1,1, ω -Trihydroperfluoroalkyl methacrylates(FMA) employed in this study are as follows:



The mixture of purified FMA and methyl methacrylate(MMA) was thoroughly degassed by repeated freezing and thawing procedure at a reduced pressure and sealed under 10^{-4} mmHg. The irradiation was carried out by γ -rays from ^{60}Co with the dose rate of 4×10^4 R/h for 17.5 hours at 25°C , till the complete conversion of monomer mixture was attained. A few copolymer samples were prepared by ultraviolet ray irradiation at 25°C . The bulk copolymers were dissolved in acetone and reprecipitated in the large amount of methanol or methanol-water mixture (95:5 by volume) to obtain the powdered copolymers. After filtering and drying the recovery of copolymers was more than 97%. Another detail of the polymerization procedure is seen in the previous article.²

Thermogravimetric Measurements

The thermogravimetric analysis (TGA) with derivative thermogravimetry (DTG), and differential thermal analysis (DTA), together with the analysis of volatile products by the automatic sampler-gas chromatography system were performed on a pulverized copolymer as well as on a bulk copolymer as obtained. The apparatus and the measuring conditions have already been written elsewhere,¹ and the latter is also seen in each figure.

RESULTS AND DISCUSSION

Effect of Copolymer Composition

Figure 1 shows the molecular weight distribution curves of the FMA_2 copolymer adopted for the thermal depolymerization in this study. Each copolymer exhibited a single peak in the distribution curve, which fell within the restricted region of molecular weight (referred to that of standard polystyrene) altogether, irrespective of the copolymer composition. The abscissa of the figure was plotted by the corresponding molecular weight of standard polystyrene. The difference in peak-height in spite of the same concentration of copolymer may depend on the difference of refractive index with the composition of copolymer.

Figure 2 shows the thermal decomposition of FMA_2 copolymers having various comonomer compositions in helium at constant temperature elevation. While the two-stepwise decomposition of FMA homopolymer in inert atmosphere has already been reported,¹ such phenomena were also ob-

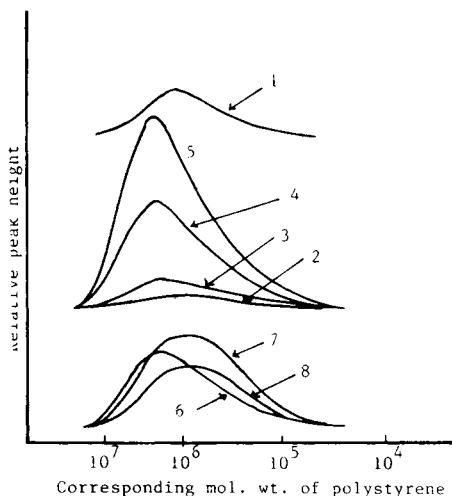


Fig. 1. Molecular weight distribution of poly(FMA-co-MMA) determined by gel permeation chromatography: column, Shodex 80MS; solvent, DMF; temperature, 70°C. 1 polyFMA₂, 2 poly(FMA₂-co-MMA)(70:30), 3 poly(FMA₂-co-MMA)(50:50), 4 poly(FMA₂-co-MMA)(30:70), 5 poly(FMA₂-co-MMA)(10:90), 6 poly(FMA₁-co-MMA)(10:90), 7 poly(FMA₂-co-MMA)(10:90), 8 poly(FMA₃-co-MMA)(10:90); 1 ~ 5 were prepared by γ -ray irradiation and 6 ~ 8 were prepared by UV-ray irradiation; (a:b) means the volume ratio of comonomers to prepare copolymer.

servable on copolymers, especially on those which were rich in FMA content. Generally the depolymerization of the initial step proceeded in the temperature ranging from 170 to 300°C, while the second step seemed to proceed at temperature higher than 300°C.

Another aspect of Figure 2 is that, the aggregated state of copolymer was supposed to considerably affect the ease with which the copolymer depolymerized. Thus, the polymer block as obtained by complete polymerization decomposed very rapidly in lower temperature region, whereas the pulverized copolymer depolymerized more reluctantly. It may be because air which suppressed the proceeding of the first-step depolymerization was not

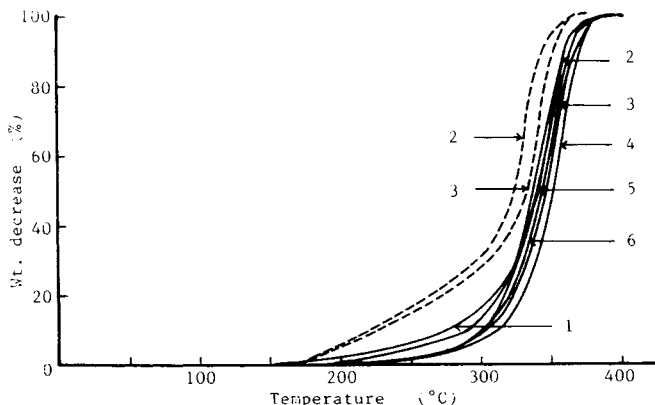


Fig. 2. Thermal decomposition of FMA₂ copolymers in inert gas: rate of temperature elevation, 5°C/min; in the stream of He (100 mL/min); —, reprecipitated copolymer; ---, block copolymer; 1 polyFMA₂, 2 poly(FMA₂-co-MMA)(70:30), 3 poly(FMA₂-co-MMA)(50:50), 4 poly(FMA₂-co-MMA)(30:70), 5 poly(FMA₂-co-MMA)(10:90), 6 polyMMA.

occluded in the bulk copolymer, but in the pulverized one the interposed air could not be removed completely by the mere flow of inert gas during experiment. The effect of air was examined on the reprecipitated powder of copolymers except for particularly noted cases.

The decomposition products of copolymer were examined by sampling the evolved gas at a constant interval during the constant temperature elevation. The gas was guided to a gas chromatograph through the pipe heated at 150°C. The results are shown in Figure 3.

The products were proved to be the mixture of regenerated FMA₂ and MMA throughout the whole temperature range, and no other product was detected. The typical gas chromatographic diagram is also seen in Figure 3. The relative amounts of FMA₂ and MMA evolved from (50:50)-copolymer manifested almost the same pattern against temperature. Both quantities of component monomers showed clear peaks at 200 ~ 220°C, and 345°C, corresponding to the two-step depolymerization, and in consequence the ratios of the first and the second peak heights were also the same with FMA₂ and MMA; $M_1/M_2 = 0.085$ on FMA₂ and $M_1/M_2 = 0.089$ on MMA, where M_1 and M_2 pertain to the heights of the first and the second peak, respectively.

Figure 4 shows the results of the same kind of experiment as above on the mixture composed of polyFMA₂ and polyMMA, 1:1 by weight, prepared

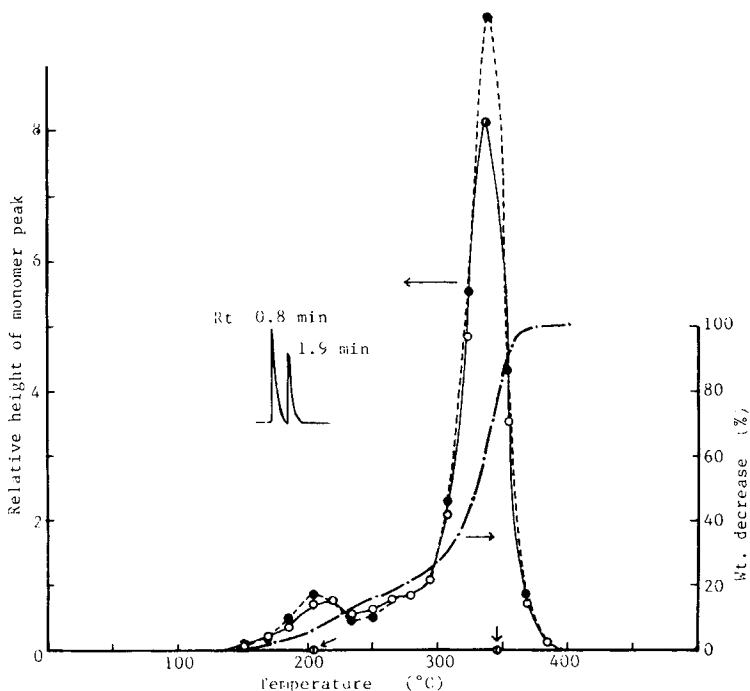


Fig. 3. Relative amounts of the regenerated monomers at respective temperatures during the thermogravimetry of poly(FMA₂-co-MMA)(50:50) in helium: rate of temperature elevation, 2.5°C/min; gas chromatography, PEG 6000, 1 m column, at 150°C; measuring interval, 6 min by 10 s sampling, flow-rate of He, 50 mL/min; (○) on the abscissa shows the temperature at which DTG curve reached maxima; —(○)—, FMA₂; --(●)--, MMA; —,—, TGA curve.

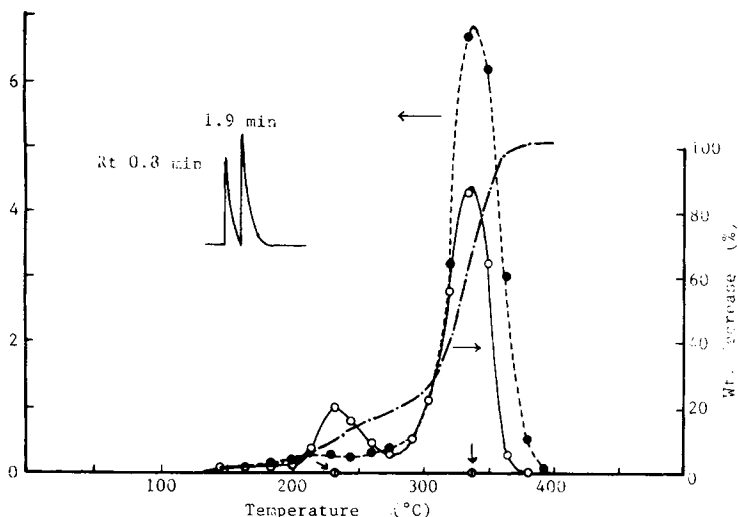


Fig. 4. Relative amounts of the regenerated monomers at respective temperatures during the thermogravimetry of the mixture of polyFMA₂ and polyMMA (50:50) in helium: rate of temperature elevation, 2.5°C/min; gas chromatography, the same as described in Fig. 3; (—○—), FMA₂; (---●---), MMA; (—), TGA curve.

by coprecipitation from the mixed solution of each polymer. The overall feature looks similar to that of Figure 3, except the lower temperature region. Both FMA₂ and MMA were detected more or less in every gas sample extracted by the automatic gas sampler, but no apparent peak of MMA seemed to exist in lower temperature range, while FMA₂ attained the clear maximum at 235°C; $M_1/M_2 = 0.23$ on FMA₂ and $M_1/M_2 = 0.049$ on MMA (the value was calculated from the height of plateau in MMA curve). When compared with Figure 2 of our former report,¹ which showed the depolymerization of polyFMA₂, it was obvious that the depolymerization was not affected by the presence of the other polymer, polyMMA. The peak temperatures of copolymer in Figure 3, however, were slightly different from both homopolymers, that is, the first peak was about 20°C lower whereas the second one was higher by 10°C than those of homopolymeric FMA₂. Otherwise the results seemed to be consistent with those of homopolymer depolymerization.

Concerning the overall thermal stability of copolymer in inert atmosphere, the monomeric composition of copolymer was considered to affect the thermal stability in the sense that the copolymer rich in FMA monomeric units contained the larger fraction of copolymer which decomposed at lower temperature. In Figure 5, the rate of depolymerization of copolymer was compared with that of homopolymer, where both were kept at 210°C at first, and next at 262°C. In inert atmosphere the depolymerization at 210°C which corresponded to the peak temperature of the first step proceeded at considerable rates, with the rate of depolymerization of homopolymer being larger than that of copolymer. But at 262°C which corresponded to the temperature where the second step depolymerization took place, the relative rate was reversed, that of copolymer being larger than that of homopolymer (the samples were kept to 210°C preliminarily to the completion of the first-step depolymerization).

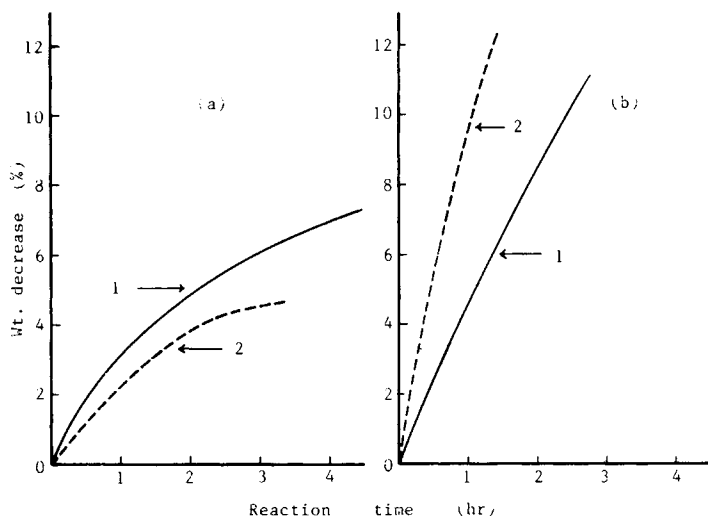


Fig. 5. Depolymerization of polyFMA₂ and poly(FMA₂-co-MMA) at fixed temperatures in inert atmosphere: (a) 210°C, (b) 262°C. Preliminarily, polymer samples were kept at 210°C for several hours (see (a) for the observed results), and then brought to 262°C for further depolymerization; He, 100 mL/min; 1 polyFMA₂, 2 poly(FMA₂-co-MMA)(50:50).

The two-stepwise depolymerization has been ascribed to the presence of the polymer fraction which had relatively lower heat stability in the polymer preparation.¹ The similar reason may be valid in the present case on copolymer of FMA. The copolymer moiety which possessed an unsaturated chain end would be formed as a result of the termination reaction by disproportionation mechanism, and its unzipped reaction seemed to occur at lower temperature than that of the saturated chain end.

Effect of Air on Depolymerization

When the thermogravimetry was performed in air, the rate of depolymerization was considerably affected by the aggregation state of copolymers. Figure 6 shows that the copolymer of the same origin behaved quite differently according to whether it was reprecipitated or not. Even in inert atmosphere the depolymerization of the copolymer block as obtained by bulk polymerization had begun to take place at somewhat lower temperature than that of the reprecipitated one (Fig. 2). The reason has been attributed to the retardation effect of the interposed oxygen. Especially in air, the inner part of the block copolymer seemed to depolymerize as in the no-oxygen circumstance, and therefore the weight decrease proceeded as rapidly as in inert atmosphere from the temperature nearly 100°C lower than that of reprecipitated one.

Figure 7 shows the overall depolymerization of copolymers in air. By comparing it with Figure 2, it can be seen that the initiation temperature where the depolymerization was introduced shifted to considerably higher temperature, and it was concluded that the first step of the two-step depolymerization disappeared completely and merged into a single step. But the final temperature where the depolymerization completed was much the

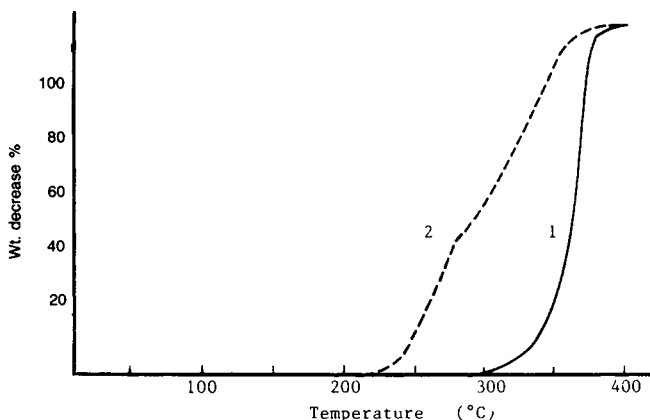


Fig. 6. Effect of aggregation state on the depolymerization in air of poly(FMA₂-co-MMA)(50:50): rate of temperature elevation, 5°C/min; 1 reprecipitated copolymer, 2 block state as copolymerized.

same irrespective of atmosphere. It seemed to be difficult to detect the relationships between depolymerization behavior and the composition of copolymer, because the thermograms did not differ greatly.

The change in feasibility of depolymerization by the atmosphere was made clearer when the weight decreases of copolymers kept at constant temperature were measured. Figure 8 shows the weight decrease of a few copolymers at 210°C and 262°C in air. In helium the depolymerization proceeded at considerable rates as shown in Figure 5, while in air the rates were low generally and in the extreme case some copolymers did not show any sign of weight decrease at this temperature. At 262°C, however, the rates of depolymerization remarkably increased and approached to those obtained in inert atmosphere [Fig. 5(b)]. The temperature range in which the major part of depolymerization proceeded in air roughly corresponded to that of the second-step depolymerization in inert atmosphere.

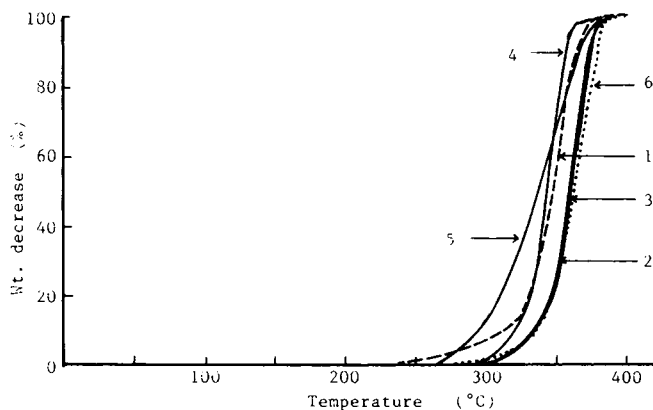


Fig. 7. Thermal decomposition of FMA₂ copolymers in air: rate of temperature elevation, 5°C/min; 1 polyFMA₂, 2 poly(FMA₂-co-MMA)(70:30), 3 poly(FMA₂-co-MMA)(50:50), 4 poly(FMA₂-co-MMA)(30:70), 5 poly(FMA₂-co-MMA)(10:90), 6 polyMMA.

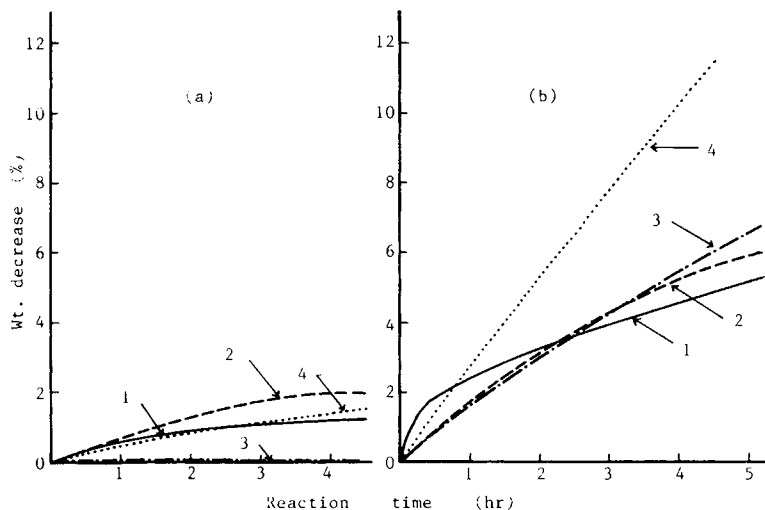


Fig. 8. Depolymerization of polyFMA₂ and poly(FMA₂-co-MMA) at fixed temperatures in air: (a) 210°C, (b) 262°C. Preliminarily, polymer samples were kept at 210°C for several hours (see (a) for the observed results), and then brought to 262°C for further depolymerization; 1 polyFMA₂, 2 poly(FMA₂-co-MMA)(70:30), 3 poly(FMA₂-co-MMA)(10:90), 4 polyMMA.

The effect of the kind of FMA monomer in copolymer on the depolymerization was examined and the result is shown in Figure 9, where each copolymer contained 10% by volume of FMA₁, FMA₂, or FMA₃. In inert atmosphere the difference due to FMA species was not observed, while some differences were manifested in air on the ease in depolymerization. And the results naturally reflected to their thermal stabilities in air at a constant temperature stagnation.

The order of FMA₃ - > FMA₂ - > FMA₁-copolymer in the ease of depolymerization in air corresponded well to that of FMA homopolymers.¹ The reason why such tendency did not appear in inert atmosphere, however, remains unsolved. It is remarkable that FMA₁ copolymer showed a good thermal stability up to nearly 280°C in air.

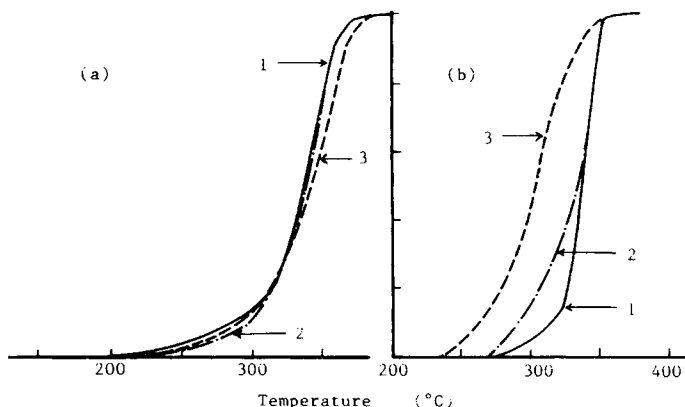


Fig. 9. Effect of the kind of FMA on the depolymerization of copolymers: rate of temperature elevation, 5°C/min; (a) in He, 100 mL/min, (b) in air; 1 poly(FMA₁-co-MMA)(10:90), 2 poly(FMA₂-co-MMA)(10:90), 3 poly(FMA₃-co-MMA)(10:90), polymer samples were prepared by UV-ray irradiation.

We have already discussed the cause of such an apparent stabilizing effect of air against thermal depolymerization in our previous report. Once-formed polymer radicals in thermally less stable polymer would be attacked by oxygen and altered to more stable forms, hydroperoxide or peroxide presumably, which endured the depolymerization up to near 280°C or more. Such a hypothesis assumed for the depolymerization of FMA homopolymers can also explain the thermal behaviors of FMA copolymers in air, although the effect would be reduced according to the content of comonomer, MMA.

Naturally such a stabilizing effect of oxygen is more prominent for thin film or for powdered polymer, and FMA copolymers are usable as methacrylic plastics of excellent thermal stability in air.

References

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