

The Effect of UV Light on the Subsequent Thermal Volatilization of Poly(methyl Acrylate)

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Synopsis

Films of poly(methyl acrylate) were exposed to UV light for periods of up to 45 min and were then degraded thermally under vacuum and at atmospheric pressure in nitrogen. Short exposures caused a marked decrease in the initial rate of thermolysis, and this was attributed to the removal of active centers. The formation of crosslinks during photolysis severely decreased the subsequent rate of volatilization of the polymer by inhibiting the unbuttoning chain reaction mechanism. Volatilization of exposed films under vacuum was slower than at atmospheric pressure in nitrogen, and this was attributed to the loss by evaporation of active centers. Activation energies for thermolysis before and after UV exposure were 160 and 167 kJ/mole, respectively. The subsequent thermal behavior of films exposed to UV light in oxygen and nitrogen atmospheres was closely similar.

INTRODUCTION

Poly(methyl acrylate) (PMA) has been shown¹ to degrade thermally by a random free-radical chain mechanism. This led to an acceleration of the rate of volatilization in the early stages of reaction, with a maximum in the rate in the region of 5–10% conversion. The maximum was ascribed to the build-up of material of low molecular weight that could volatilize following internal scission. Polymer fragments of average molecular weight 633 have been reported,² while on pyrolysis at 980°C a trimer constituted 53% of the volatile products.³ GPC studies on the soluble fraction of PMA remaining during photolysis have shown the accumulation of material of low molecular weight,⁴ and it has been suggested that a random chain scission mechanism similar to that occurring during thermolysis took place on photolysis. It was decided to investigate the degradation of PMA further by studying the effects of prior UV degradation on its subsequent thermal degradation.

EXPERIMENTAL

The polymer was prepared in a nitrogen atmosphere from freshly distilled methyl acrylate using azobisisobutyronitrile as initiator.⁵ Thin films (50 μ) were subjected to radiation from a high-pressure Hg lamp in a cell fitted with a quartz window and designed to allow exposures at room temperature in dried nitrogen and oxygen atmospheres.

A du Pont thermogravimetric system was used for thermal degradation

studies. Degradations were conducted under a vacuum of 10^{-2} torr as well as at atmospheric pressure in a stream of nitrogen. Samples were pumped at 90°C for 30 min to ensure the complete removal of small product molecules from the photolysis reaction. The sample temperature was then raised rapidly ($100^{\circ}\text{C}/\text{min}$) to the preselected isothermal degradation temperature. Sputtering was found to occur on thermal degradation above 270°C , but slow degradations at lower temperatures (250°C) gave reproducible results without resort to the use of a layer of copper powder which has been shown to influence degradation.¹ For the calculation of activation energies, dynamic runs were conducted at heating rates of 2° , 5° , 10° , 20° , and $50^{\circ}\text{C}/\text{min}$.

Molecular weight changes on heating were studied by placing the polymer in an evacuated tube in a furnace controlled at 250°C . Details of the GPC system were described earlier.⁴

RESULTS

On raising previously exposed samples rapidly to the selected degradation temperature, a sharp drop in weight occurred (Fig. 1). It can be seen from Figure 2 that for samples heated under vacuum, these weight losses were larger than for samples heated in nitrogen at atmospheric pressure, and the difference could be ascribed to the evaporation, under vacuum, of some larger fragments which did not come off at atmospheric pressure. To check on whether this initial weight loss was in fact due to the evolution of low molecular weight material produced on photolysis or due to volatiles formed from active centres produced by the light, exposed samples were rapidly heated to 200°C when a substantial loss occurred rapidly with no further change in weight. Raising the temperature in steps of 10°C brought about further small instantaneous losses which were attributed to the evaporation of correspondingly heavier chain fragments. No thermal degradation was measurable in unexposed polymers at these temperatures.

Following short exposures, the initial rate of thermal decomposition of samples was very much slower than that of unexposed samples, while prolonged irradiation led to a progressive increase in the initial rates (Fig. 3).

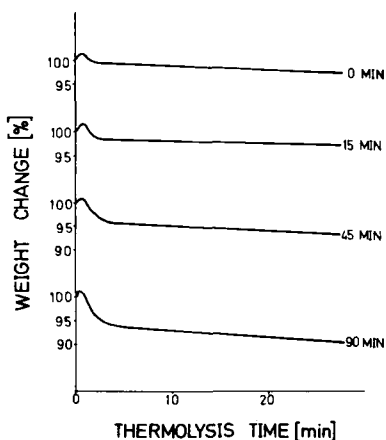


Fig. 1. TGA of polymer films after various exposure times.

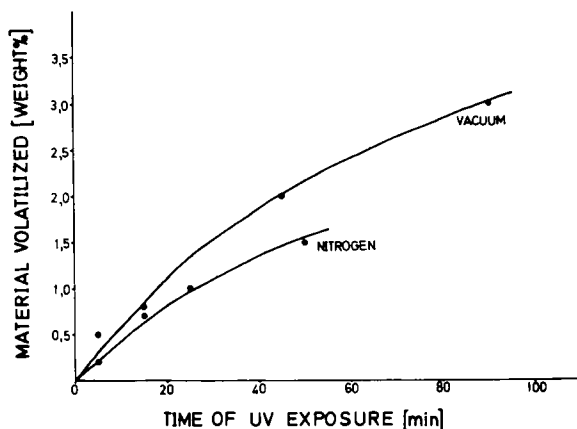


Fig. 2. Curves showing percentages of material lost by evaporation on heating air exposed films under vacuum and in nitrogen, respectively.

These rates were determined from the initial slope of the TGA thermogram, but the determination was complicated by allowance having to be made for the simultaneous evaporation of low molecular weight photolysis fragments during the first few minutes of heating. On continued thermal degradation of exposed films, the rate of volatilization decreased rapidly with increased percentage volatilization, dropping well below those found for unexposed films after similar degradation times and/or percentages volatilization. The thermal behavior of films following their irradiation in nitrogen closely resembled their thermal behavior after photolysis in oxygen. Figure 4 shows curves for the rate of volatilization as a function of percentage volatilization for unexposed polymer. These curves were obtained by differentiating the curves of cumulative percentage weight loss versus time of heating. The phenomenon of a maximum in the rate curves as shown by the polymer degraded in nitrogen is well known.¹ On the other hand, polymer degraded under vacuum showed a steady decrease in the rate of volatilization with time, and none of the previously exposed films exhibited maxima in their rates of volatilization.

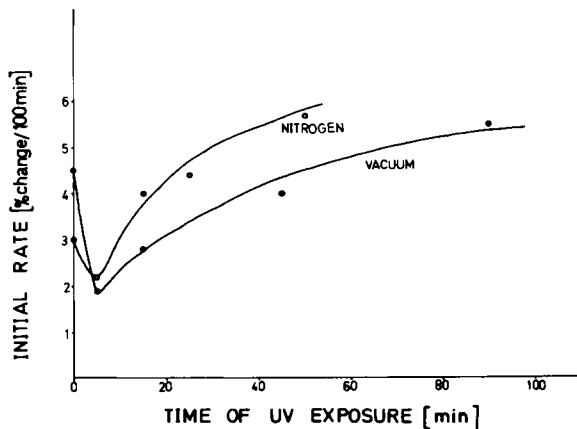


Fig. 3. Curves showing the initial rates of thermolysis following varying periods of UV exposure in air.

The activation energy for the thermal decomposition under vacuum of unexposed polymer was determined from a series of runs at different heating rates following the method of Flynn and Wall.⁶ Activation energy plots are shown in Figure 5 for different percentages of polymer volatilized. The activation energy remained constant at 160 kJ/mole from 5% to 80% volatilization. During the very early stages of degradation, lower activation energies pertained: 104 and 132 kJ/mole at 1% and 2% volatilization, respectively. Activation energies for exposed films were calculated from data given in Figure 6.

DISCUSSION

The results supported the conclusions of Cameron and Kane¹ regarding the occurrence of a chain reaction leading to random scission. The position of the maximum in the curves of rate of thermolysis versus percentage volatilization (Fig. 4) is sensitive to a number of factors including the relative rates of formation and evaporation of smaller fragments. In a nitrogen atmosphere, larger fragments would not be lost until they had undergone further internal scission and a build-up of such fragments would occur, leading to the observed maximum in the rate of thermolysis. The absence of a maximum in the vacuum thermolysis curve could be attributed to the more ready evolution of fragments at reduced pressures enabling relatively larger fragments to volatilize. Vacuum thermolysis studies showed^{1,2} that the maximum became much less pronounced at reduced temperatures and the absence of a maximum in vacuum at 250°C was not inconsistent with earlier studies. It was noteworthy that extrapolation of the rate of vacuum thermolysis, and the declining rate section of the nitrogen thermolysis curves, to zero percentage volatilization coincided.

The larger percentage of material lost (Fig. 2) on initial heating of a photolyzed film under vacuum than under atmospheric nitrogen pressure was simply due to the evaporation of larger fragments at reduced pressures. This further supported the above conclusions relating to the maxima in the thermolysis rate curves.

The very marked decrease (Fig. 3) in the initial rate of thermolysis fol-

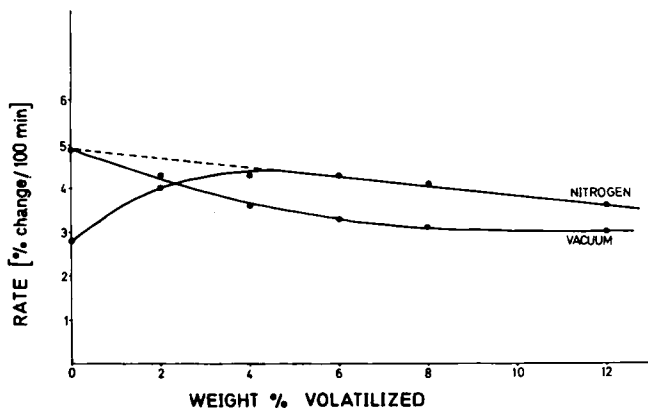


Fig. 4. Rate of volatilization as a function of conversion to volatiles for unexposed films.

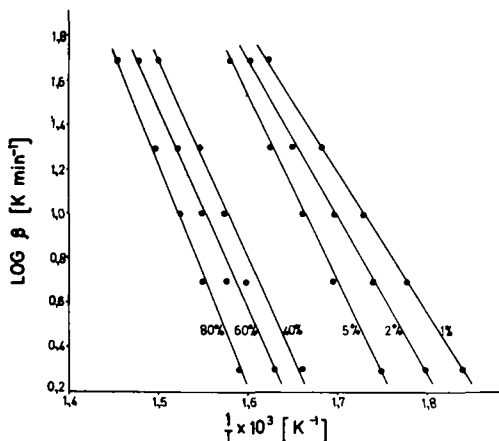


Fig. 5. Activation energy plots for unexposed film at different percentages volatilization.

lowing short UV exposures showed the presence in the polymer of active centers which were removed during photolysis. This was confirmed by activation energy plots (Fig. 5) of unexposed polymer, which showed that the activation energy for thermolysis increased progressively during volatilization of the first 5% of the polymer. Once these more active centers had reacted, the activation energy remained constant up to at least 80% volatilization. Activation energies for thermolysis of 146 and 142 kJ/mole have been reported.^{1,2} These values compare favorably with those found in this study viz., 104 kJ/mole at 1% volatilization, increasing to 160 kJ/mole at 5% to 80% volatilization.

An accumulation of lower molecular weight material on prolonged photolysis has been clearly established,⁴ and the observed increase in the initial rate of thermolysis following longer UV exposures (Fig. 3) supported the suggestion that smaller chain fragments produced volatile material on internal scission. Initial rates of volatilization of exposed films under vacuum were lower than initial volatilization rates in nitrogen, while the reverse was the case for unexposed films (Fig. 3). On continued degradation, rates of volatilization

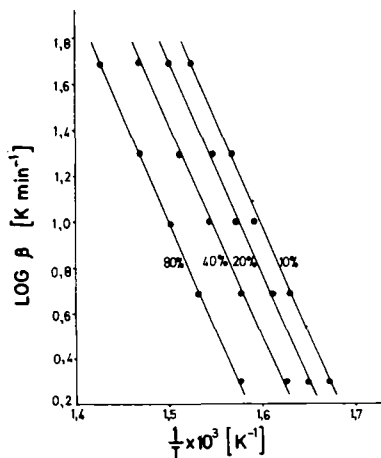


Fig. 6. Activation energy plots at different percentages volatilization for a film that had suffered 45 min of UV exposure.

under vacuum of unexposed film also decreased below those for unexposed polymer in nitrogen. These results showed that the more rapid evaporation of product fragments under vacuum removed some of the active centers from the system, thus preventing their initiating a chain reaction. This removal of chain-initiating centers was particularly marked in films that had suffered prolonged exposure and that therefore contained a large percentage of lower molecular weight material that could volatilize on internal scission.

In all cases, the rates of volatilization of previously exposed films decreased rapidly on continued thermolysis and soon became less than the rates for unexposed polymer at the same percentage volatilization. The high initial rates of volatilization of films that had suffered prolonged exposures was due to the increased formation of material of lower molecular weight; but an inhibiting effect was clearly operative in exposed polymers, and this became more noticeable on continued thermolysis once part of the low molecular weight material had reacted. Polymer films exposed to UV radiation in oxygen for 20 min showed the same activation energy (167 kJ/mole) for thermolysis as unexposed polymer (160 kJ/mole), indicating that photolysis had not altered the mechanism of the thermal degradation process. Instead, photolysis had produced centers that inhibited the rate of the subsequent thermal degradation. Since films photolyzed under nitrogen and oxygen showed closely similar behavior on thermolysis, the inhibition effect of photolysis was ascribed the formation of crosslinks in the polymer and not to the introduction of hydroperoxides. Cameron and Kane¹ proposed a random free-radical chain mechanism involving both intra- and intermolecular reactions for the production of chain fragment on thermolysis. Crosslinks would inhibit the unbuttoning intramolecular chain reaction by reducing the number of steps in the chain sequence. The large decrease in rate found on crosslinking showed that the intramolecular reaction played a major role in degradation.

Haken et al.³ showed that on pyrolysis the major product was a trimer resulting from a six-membered transition state following chain scission, and this reaction, too, would be inhibited by crosslinks. Crosslinking also occurred on vacuum thermolysis of unexposed polymer while the average molecular weight of the soluble fraction decreased progressively. However, films that had suffered even short exposures contained more crosslinked material than thermally degraded samples that had lost, say, 5% of their original

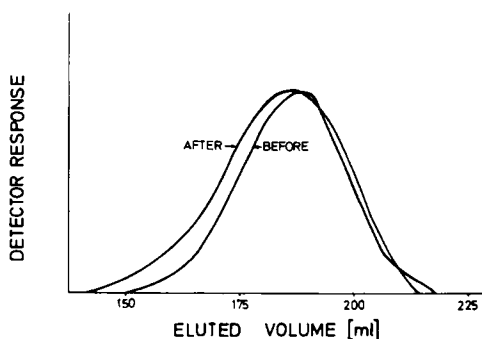


Fig. 7. GPC curves for a polymer film that had suffered 45 min of UV exposure before and after heating of the film to 250°C for 5 min.

weight by volatilization. The inhibiting effect on the unbuttoning reaction of the radiation induced crosslinks was therefore more noticeable.

When an air-exposed film was heated under vacuum for 5 min at 250°C, a small amount of crosslinking occurred (Fig. 7). This could be attributed to the reaction of peroxide or hydroperoxide groups introduced during photolysis. Films exposed in a nitrogen atmosphere did not show this effect on heating.

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