Molecular Weight Changes in Polyacrylates on Ultraviolet Irradiation

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Synopsis

Films of poly(methyl acrylate), poly(ethyl acrylate), and poly(n-butyl acrylate) were irradiated by means of a high-pressure mercury lamp in oxygen and nitrogen atmospheres, and the molecular weight changes accompanying degradation were studied as a function of radiation dose. Crosslinked material was formed in all cases though less crosslinking occurred in oxygen than in nitrogen atmospheres. Scission was the major reaction in the photo-oxidation of poly(ethyl acrylate), and this was explained in terms of acetal formation. In a nitrogen atmosphere, the proportion of units fractured to the proportion of units crosslinked per unit radiation dose was constant for the three polymers. Gel permeation chromatographic studies showed the accumulation of low molecular weight fragments on prolonged photolysis, and this was explained in terms of a chain reaction mechanism.

INTRODUCTION

The evaluation of molecular weight changes occurring during the photolysis of polyacrylates is complicated by the simultaneous occurrence of crosslinking and chain scission. Jacobs and Steele[1] have shown that the vacuum photolysis of poly(ethyl acrylate) (PEA) leads to a decrease in the swelling ratio of the polymer as well as to a decrease in viscosity of the soluble fraction, while Fox et al.[2] noted similar effects for poly(methyl acrylate) (PMA). They found much less crosslinked material on photo-oxidation than on vacuum photolysis.

We recently reported fully on the degradation products resulting from the photolysis in vacuum[3,4] and oxygen[5,6] of PMA, PEA, and poly(n-butyl acrylate) (PBA) and here detail the molecular weight changes accompanying evolution of volatiles. The molecular weight changes observed support aspects of the previously proposed degradation mechanism.

EXPERIMENTAL

The polymer preparation was described earlier.[3,4] Polymer samples having a narrow molecular weight distribution were prepared by the normal nonsolvent addition method[7] from 1 liter of a 10% (weight/volume) solution in acetone at 25°C. Distilled water was used as nonsolvent, and once the desired 10% weight fraction had precipitated, the solution was heated to 45°C to redissolve the precipitate. The system was allowed to cool overnight to 25°C during which time the fraction reprecipitated.

Films, approximately 50 μm thick, were irradiated in a special cell fitted with a quartz window. Dry nitrogen or oxygen was continuously passed through the system during irradiation with a high-pressure mercury lamp. After exposure, the films were pumped in a vacuum desiccator to ensure removal of all volatile products before the films were soaked in tetrahydrofuran for 24 hr to extract soluble material. The amount of crosslinked polymer formed was calculated from the weight of material retained on filtration of the solution through a specially prepared sintered glass filter. Changes in the molecular weight of the soluble fraction were studied by means of a Waters gel permeation chromatograph. Two-milliliter samples of a 0.25% (weight/volume) solution of polymer in tetrahydrofuran were injected into the GPC at 25°C. Six styragel columns with molecular exclusion limits of 10^2, 9×10^2, 2.5×10^3, 10^4, 5×10^4 and 2×10^5 nm, respectively, were used. Calibration was by means of polystyrene standards supplied by Waters Associates, and since only changes in molecular weight were considered, no attempt was made to convert the calibration to absolute values for the various polyacrylates used.

RESULTS

Scission and crosslinking occurred in all three polymers during exposure in both oxygen and nitrogen atmospheres. The increase in the amounts of insoluble material produced with increased radiation times is shown in Figures 1 and 2. Insoluble material initially formed at much the same rate on photolysis in oxygen and in nitrogen atmospheres for PMA and PBA, though the amounts of insoluble material produced on prolonged oxidation were slightly less. PEA formed very much less insoluble material on photo-oxidation than on photolysis in nitrogen.

The gel permeation chromatography curves for the soluble fraction of exposed films showed a spread of molecular weights to both higher and lower weight values, indicating that crosslinking and scission occurred simultaneously. On prolonged exposure, an accumulation of material of lower molecular weight was observed in both oxygen and nitrogen atmospheres (Fig. 3). The changes in $\bar{M}_w/\bar{M}_n$ for the soluble fraction are shown in Table I for short exposures.

TABLE I
Change in $\bar{M}_w/\bar{M}_n$ for the Soluble Polymer Fraction

Exposure time, min	PMA		PEA		PBA	
	N_2	O_2	N_2	O_2	N_2	O_2
1			2.15	2.57	3.84	3.49
2	1.90	1.98	3.13	3.06	3.74	3.79
3			3.70	3.50	4.26	4.53
4	2.30	2.46			4.55	4.31
5			4.83	4.10		
6	2.50				4.74	4.85
7				5.30		
8	3.10	3.60				

DISCUSSION

The radiation-induced crosslink formation and main-chain scission was investigated using the expression

$$S + S^2 = \frac{p_0}{q_0} + \frac{1}{u_1 r q_0}$$

derived by Charlesby and Pinner[8] for polymers with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \rightarrow 2$). Using the radiation time as a measure of radiation dose r, the inverse of radiation time was plotted against $S + S^{1/2}$ for the soluble fraction S (Fig. 4). The intercept of the plots yielded p_0/q_0, the proportion of units fractured to the proportion of units crosslinked per unit radiation dose; u_1 is the number-average degree of polymerization.

The ratio p_0/q_0 was found to be 0.43 for PMA, 0.39 for PEA, and 0.42 for PBA during photolysis in nitrogen. These values were constant within the experimental error and slightly lower than the value of 0.5 scissions/crosslink found by Jacobs and Steele[1] during the photolysis of PEA under vacuum. On radiolysis, Shultz and Bovey[11] and Burlant et al.[12] observed an increase of crosslinking efficiency with increasing length of the alkyl ester group. The latter author's value of 0.45 for the ratio p_0/q_0 for PEA agreed well with our values, but for PBA their value decreased to 0.28. Figures 1 and 2 showed that on photolysis the rate of crosslinking and the final percentage of crosslinked material formed was somewhat less in the case of PMA than in PEA and PBA, but no distinction was noticeable between the latter two polymers. The constancy of the p_0/q_0 ratio, therefore, showed that the rates of main-chain scission must also be equal to the three polymers. The constancy of the p_0/q_0 ratio was in agreement with the radiolysis studies of Rosenberg and Heusinger[9] on PEA. They found that not only crosslinking but also main-chain scission decreased with deuteration of the ester side group, the ratio of
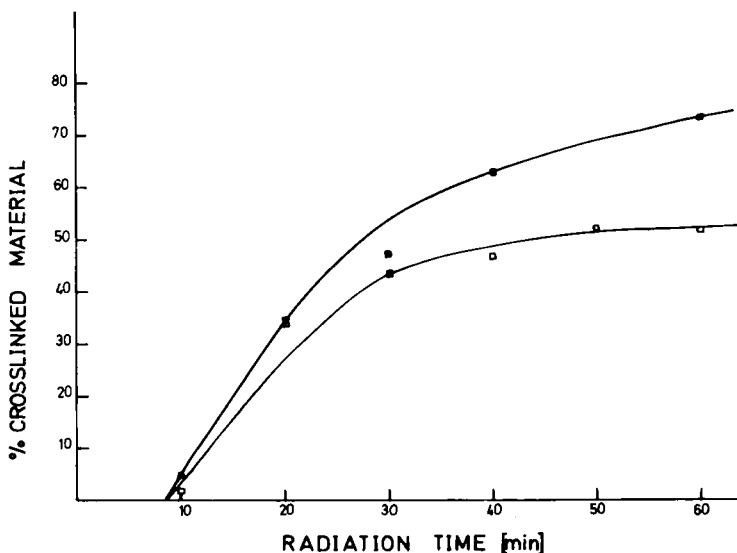

Fig. 1. Increase in the percentage crosslinked material produced with increased radiation time: (■) PMA in N_2 (□) PMA in O_2.
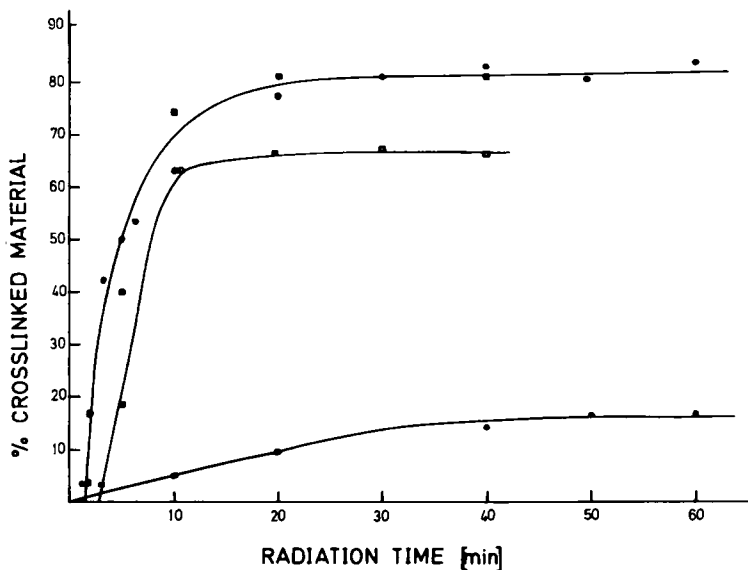
Fig. 2. Increase in the percentage crosslinked material produced with increased radiation time: (●) PEA in N_2; (○) PEA in O_2; (■) PBA in N_2; (□) PBA in O_2.
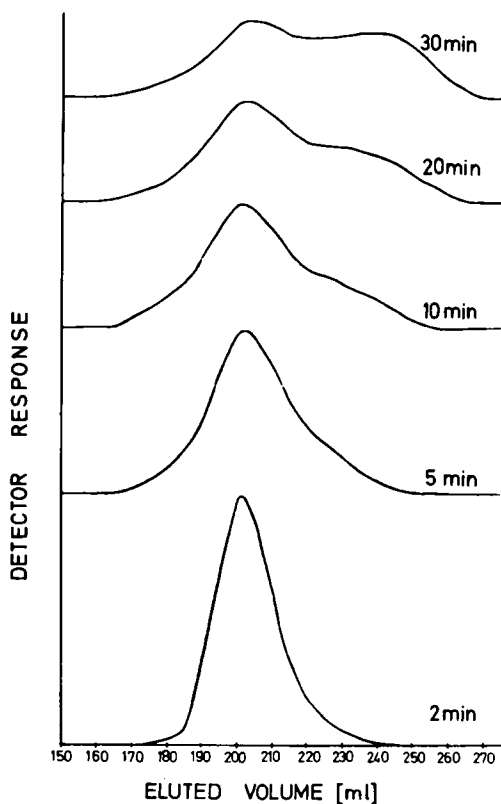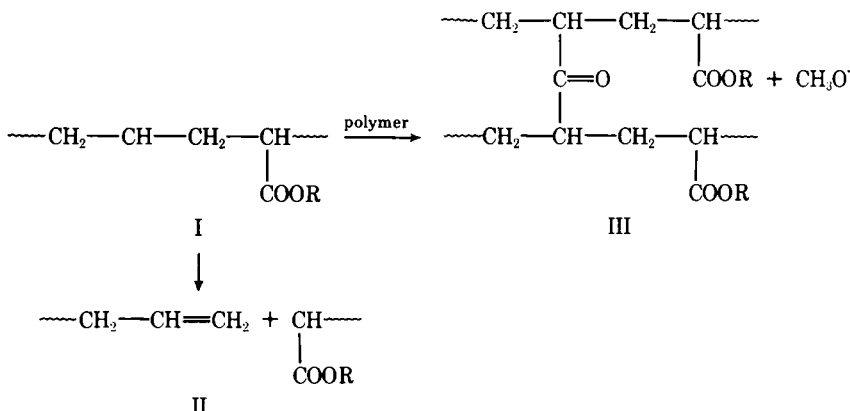

Fig. 3. GPC traces showing accumulation of low molecular weight material on prolonged exposure of PMA in a nitrogen atmosphere.

scission to crosslinking remaining constant. Both processes had the same precursor, and any factor affecting crosslinking would therefore also affect scission. We found similar volatile products during the photolysis of the three polymers.[3,4] This was consistent with, but did not prove, decomposition of the side group preceding crosslinking and scission, as suggested by Rosenberg and Heusinger[9] for the radiolysis of PEA.

GPC studies showed the build-up of low molecular weight material on prolonged exposures (Fig. 3). This material appeared as a distinct peak and not merely as a broadening of the initial distribution by polymer of progressively lower molecular weight. The build-up of smaller molecules can be attributed to random scission of polymer molecules by a free-radical chain reaction. Cameron and Kane[10] explained the maxima in the rate of thermal decomposition of PMA in terms of such a mechanism leading to the accumulation of chain fragments sufficiently small to produce a volatile fragment in internal scission. At the lower temperatures applicable in the case of UV degradation, this low molecular weight polymer was not volatile and was thus detected in the solid phase. Taking all the above observations into consideration, the following reaction sequences are proposed as the most probable mechanisms involved in scission and crosslinking:

$$\begin{array}{ccccc}
\text{---CH}_2\text{---CH---CH}_2\text{---CH---} \\
| \qquad\qquad | \\
\text{C=O} \qquad \text{COOR} + \text{CH}_3\text{O}^{\cdot} \\
|
\end{array}$$

$$\text{---CH}_2\text{---CH---CH}_2\text{---CH---} \xrightarrow{\text{polymer}} \text{---CH}_2\text{---CH---CH}_2\text{---CH---}$$

$$\begin{array}{cc}
| & | \\
\text{COOR} & \text{COOR} \\
\text{I} & \text{III}
\end{array}$$

$$\downarrow$$

$$\text{---CH}_2\text{---CH=CH}_2 + \text{CH---}$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad \text{COOR}$$
$$\qquad\quad \text{II}$$

Rosenberg and Heusinger[9] proposed compound I as the common precursor for scission and crosslinking in the radiolysis of PEA, while II could initiate a scission chain mechanism leading to the formation of low molecular weight fragments as proposed by Cameron and Kane.[10] Crosslinking involving two free radicals[9] of type I would appear unlikely in view of the fact that the rate of crosslinking exceeded that of scission in spite of the chain mechanism involved in scission. The formation of III during crosslinking was consistent with the high (alcohol + aldehyde)/CO ratios obtained on photolysis.[3,4] Burlant et al.[12] found no gel on radiolysis of PMA, while PEA formed a gel only after a certain exposure time, and concluded that crosslinking took place predominantly on the hydrocarbon side chains. We found crosslinked material in all cases, though no gel was detected during the first 8 min of exposure of PMA (Fig. 1). Cameron and Kane[13] reported that the degree of crosslinking in PMA on radiolysis differed for polymers prepared at different temperatures.

In photo-oxidation, the p_0/q_0 ratio increased and totally different ratios were obtained for the three polymers (Fig. 4). For PMA, we found only
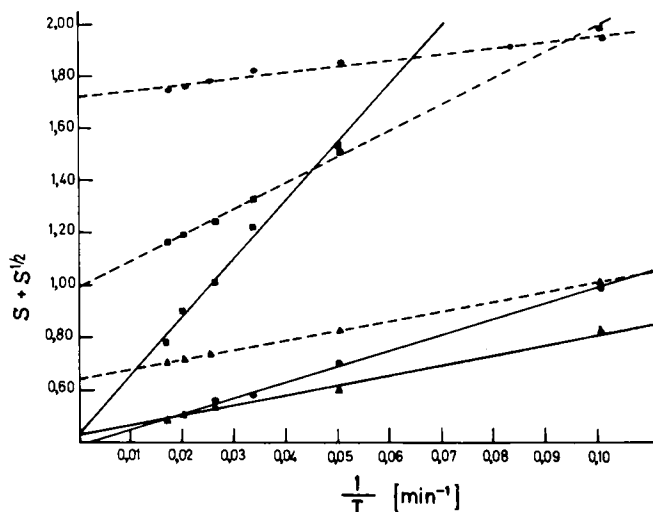
Fig. 4. Plots of the soluble fraction S vs. the inverse of the radiation time T according to the equation of Charlesby and Pinner: (■) PMA; (●) PEA; (▲) PBA. Full lines in N_2, dotted lines in O_2.

slightly less crosslinked material in oxygen than in nitrogen atmospheres, while Fox et al.[2] noticed a very marked decrease in crosslinking in oxygen. They suggested that oxygen may act as a radical scavenger, thus inhibiting the formation of crosslinks. However, there is no reason to believe that oxygen would not act similarly in PEA and PBA causing an equal increase in the p_0/q_0 ratio. Furthermore, oxygen attack at radical sites normally available to initiate crosslinking and scission would inhibit both reactions, and another explanation must be sought as to why scission increased relative to crosslinking in an oxygen atmosphere. The tertiary hydroperoxide groups formed on oxygen attack at free-radical sites may decompose to yield an α-keto ester with simultaneous chain scission, thus causing scission to increase in frequency relative to crosslinking. In passing from PMA to PBA, the oxy radicals produced on hydroperoxide decomposition would become less stable due to the electron-withdrawing effect of the ester carbonyl group, thus increasing scission via this route. This may explain the increase in the p_0/q_0 from 1.0 to 1.7 for PMA and PBA, respectively. The p_0/q_0 ratio for PEA does not fit in the series. Only a very small amount of insoluble material was produced on photo-oxidation, and equilibrium between scission and crosslinking was soon reached (Fig. 2). This behavior could be explained in terms of acetal formation.[6] Acetal formation would lead the production of more polymer radical sites in PEA than was the case for PMA and PBA. Increased oxygen attack at these sites would lead to increased hydroperoxide formation and subsequently to increased chain scission following decomposition of the hydroperoxides.

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