

Ultraviolet Irradiation of Poly(ethyl Acrylate) in Vacuum. II. Mechanism of the Reaction*

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In Part I¹ it was shown that the irradiation of films of poly(ethyl acrylate) with ultraviolet light in a vacuum produced changes in solubility, swelling, and viscosity which could be interpreted in terms of simultaneous crosslinking and chain scission processes. The present research was carried out to study the mechanism by which these processes may take place. The volatile products of the reactions have been collected and analyzed in the mass spectrograph. The effects of film thickness, light intensity, and temperature of irradiation on extent of crosslinking and scission have been determined. Susceptibility to crosslink formation was found to change rapidly in the neighborhood of the glass transition temperature.

Experimental

The preparation of poly(ethyl acrylate) films and the apparatus for irradiating them at room temperature were described in Part I. The same type of lamp was used as before, a Sylvania germicidal lamp which emits chiefly at 254 μ . Data on films irradiated in this set-up for various lamp-to-film distances are given below. For determining the effect of film thickness, smaller samples (0.5 \times 0.25 in.) were placed on an aluminum strip in the quartz tube and the rotating device was shut off. The smaller sample size provided films of more uniform thickness and since five samples could be irradiated at one time the variation in the amount of light falling on each sample was expected to be small.

In the temperature experiments only one side of the film was irradiated but the larger sample size (2.5 \times 0.25 in.) was used. For runs above room temperature the film was supported on an aluminum strip which was attached to the bulb of a thermometer with aluminum foil. The thermometer was en-

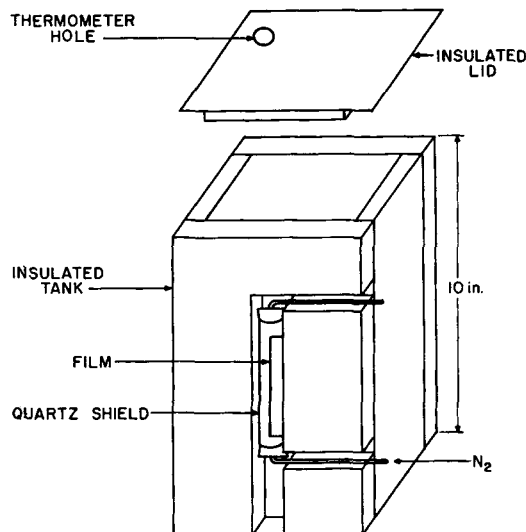


Fig. 1. Apparatus for maintaining films at low temperatures during irradiation.

closed in a quartz tube which was evacuated to a pressure of not more than 0.1 mm. of mercury. Thermometer readings were kept within $\pm 2^\circ\text{C}$. of the desired temperature by intermittent heating with an infrared lamp. For low temperature runs the apparatus shown in Figure 1 was used. A small sheet metal tank holding about 2 liters was heavily insulated except for a narrow area as shown. In this area an aluminum strip holding the film sample was bolted to the tank wall and covered with a quartz shield made by cutting a section of tubing in two longitudinally and sealing it to the tank wall. The ends of the shield were closed except for small gas inlet tubes through which a slow stream of oxygen-free nitrogen was passed. The tank was filled with acetone which was kept at the desired temperature by intermittent additions of powdered solid carbon dioxide. By this method the acetone could easily be kept within 1° of the desired temperature. The lamp-to-film distance was 2 in.

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The techniques used to determine gel content, swelling ratio and intrinsic viscosity have been previously described.¹ Crosslink contents were determined from gel content and swelling ratio data using the Charlesby² and Flory-Rehner³ theories, respectively.

Results and Discussion

Light Intensity

The effect on the crosslink content of varying the distance between the ultraviolet lamp and a 10 mil film is shown in Figure 2. The values of ν_e/V_0 , moles of effective network chains/unit volume, were calculated from the experimental swelling ratios according to the equation given by Flory and Rehner.³

$$-\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 = v_1(\nu_e/V_0)(v_{2m}^{1/3} - v_{2m}/2)$$

A value of 0.46 (ref. 1) was used for χ_1 , the thermodynamic interaction parameter. The reciprocal of the swelling ratio and molar volume of the solvent (acetone) are represented by v_{2m} and v_1 , respectively.

At each distance the data are satisfactorily represented by a straight line, indicating that the extent of crosslinking is directly proportional to the amount of light absorbed. Also, a finite time elapses prior to the appearance of an insoluble gel. Extrapolating to $\nu_e/V_0 = 0$ shows that the gelation time increases with decreasing light intensity. No simple relationship between ν_e/V_0 and light in-

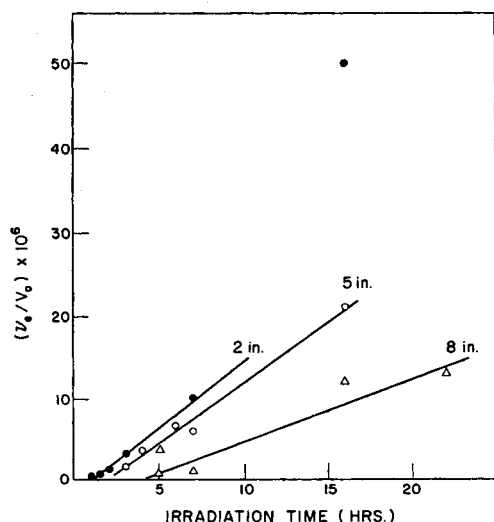


Fig. 2. Effect of lamp-to-film distance on crosslink content of irradiated poly(ethyl acrylate).

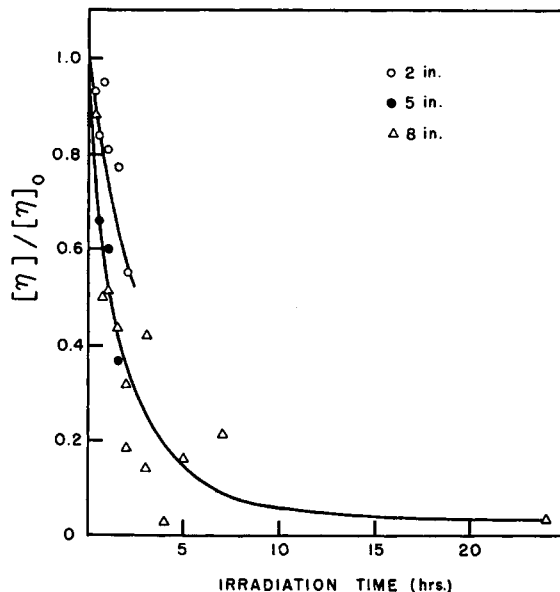


Fig. 3. Viscosity changes in irradiated poly(ethyl acrylate). Effect of lamp-to-film distance.

tensity is apparent. This is probably due to the fact that the light source is large compared with the sample and is kept near the sample. As a result the inverse square law is not applicable here.

The relative intrinsic viscosities of the soluble portions remaining after irradiation are given in Figure 3. The rapid decrease in intrinsic viscosity with time at each lamp-to-film distance is expected if chain scission occurs. Though the rate of decrease of intrinsic viscosity is less at 8 in. than at 2 or 5 in., there does not appear to be a difference in rate at 2 and 5 in. At these shorter distances the effect of the source size on the expected inverse square intensity relationship would be most pronounced. The fact that no intrinsic viscosity increase was found for pre-gelation irradiation times should not be taken as evidence against crosslinking, since the maximum increase in intrinsic viscosity predicted by the theory is only about 10%.⁴ A decrease in intrinsic viscosity prior to gelation has also been observed for polypropylene⁵ and poly(1-pentene) and poly(1-hexene)⁶ exposed to ionizing radiation.

Film Thickness

In Figure 4, δ/l , the number of crosslinked units per original primary weight-average molecule divided by the thickness of film, is plotted against thickness. The δ values are calculated from solubility data according to Charlesby's equations² using 0.5 (ref. 1) for the value of β/α , the ratio

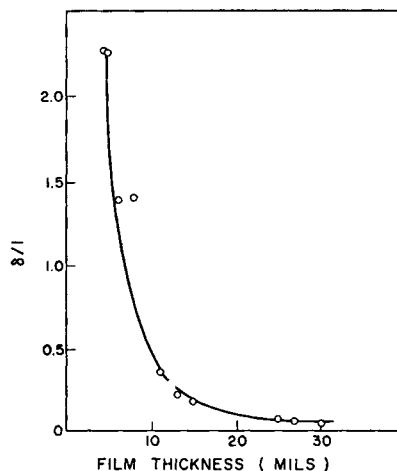


Fig. 4. Film thickness vs. extent of crosslinking for irradiated poly(ethyl acrylate).

of the number of main-chain fractures produced to the number of crosslinked units formed. The data show that the extent of crosslinking decreases with increasing film thickness. A crosslinked "skin" was not observed to form over uncrosslinked polymer at any stage, but the density of crosslinking must decrease with increasing distance from the polymer surface.

Temperature

The data in Figure 5 show that increasing the temperature does not affect the rate of crosslinking relative to scission. The curve drawn through the

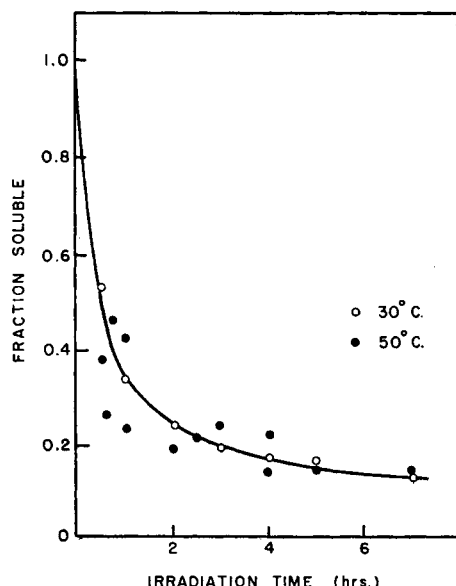


Fig. 5. Acetone solubility of poly(ethyl acrylate) after irradiation at 30 and 50°C.

30° points also fits the data at 50°C. If increasing the temperature over this interval has any effect on the rate of crosslink formation, a comparable change must take place in the scission reaction so that the net crosslink content, measured by the gel fraction, appears to be the same at the two temperatures. Very likely, it is not that a change of temperature alters the rate of both reactions, but that there are no rate determining reactions which show any temperature dependence over this temperature range.

A very pronounced change in mechanism is indicated when poly(ethyl acrylate) is irradiated at low temperatures. In a preliminary experiment carried out with the film under liquid nitrogen ($-196^{\circ}\text{C}.$), irradiation times which at room temperature had brought about insolubility and reduced swelling did not produce gelation. However, there was a decrease in intrinsic viscosity:

Irradiation time, hr.	$[\eta]$
0	5.47
3.0	3.28
7.0	3.06

The polymer films fluoresced rather strongly during irradiation under liquid nitrogen and the fluorescence persisted for 1 or 2 sec. after the source was extinguished.

Crosslinking presumably occurs by the combination of polymer free radicals formed by some primary irradiation process. In view of the above observations it seemed reasonable to assume that crosslinking did not occur at very low temperatures because of the decreased mobility of the molecular chains. This suggested that data around the glass transition temperature might be of interest.

The glass temperature of poly(ethyl acrylate) is $-17^{\circ}\text{C}.$, as determined from the temperature dependence of the torsional modulus of films. We have therefore studied the effect of irradiation at various temperatures between 26 and $-20^{\circ}\text{C}.$ using the apparatus described above and shown in Figure 1. It should be noted that in these runs oxygen was excluded by sweeping the sample chamber with nitrogen rather than by evacuation. The solubility data are plotted in Figure 6, and it is clear that the time necessary to produce insoluble polymer increases with decreasing temperature of irradiation. At $-20^{\circ}\text{C}.$, no insoluble polymer is

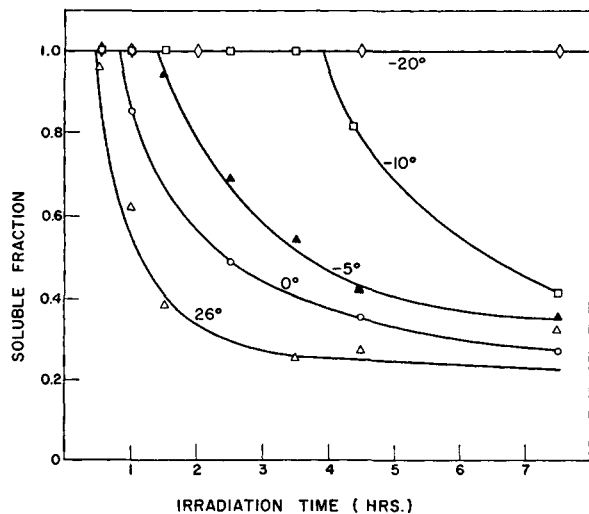


Fig. 6. Effect of temperature on the acetone solubility of irradiated poly(ethyl acrylate).

found even after 7.5 hr. In view of the results at 30 and 50°C., the change which occurs between 0 and -20°C . is most striking. Possibly very long irradiation times would produce insoluble polymer at -20°C ., but even so, the fact that there is a large increase in the time necessary to produce gelation as the glass temperature is approached suggests that the original premise is correct and that chain mobility is important in the crosslinking process. As the temperature of a polymer is lowered, the molecular mobility decreases, the rate of decrease being most rapid at the glass temperature. If crosslinking results from the combination of two polymer radicals, the longer gel times which occur as the temperature is lowered near the glass temperature would result from the lessened mobility of the radicals.

Since the completion of this work a similar effect has been noted with electron-irradiated polyethylene.⁷ It was observed that crosslinking efficiency is not very temperature dependent below the glass temperature or above the crystal melting temperature. However, between these temperature extremes, where the crystalline-to-amorphous content is rapidly changing, crosslinking efficiency increases with increasing temperature. Our results show a similar change in crosslinking efficiency around the glass transition temperature. However, above room temperature, the crosslinking efficiency in the irradiation of amorphous poly(ethyl acrylate) seems to be independent of temperature.

Figure 7 shows that the large changes in solubility

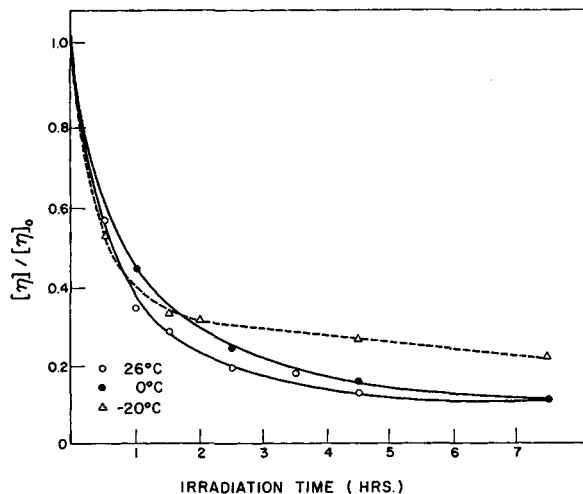


Fig. 7. Effect of temperature on viscosity change in irradiated poly(ethyl acrylate).

due to irradiation temperature are not reflected in the viscosity. The rate of decrease of intrinsic viscosity depends only slightly on the temperature. This suggests that by lowering the temperature the crosslinking reaction can be slowed down or eliminated while scission continues at about the same rate. The latter does not necessarily imply that main-chain scission is a direct result of light absorption. The carbonyl group is probably the locus of the absorption, and it is more likely that the primary process is a split in the pendant group. This seems more reasonable than assuming that energy absorbed by the carbonyl is redistributed in such a way that main-chain C—C bonds receive an excess of energy and are ruptured. It is suggested in the mechanism below that the polymer radical which forms after side-chain loss undergoes a chain splitting reaction. Neither of the postulated reactions, light absorption to produce side-chain-loss or polymer radical splitting, would be expected to show a large dependence on temperature or glass transition temperature.

Reaction Products

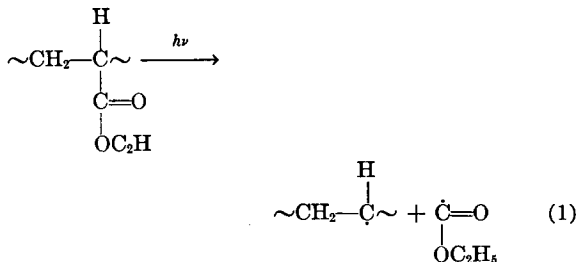
Mass spectrometer analyses were made of the gas in initially evacuated quartz tubes containing irradiated polymer films. The samples of gas were found to contain hydrogen, methane, carbon monoxide, and carbon dioxide. An unidentified high molecular weight compound was detected in some of the samples. Results for irradiation times of 4 hr. (average of two experiments) and 16 hr. are:

Irradiation time, hr.	Per cent by volume			
	CH ₄	CO	CO ₂	H ₂
4	33.9	59.2	6.2	0.7
16	44.7	45.6	8.9	0.8

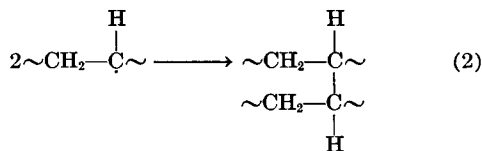
The oxygen-containing compounds CO and CO₂ are probably formed as a result of scission of C—O bonds in the side chains, perhaps as a direct result of UV absorption by the carbonyl group. The small yield of hydrogen seems to be constant, which suggests that it is being produced from an impurity or from a photochemically reactive end group. In either case the presence of hydrogen is not thought to result from or affect the scission or crosslinking reactions. No simple explanation can be given for the presence of methane. It is probably formed in reactions following the original side-chain scission.

Reaction Mechanism

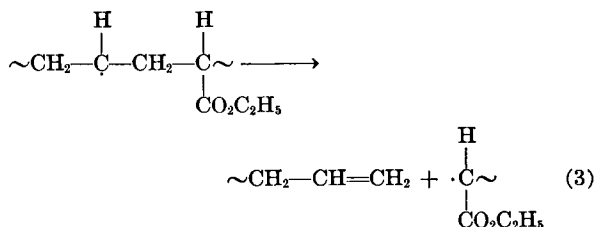
Since the reaction is initiated by ultraviolet light, it is likely that the site of the initial reaction is near the ultraviolet-absorbing group in the ester side chains. The bond strengths involved here decrease in the order, C=O > C—H > C—O > C—C, so that the following reaction may be postulated as the primary process:



Further reactions of the $\cdot\text{CO}_2\text{C}_2\text{H}_5$ radical could produce CO and CO₂. Crosslinking results from the combination of two polymer radicals.



Below the glass temperature, the likelihood of this reaction occurring decreases because of reduced chain mobility. We have found that the crosslinks are quite stable to alkali, which supports a crosslink of the type suggested rather than one involving a side group. The polymer radicals can also decompose according to eq. (3), which results in main chain scission:



A reaction of this type would be expected to have a low temperature dependence as was in fact found for the intrinsic viscosity changes. It is also possible that the original polymer radical abstracts a tertiary hydrogen from another polymer chain, and thus transfers radical sites from one molecule to another.

The methane identified in the mass spectrometer analysis is somewhat puzzling. There is no evidence to indicate whether it comes from the cleaved side-chains or from further decomposition of the broken main chains, although the latter seems intuitively more likely.

The combination and disproportionation reactions leading to crosslinking and scission have been proposed for the mechanism of other degradations. Grassie has pointed out⁸ that the two can be separated by working in solution, where the bimolecular combination process would be slow. For poly(ethyl acrylate) such a separation can be obtained by working below the glass transition temperature. This would eliminate any possibility of side reactions due to the solvent.

Conclusion

This study of the effect of ultraviolet light on poly(ethyl acrylate) has led to a postulated mechanism for the degradation process which may be summarized as follows. The irradiation results primarily in a splitting off of the ester side chains from the polymer backbone. The polymer radicals produced in this process can form crosslinks by combination with each other or can decompose with chain scission. Since chain mobility would be an important factor in the recombination (crosslinking) reaction, the strong temperature dependence observed for this reaction near the glass transition temperature is to be expected. On the other hand, chain mobility should not affect the decomposition leading to chain scission and this is consistent with the observed lack of change in the rate of viscosity change with temperature.

The mass spectroscopic analysis was carried out for us by Dr. Alan Weiss.

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Synopsis

Irradiation of poly(ethyl acrylate) films in the absence of oxygen with ultraviolet light of 254 $m\mu$ wavelength results in chain scission and crosslinking. The effects of film thickness, light intensity, and temperature of irradiation on this process have been determined, and the volatile reaction products have been analyzed in the mass spectrograph. The data suggest that the primary result of irradiation is splitting off ester side chains. The polymer radicals remaining can be crosslinked by combination with one another or cleaved by a decomposition reaction. There is a large change observed in the rate of the crosslinking reaction in the neighborhood of the glass transition temperature (-17°C .), but the scission reaction shows only a very small temperature dependence in this region.

Résumé

L'irradiation de films de polyacrylate d'éthyle, en absence d'oxygène, par de la lumière ultraviolette de longueur

d'onde de 254 $m\mu$, donne une rupture de chaîne et provoque du pontage. On a déterminé les influences de l'épaisseur du film, de l'intensité de la lumière et de la température d'irradiation sur ce processus et les produits de réaction volatils ont été analysés au spectrographe de masse. Ces données suggèrent que le premier résultat de l'irradiation est d'éliminer les chaînes latérales esters. Les polymères radicalaires restants peuvent être pontés en se combinant avec un autre ou peuvent se couper par une réaction de décomposition. On observe une grande variation dans la vitesse de la réaction de pontage au voisinage de la température de transition vitreuse (-17°C), mais il semble que la réaction de rupture en dépende seulement très peu dans la même région de température.

Zusammenfassung

Bestrahlung von Poly-(äthylacrylat)-filmen bei Sauerstoffausschluss mit ultraviolettem Licht der Wellenlänge 254 $m\mu$ führt zur Kettenspaltung und Vernetzung. Der Einfluss der Filmdicke, der Lichtintensität und der Bestrahlungstemperatur auf diesen Prozess wurde bestimmt und die flüchtigen Reaktionsprodukte im Massenspektrographen analysiert. Die Ergebnisse sprechen dafür, dass das primäre Ergebnis der Bestrahlung die Abspaltung von Esterseitenketten ist. Die entstehenden Polymerradikale können durch eine gegenseitige Vereinigung vernetzt oder durch eine Zersetzungsreaktion gespalten werden. In der Umgebung der Glasumwandlungstemperatur (-17°C) wird eine starke Änderung der Geschwindigkeit der Vernetzungsreaktion beobachtet, hingegen zeigt die Spaltungsreaktion in diesem Gebiet nur eine sehr kleine Temperaturabhängigkeit.

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