

The Crosslinking of Plasticized Poly(methyl Methacrylate) by Ionizing Radiation

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INTRODUCTION

The response of poly(methyl methacrylate) (PMMA) to ionizing radiation has been extensively investigated.¹⁻³ The polymer undergoes random mainchain fracture with a G value of 1.6 and without exhibiting any concurrent crosslinking reactions. Partial protection against degradation has been achieved by incorporating benzoquinone and other radical traps. The instability of the polymer towards radiation extends to its copolymers, and Shultz has demonstrated that crosslinked methyl methacrylate-ethylene dimethacrylate copolymers are converted into soluble polymer by low radiation doses.⁴

Recently reported work on the irradiation of poly(vinyl chloride) and cellulose acetate in admixture with allyl esters^{5,6} has now been extended to an examination of the effect of radiation on PMMA plasticized with diallyl sebacate. When irradiated in the pure state, this allyl ester undergoes conversion to polymer with a G value for loss of allyl unsaturation of 30. Similar rates of conversion have been obtained for solid solutions of PMMA in diallyl sebacate while, at the same time, the polymer is rendered insoluble.

EXPERIMENTAL

I.C.I. Perspex sheet was cut up into fragments, milled with diallyl sebacate, and pressed into sheets. The initial compositions of the sheets were determined by dissolving samples in methylene chloride and adding the solution slowly to excess methanol. The precipitated PMMA was separated by centrifuging and drying to constant weight *in vacuo* at 60°. The composition found in this way showed very good agreement with that found spectroscopically.

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Densities of the unirradiated and irradiated samples were measured at 20° by floating fragments in 10 cc. of aqueous potassium carbonate of known strength. Distilled water was added dropwise from a buret until the fragments began to sink. The concentration of the solution could be calculated so that its density and hence that of the samples could be found by interpolation.⁷

Transition temperatures were measured by using a falling ball rebound apparatus similar in essentials to that described by Gordon.⁸ The rebound height of a ball impinging on the sample is determined as a function of temperature so that when the frequency imposed by the ball matches the natural mode of vibration of the specimen the energy absorption passes through a maximum. The peak absorption temperature under these conditions corresponds to the transition temperature at an applied frequency of about a millisecond.

The loss of allyl unsaturation in the plasticized samples after irradiation was established spectroscopically by measuring the absorption change produced in the 1.65- μ band in the near infrared.

The samples were irradiated at normal temperatures with 2-m.e.v. electrons produced by a Van de Graaff accelerator under operating conditions such that each pass through the beam resulted in a delivered dose of 1 megarad.

RESULTS

Measurements of density changes following irradiation were used as a preliminary indication of the conversion of allyl groups. A control experiment showed that the density of unplasticized Perspex (1.188 at 20°) underwent no detectable change after 80 megarads. The results obtained with the plasticized samples are shown in Figure 1. Additional and quantitative evidence of the loss of unsaturation is furnished by the spectroscopic results plotted in Figure 2. The reduction in

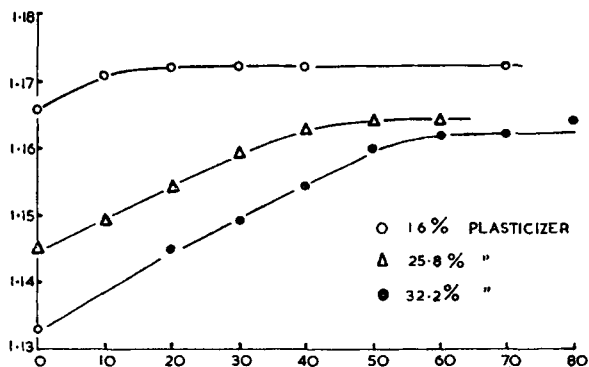


Fig. 1. Poly(methyl methacrylate) plasticized with 16, 25.8, and 32.2% diallyl sebacate. Abscissa: radiation dose, megarads; ordinate: density at 20°C.

allyl group concentration per megarad is independent of the initial concentration and linear with dose, at least in the early stages of the reaction. (This has also been observed with the conversion of triallyl citrate in the presence of cellulose acetate⁶). The average conversion rate of allyl groups is 29.8 $\mu\text{mole/g./Mrad.}$, which corresponds to a G value of 30. The same value applies to the monomer when irradiated under the same conditions.

Irradiated samples were immersed in methylene chloride at room temperature in order to indicate whether insoluble and, by implication, crosslinked structures had been formed. Over a certain dose range, which depended on the initial plasticizer concentration, coherent, swollen gels were obtained.

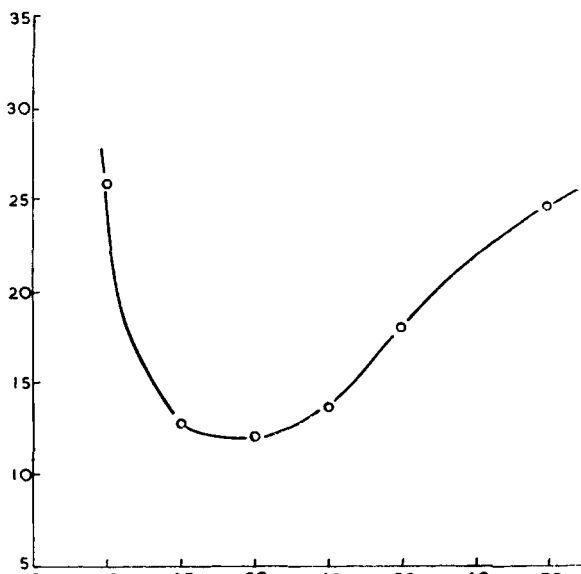


Fig. 3. Poly(methyl methacrylate) plasticized with 16% diallyl sebacate; extracted with CH_2Cl_2 , for 15 hr. Abscissa: radiation dose, megarads; ordinate: % soluble material.

At lower doses dissolution occurred, giving slightly turbid solutions; at high doses, the samples disintegrated to insoluble globules. The solution behavior was established more rigorously by exhaustive extractions with methylene chloride in a Soxhlet apparatus. Figure 3, which is based on these results, shows the unusual type of solu-

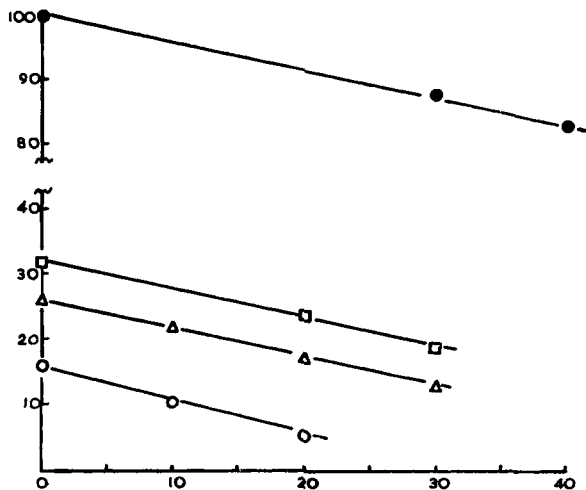


Fig. 2. Effect of radiation on concentration of allyl groups in poly(methyl methacrylate) plasticized with (O) 16, (Δ) 25.8, and (\square) 32.2% diallyl sebacate; (\bullet) pure plasticizer. Abscissa: radiation dose, megarads; ordinate: % unsaturation.

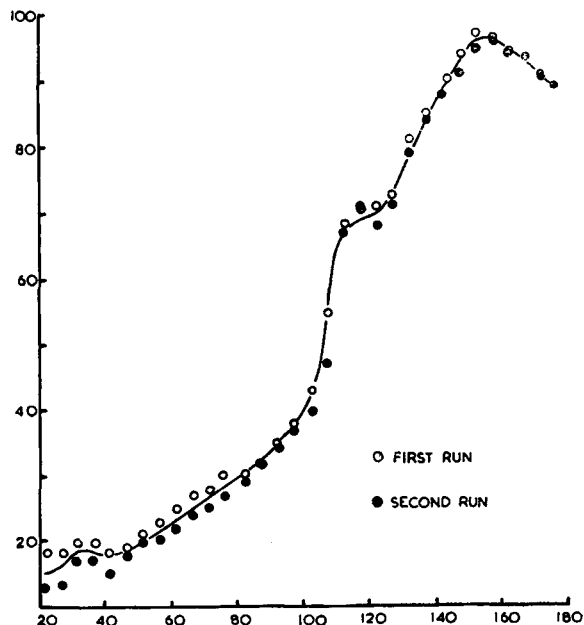


Fig. 4. Energy absorption spectrum of unplasticized, unirradiated poly(methyl methacrylate). Abscissa: temperature, °C.; ordinate: % energy absorbed.

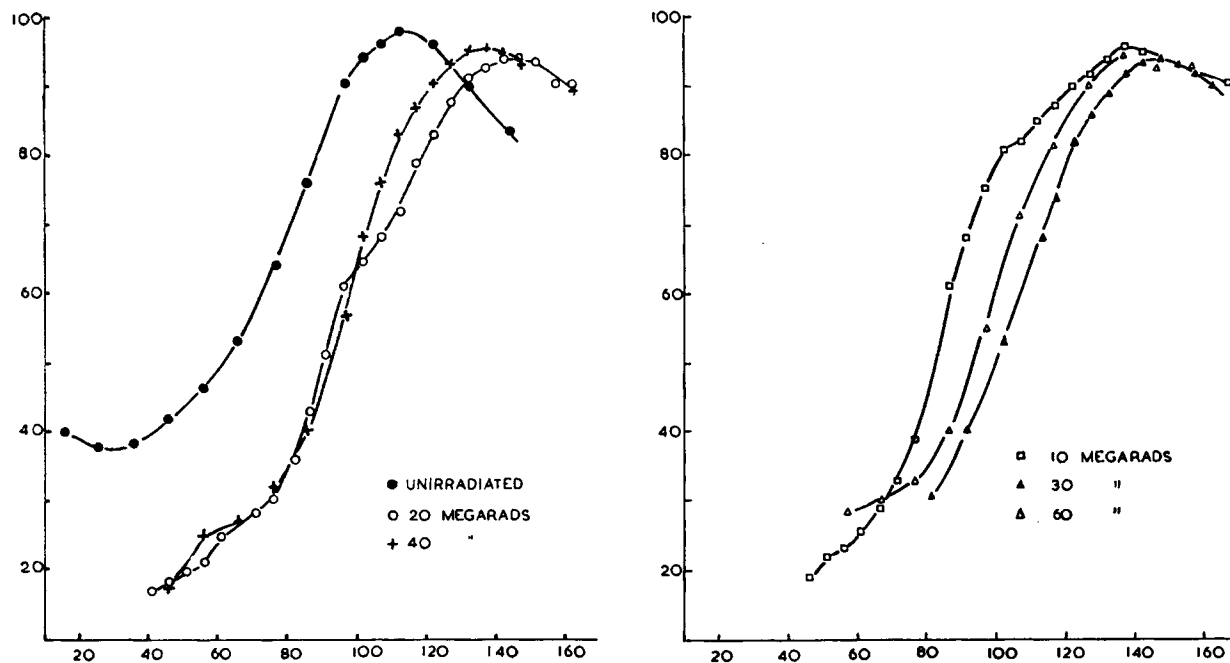


Fig. 5. Energy absorption spectra of poly(methyl methacrylate) plasticized with 16% diallyl sebacate and irradiated at various doses: (a) 0, 20, and 40 Mrad; (b) 10, 30, and 60 Mrad. Abscissa: temperature, °C.; ordinate: % energy absorbed.

bility curve obtained. Obviously, a reversal of the crosslinking process has occurred, and the curve superficially resembles those obtained with poly-(dihydroperfluorobutyl acrylate),⁹ where degradative attack by fluorine liberated from side chains was postulated. The most coherent swollen gel was obtained at 10 megarads, well before the minimum in the sol curve.

The influence of radiation on the plasticized PMMA was also revealed by dynamic relaxation measurements. Figure 4 shows the energy absorption spectrum of unplasticized unirradiated PMMA. The peak temperature occurs at 155°, which is in good agreement with a published value of 160° obtained with the use of a similar apparatus.^{8,10} The prominent shoulder at 110° is attributed to the mobility of the methyl ester side groups in the glassy state,¹¹ although its position on the curve is at variance with that reported elsewhere.^{8,10} (Irradiation, in causing scission of the side chains would be expected to affect the shape of the curve in the region of the shoulder. It was found that, after a dose of 10 megarads, the shoulder was much less perceptible; furthermore, the specimen began to bubble at 145°). A family of energy absorption curves for an irradiated series of one plasticized PMMA composition has been separated in Figures 5a and 5b for clarity. The effect of radiation is to

increase the transition temperature (i.e., the peak temperature) to a constant value between 20 and 30 megarads, after which it shows a decline. The shoulder is apparent only at 10 and 20 megarads. An initial increase in transition temperature is in accordance with expectation and corroborates the solubility curve in reflecting the overall reduction in internal mobility consistent with the formation of a network. When the crosslink density reaches its optimum, degradation begins to make a larger contribution, and plasticization of the structure by degradation products causes the transition temperature to fall (see Table I).

TABLE I
Gel Fractions and Resonance Peak Temperatures of Irradiated Plasticized PMMA

Dose, Mrad	16% Diallyl sebacate		25% Diallyl sebacate	
	Gel, %	T_p , °C. ^a	Gel, %	T_p , °C. ^a
0	0	113	0	88
10	74.1	136	0	99
20	87.2	147	—	107
30	87.9	147	68.9	—
40	86.3	134	—	—
50	82.0	—	—	—
60	—	137	87.4	—
70	75.3	—	—	—

^a T_p for unplasticized, unirradiated PMMA was 155°C.

DISCUSSION

The simplest approach in interpreting the effect of radiation on this system is to consider that each component reacts independently in its own characteristic manner. This postulate requires the diallyl sebacate to polymerize and form an insoluble network as soon as the critical conversion for gelation is exceeded. From results reported for this monomer by Holt and Simpson¹² it may be deduced that the critical conversion in terms of loss of allyl unsaturation is 15%. Simultaneously, the PMMA suffers degradation with a dislinking parameter¹³ $p_0 = 1.7 \times 10^{-4}$.

The rate of loss of unsaturation is available from the present data, and the average primary chain length of the poly(diallyl sebacate) is assumed to be the same as the value of 19.4 found by Holt and Simpson.¹² Accordingly, the G value for radical initiation in the system is 1.5. This will include all initiating radicals, whether formed directly in the diallyl sebacate, by hydrogen abstraction reactions from the PMMA, or as a consequence of disruption of the PMMA molecules. Since the weight of gel exceeds the weight of plasticizer present, it follows that the PMMA must become linked to the network at a rate exceeding the fracture rate. This can be achieved simply by the initiation of allyl polymerization chains by polymeric radicals.

The condition necessary for crosslinking to occur is that the probability of forming a crosslinked unit should be at least half the probability of dislinking, i.e., $p_0/q_0 < 2$. If p_0 for PMMA is unaffected by the presence of diallyl sebacate, then q_0 must exceed 0.85×10^{-4} , or the G value for junction point formation must exceed 0.8. However, this merely states the condition necessary for gel to appear. Larger ratios of q_0/p_0 are indicated here by the substantial proportions of gel observed. According to the theory developed for gel accumulation in systems undergoing simultaneous crosslinking and dislinking, p_0/q_0 is equal to the minimum value of $(s + \sqrt{s})$, where s denotes the sol fraction. From Figure 3, the ratio of soluble PMMA at the minimum is 0.14, whence $(s + \sqrt{s}) = 0.5$. Thus p_0/q_0 is 0.5, and the limiting crosslink density is 4 crosslinked units per weight-average molecule. Since the maximum G value for initiation is 1.5, this implies a maximum value of 0.75×10^{-4} for p_0 , approximately 44% of that found for pure PMMA.

Further implications of the proposed mechanism may now be considered. Gel should not be formed

at doses insufficient to convert 15% of the diallyl sebacate. Furthermore, after 30 megarads, when 81% of the allyl groups have reacted, the G (initiation) value must tend to fall below the minimum necessary to sustain the gel. Thereafter radiation can be assumed to produce degradation only. Both features are shown in Figure 3, viz. absence of gel below 5 megarads and an increase in sol fraction above 30 megarads.

In the range 40–70 megarads the sol fraction increases at approximately 0.3% per megarad. This rate is considerably less than that observed by Shultz⁴ for highly crosslinked methyl methacrylate–ethylene dimethacrylate copolymers. Shultz's equation for the formation of sol by degradation of a random PMMA network can be written:

$$(s_1 - s_2) + (\sqrt{s_1} - \sqrt{s_2}) = (r_1 - r_2)p_0M_c/100$$

where s_1 and s_2 are the sol fractions at doses r_1 and r_2 and M_c is the average molecular weight between junction points. For a maximum value of 0.75×10^{-4} for p_0 , the present data lead to the value $M_c = 9000$ as characterizing the network at the minimum in the sol curve. Since it has been deduced above that there are four junction points per molecule, a molecular weight of 45,000 is indicated for the primary chain of the network at the sol minimum.

CONCLUSIONS

The semiquantitative interpretation of the curve in Figure 3 has served merely to test the validity of the assumption that the two components of the sample respond independently to radiation. This assumption has not been controverted, although the evidence points to a lower dislinking probability for the plasticized PMMA than for the pure polymer. This is not unexpected in view of the many examples of protection of PMMA degradation exercised by additives.

The disappearance of allyl unsaturation per unit radiation dose is identical, within experimental error, in the presence of PMMA as in the pure diallyl sebacate. The gel/dose curve can be accounted for by assuming radicals produced by radiation on the PMMA chains to be the principal initiating species. When the gel is depleted of allyl monomer, further radiation causes degradation. A similar reversal of behavior is apparent from the energy absorption curves.

The authors wish to thank the Chairman of Tube Investments Ltd. and the Chairman of BX Plastics Ltd. for permission to publish.

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Synopsis

Poly (methyl methacrylate) (PMMA) normally undergoes random main-chain fracture when exposed to ionizing radiation. In the presence of radical traps, partial protection against degradation may occur, but no crosslinking reactions have hitherto been observed. In this work, diallyl sebacate has been incorporated into PMMA prior to exposure to ionizing radiation (2 m.e.v. electrons). The plasticized PMMA had a low softening point, which was increased by irradiation due to polymerization of the diallyl ester. At the same time, the PMMA was rendered insoluble. With methylene chloride as solvent, the gel fraction greatly exceeded the fraction of allyl ester present, proving that the PMMA had become crosslinked or incorporated into the allyl network. Beyond a certain dose, however, which varied with the diallyl sebacate weight fraction, continued irradiation led to increased sol fractions and reduced transition temperatures. Spectroscopic measurements showed the disappearance of allyl unsaturation per unit radiation dose to be identical, within experimental error, in the presence of PMMA as in the pure diallyl sebacate. A semi-quantitative examination of the gel/dose curve and dynamic energy absorption curves for a sample containing 16% diallyl sebacate has pointed to radicals produced by radiation on the PMMA chains to be the principal initiating species, these becoming junction points to the allyl network. When the gel is depleted of allyl monomer, further radiation causes degradation of the PMMA segments.

Résumé

Le polyméthacrylate de méthyle subit normalement des ruptures statistiques de la chaîne principale sous l'action d'une radiation ionisante. En présence de piège à radical, une protection partielle contre la dégradation peut être

obtenue mais on n'a pas observé jusqu'ici de réactions de pontage. Dans ce travail, on a incorporé du sébacate de diallyle à du PMMA avant exposition aux radiations ionisantes (électrons de 2 Mev). Le PMMA plastifié possédait un bas point de ramollissement; il a été élevé par irradiation grâce à la polymérisation de l'ester de diallyle. En même temps le PMMA devenait insoluble. Avec du chlorure de méthylène comme solvant, la fraction gelifiée dépassait largement la fraction d'ester de diallyle présente, ce qui prouve que le PMMA avait été ponté en incorporé dans le réseau allylique. Au delà d'une certaine dose, cependant, qui variant avec la fraction en poids de sébacate de diallyle une irradiation prolongée faisait augmenter les fractions de sol et abaissait les températures de transition. Des mesures spectroscopiques ont montré que la disparition de l'insaturation allylique par unité de dose de radiation était identique, dans la mesure des erreurs expérimentales, en présence de PMMA et dans le sébacate de diallyle pur. Un examen semi-quantitatif de la courbe gel/dose et des courbes d'absorption d'énergie dynamique pour un échantillon contenant 16% de sébacate de diallyle ont montré que des radicaux produits par radiation sur les chaînes de PMMA constituaient la principale espèce initiatrice, ceux-ci devenant des points de jonction avec le réseau allylique. Quand le gel est dépourvu de monomère allylique, une irradiation ultérieure cause une dégradation des segments de PMMA.

Zusammenfassung

Bei der Einwirkung von ionisierender Strahlung erleidet Poly(methylmethacrylat) (PMMA) normalerweise eine statistische Kettenspaltung. In Gegenwart von Radikalabfängern kann ein partieller Schutz gegen den Abbau vorhanden sein, es wurden aber bis jetzt keine Vernetzungsreaktionen beobachtet. In der vorliegenden Arbeit wurde dem PMMA vor der Einwirkung der ionisierenden Strahlung (2 MeV Elektronen) Diallylsebacat zugesetzt. Das weichgemachte PMMA hatte einen niedrigen Erweichungspunkt, der durch Bestrahlung infolge der Polymerisation des Diallylesters hinaufgesetzt wurde. Gleichzeitig wurde das PMMA unlöslich. Bei Verwendung von Methylenchlorid als Lösungsmittel war die Menge der Gelfraktion viel grösser als der Anteil an Diallylester; das beweist, dass das PMMA vernetzt oder in das Allylnetzwerk eingebaut worden war. Oberhalb einer gewissen Dosis, deren Grösse vom Gewichtsbruchteil an Diallylsebacat abhing, führte eine fortgesetzte Bestrahlung zu höheren Solfraktionen und zu einer herabgesetzten Umwandlungstemperatur. Spektroskopische Messungen zeigten, dass innerhalb der Versuchsfehler das Verschwinden der ungesättigten Allylgruppen pro Bestrahlungsdosis-Einheit bei Gegenwart von PMMA und im reinen Diallylsebacat identisch war. Eine halbquantitative Überprüfung der Gel/Dosis-Kurve und der dynamischen Energieabsorptionskurve bei einer Probe mit 16% Diallylsebacat liess erkennen, dass hauptsächlich die durch die Strahlung an den PMMA-Ketten erzeugten Radikale als Starter wirken und dabei zu Verbindungsgliedern zum Allylnetzwerk werden. Sobald das Gel an Allylmonomerem erschöpft ist, führt eine weitere Bestrahlung zum Abbau der PMMA-Segmente.

Received January 23, 1960