

The Glass Transition of Irradiated Poly(methyl Methacrylate) Compositions Incorporating Triallyl Cyanurate

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Synopsis

A mechanical torsion pendulum has been used to observe changes in viscoelastic behavior resulting from modification of polymer structure. Crosslinking, with consequent increase in glass temperature, has been observed in irradiated poly(methyl methacrylate) compositions incorporating triallyl cyanurate, which confers partial protection against chain scission.

EXPERIMENTAL

Sheets of plasticized poly(methyl methacrylate) (PMMA) were prepared by mixing I.C.I.A.N.Z. Diakon-grade MO CLEAR molding pellets with 15% by weight of triallyl cyanurate (TACN). Each batch was preheated, milled at 165–175°C, pressed at 180–190°C, then exposed to varying amounts of 0.19-Mrad/hr γ -radiation from a cobalt-60 source.

A mechanical torsion pendulum similar to that described by Heijboer, Dekking, and Staverman¹ was used to follow changes in shear modulus and loss tangent, and thereby to estimate the glass temperature T_{g0} , the temperature at which maximum damping occurred.

RESULTS AND DISCUSSION

The response of PMMA to ionizing radiations has been extensively investigated. The observation that PMMA undergoes random main-chain fracture without exhibiting any concurrent crosslinking reactions, or with negligible crosslinking, has been reported by Charlesby, Alexander and co-workers,²⁻⁵ Chapiro,⁶ Pinner and Wycherly,⁷ and Shultz and others.^{8,9}

Various additives to PMMA impart a degree of protection against scission by ionizing radiations. Alexander et al.² have suggested that added substances reduce the amount of degradation by absorbing energy from the excited polymer molecules. Bovey¹⁰ viewed the effectiveness of these screening agents as being due to their combination with the free radicals formed during irradiation.

Pinner¹¹ found that enhancement of crosslinking of poly(vinyl chloride) (PVC) by the presence of the allyl ester was of such magnitude that it seemed feasible to crosslink by radiation, in this way, those polymers normally de-

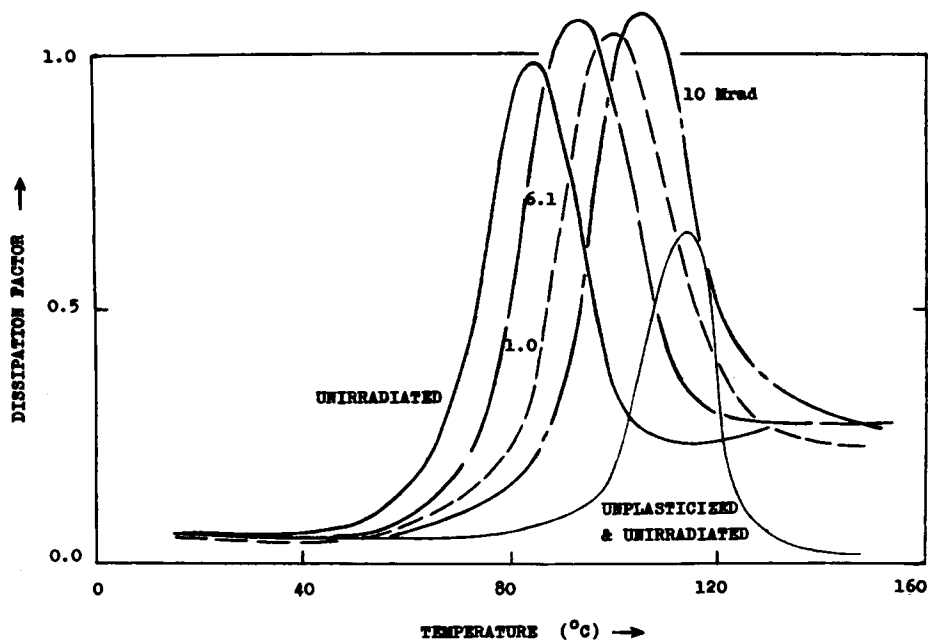


Fig. 1. Temperature variation of 0.2-Hz loss tangent for irradiated Diakon compositions.

the residual level of unsaturation decreased asymptotically with increased radiation level. This trend is consistent with removal of allyl-group unsaturation by crosslinking reactions, activated by γ -radiation, as reported by Pinner and Wycherly⁷ for diallyl sebacate. A trend in relative strengths of absorption peaks characteristic of C=C, C=O bonds and TACN is also visible in these spectra.

Progressive loss of allyl unsaturation is attributed to increased density of

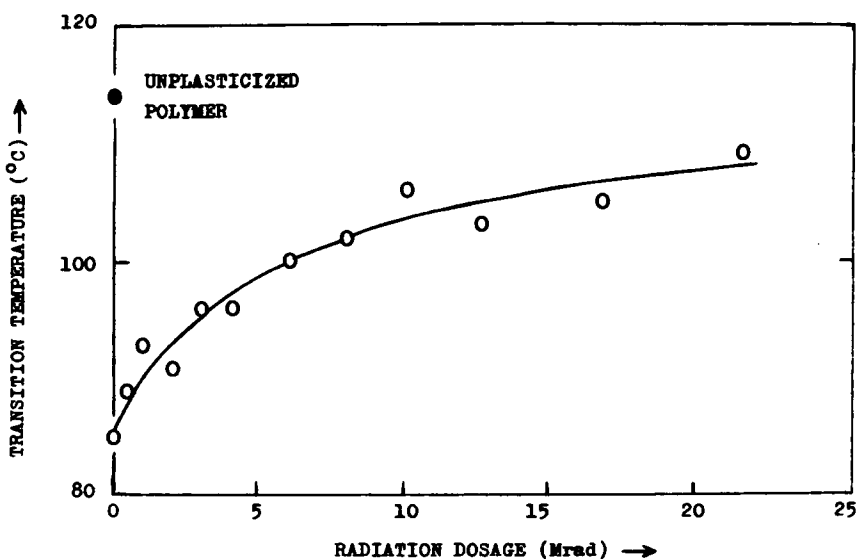


Fig. 2. Dependence of glass temperature on total incident radiation.

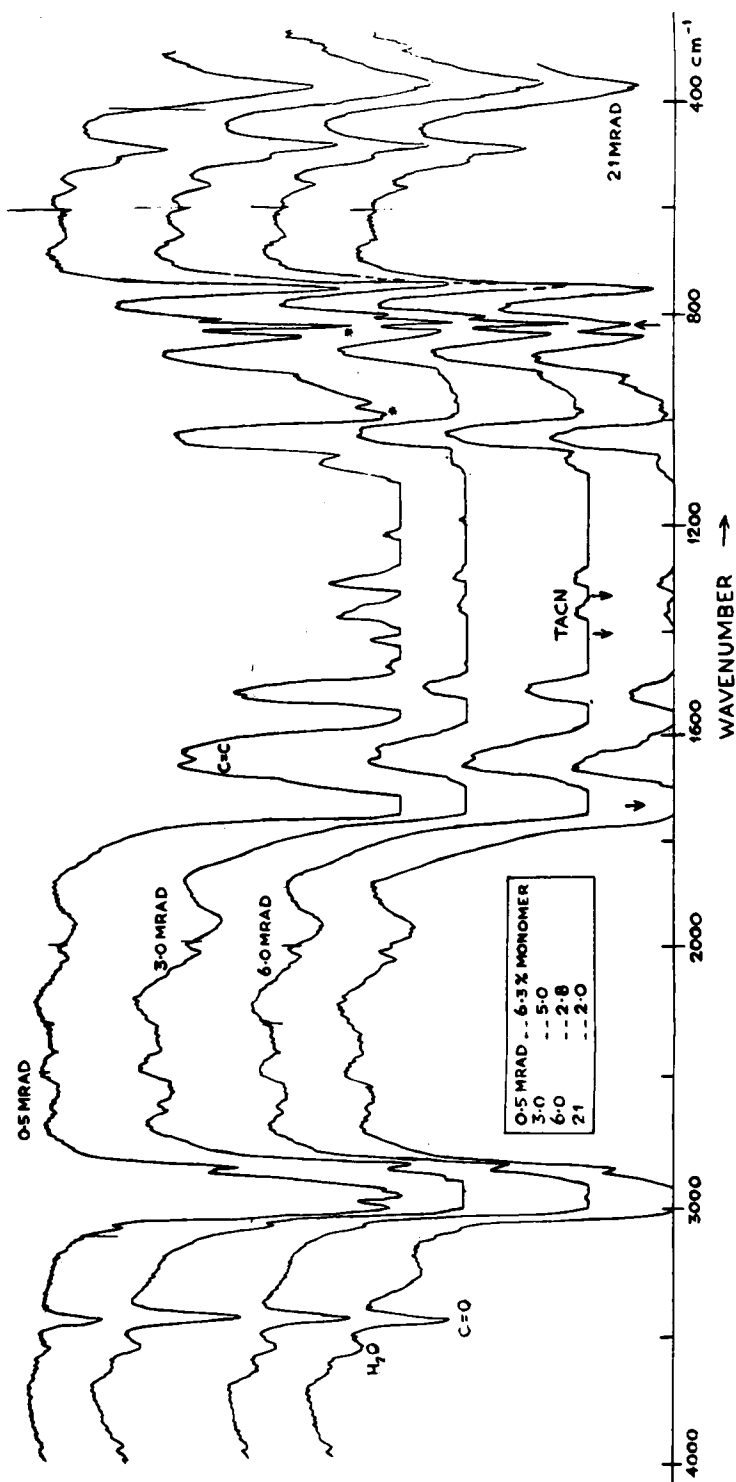


Fig. 3. Infrared spectra of representative irradiated Diakon polymers.

allyl crosslinks rather than to formation of poly(triallyl cyanurate). This view is supported by the observation of Gillham and Mentzer¹⁹ that TACN polymerizes by free-radical thermosetting reactions to form a colorless, brittle glass. They report negligible polymerization of TACN below 150°C in the presence of air, even with the addition of substantial concentrations of initiator.

The results of the infrared analyses suggest that slightly less than 2% "effective residual MMA monomer" would remain even at higher radiation levels. Such an amount of low molecular weight material would act as plasticizer and would lower the temperature of the glass transition below that of un-plasticized polymer, as in Figure 2.

Alternatively, this temperature difference may arise from concurrent radiation-induced scission of PMMA chains. Progressive lowering of T_g , attributed to reduction of molecular weight, was observed at high radiation levels in an earlier study of irradiated Perspex.²⁰ Superposition of this trend on Figure 2 gives quantitative agreement at 21.5 Mrad and implies that an eventual fall in T_g might be expected at higher radiation levels, as reported earlier by Pinner and Wycherly.⁷

The glass temperature of these plasticized Diakon polymers rises with increased radiation level. The observed nonlinear dependence of T_g on radiation dose cannot be explained by removal of plasticizer alone, since loss of allyl unsaturation is a linear function of dose⁷ and T_g is a linear function of plasticizer content.²¹⁻²⁸

It is possible that low radiation doses are more effective in introducing crosslinks into the solid PMMA polymer composition. At low crosslink density the TACN molecules may readily crosslink with adjacent PMMA chains. At higher crosslink densities the number of available crosslinking molecules is reduced and large-scale movement of unattached TACN molecules becomes necessary before crosslinks can be formed. The restricted mobility of the TACN molecules in the solid polymer then becomes important. The crosslinking efficiency of the incident radiation may, therefore, decrease at higher radiation levels.

Without such loss of crosslinking efficiency, a linear dependence of T_g on radiation might be expected, since Charlesby²⁹ reports that crosslink density is a linear function of dose, namely:

$$\rho = k \cdot R; \quad (1)$$

and Loshaek³⁰ reports that T_g is a linear function of crosslink density, namely:

$$\Delta T_g = K_x \cdot \rho \quad (2)$$

or

$$T_{gx} = T_g + K_x \cdot \rho. \quad (3)$$

However, Boyer and Spencer,³¹ Ueberreiter and Kanig,³² and Fox and Loshaek³³ note that eq. (3) is valid only for "sufficiently low crosslink density."

Alternatively, the natural tendency to chain scission of PMMA may become more dominant at higher radiation levels, as the protection imparted by TACN is diminished.

However, in addition to being affected by plasticization effects, T_g is also influenced by crosslinking,³⁴ by copolymerization,³³ and by the presence of monomer. Interaction of these factors can satisfactorily explain the pattern of behavior seen in Figure 2.

The observed changes in T_g cannot be explained by variation in the proportion of monomer, since this was effectively constant. An earlier study²⁰ also found no evidence for the generation of monomer by γ -irradiation of Perspex within the range 0–40 Mrad. Further, Geuskens, David, and co-workers^{35,36} report that irradiated PMMA depolymerizes only slightly at temperatures below 160°C.

It is possible to partially resolve the effects of the remaining factors, assuming their effects to be linear and additive. The dependence of T_g on radiation dosage for nominally pure PMMA was compared with that for the plasticized Diakon compositions. Below 10 Mrad, an increase in T_g of approximately 1.5°C/Mrad was caused by the combined effect of copolymerization and removal of plasticizer. At higher radiation levels, formation of allyl crosslinks increased the glass temperature by 0.5°C/Mrad of γ -radiation.

CONCLUSIONS

The glass temperatures of these plasticized PMMA polymers were found to increase with increased radiation level. The observed nonlinear dependence of T_g on radiation dose cannot be explained by removal of plasticizer alone, but can satisfactorily be accounted for by inclusion of crosslinking and copolymer effects.

Protection against scission is conferred by the incorporation of TACN. Spectroscopic measurements confirm the occurrence of crosslinking, with loss of allyl unsaturation.

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