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Glass transition temperature and molecular weight distribution of irradiated polymethylmethacrylates

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A mechanical torsion pendulum has been used to observe changes in viscoelastic behaviour resulting from modification of polymer structure. The linear dependence of transition temperature on reciprocal average molecular weight has been confirmed for irradiated polymethylmethacrylate polymers. Gel permeation measurements are consistent with simultaneous end-linking and chain scission at low radiation levels, leading to apparently anomalous behaviour in irradiated "Perspex".

1. Experimental

Cast I.C.I.A.N.Z. "Perspex" CLEAR sheet was cut into individual plaques 200 mm × 50 mm × 3 mm which were exposed to varying amounts of 0.19 Mrad h^{-1} γ-radiation from a cobalt-60 source. Irradiation proceeded at ambient temperatures ($\sim 30^\circ$C) in the presence of air.

A mechanical torsion pendulum, similar to that described by Heijboer *et al.* [1], was used to measure changes with temperature in the values of characteristic viscoelastic parameters. The temperature variation of these parameters was used to follow shifts in the position of the glass transition region which were caused by modification of polymer structure.

Various estimates of glass temperature have been used in the present work: T_{g1} and T_{g2}, obtained from the temperature plot of shear modulus G', are indications respectively of the lower and upper temperature limits of the transition region; and T' is in the middle of this region. The temperature T' at which the real component G' of the shear modulus is equal to 10^8 N m^{-2} has been proposed [2-4] as a reasonable estimate of the temperature of the glass-rubber transition. Symbols used to designate the various estimates of glass temperature in the present work are defined in Fig. 1.

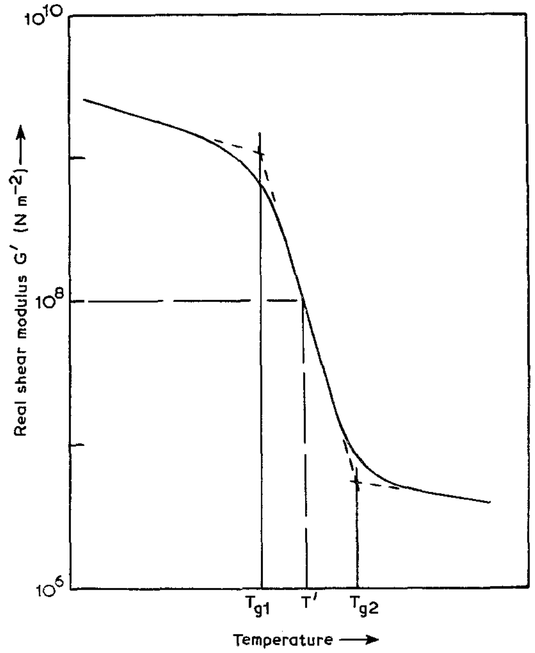

Figure 1 Designation of symbols for the various estimates of the glass transition temperature.

Solutions of the individual polymer samples were injected into G.P.C. columns at 0.25% concentration weight-to-volume of toluene, and gel permeation chromatograms run at 40°C, with a solvent flow rate of 0.75 cm^3 min^{-1} and a sample injection interval of 2 min. These chromatograms were corrected for instrument speading and axial dispersion using computer programs devised in conjunction with Smith [5].

2. Results and discussion

For normal vinyl polymers the glass temperature

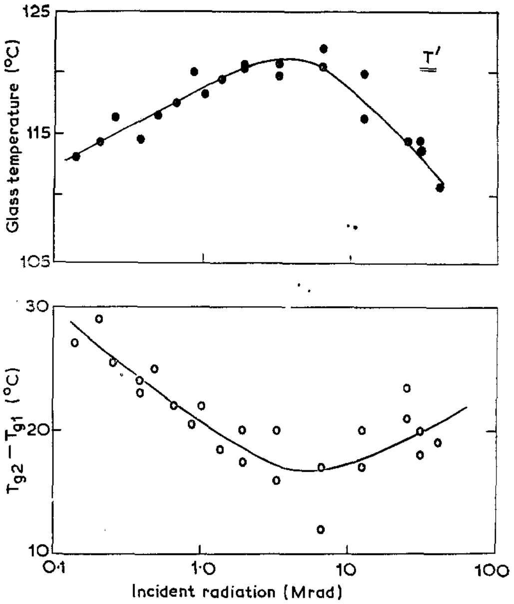

Figure 2 Variation of (a) glass temperature T' and (b) width of transition region with change in radiation level.

initially increases rapidly with increased molecular weight and gradually approaches an asymptotic value at high molecular weights [6-9]. Beevers and White [9] have reported that the asymptotic limit was reached for polymethylmethacrylate at values of number-average molecular weight $\bar{M}_n$ between 4×10^4 and 7×10^4. Similar values have been reported for polystyrene [6-8] and polyacrylonitrile [9]. Further, Ueberreiter and Kanig [7] report that the glass temperature of polystyrene fractions depended not on molecular weight distribution but on number-average molecular weight alone.

The response of polymethylmethacrylate (PMMA) to ionizing radiations has been extensively investigated. The observation that PMMA undergoes random main chain fracture without exhibiting any concurrent cross-linking reactions, or with negligible cross-linking, has been reported by Charlesby, Alexander and co-workers [10-13], Chapiro [14], Pinner and Wycherley [15], and Shultz *et al.* [16, 17].

The effect of large doses (in excess of 10 Mrad) is embrittlement, loss of strength [18], and a general deterioration of the desirable mechanical and electrical characteristics of PMMA. Shultz [19] considers this deterioration to be due to the inferior bulk properties of the low molecular weight material which is created by chain scission.

Charlesby, Moore and others [10, 19-21] report that exposure of PMMA to either ultraviolet, gamma- or pile radiation at low temperatures results in rapid reduction in molecular weight by main chain scission and the evolution of gases from rupture of side chains. Morimoto and Suzuki [22] report that cross-linking and decomposition take place simultaneously in polyalkylacrylates and methacrylates other than PMMA, and suggest that degradation in PMMA could involve depolymerization or random scission.

In addition to scission of main chains and side groups, irradiation of PMMA introduces double bonds into the polymer chain [23, 24], produces discolouration of the polymer [10, 14, 18, 25-27], and generates trapped electrons, free radicals and electron hole pairs.

Glass temperature T' and the width of the transition region are shown as functions of the logarithm of incident radiation level in Fig. 2.

For lightly irradiated "Perspex" the various estimates of glass temperature increased consistently with increase in dosage. However, the changes were not large: T_{g2} was effectively constant at 131 ± 1°C; T_{g1} increased by approximately 7°C; and T' increased by 5°C as radiation dosage increased from zero to 1.3 Mrad. In consequence, the width ($T_{g2} - T_{g1}$) of the transition region steadily decreased from 26°C for the unirradiated polymer to 16°C at 5 Mrad, as shown in Fig. 2a. As discussed below, this "sharpening" of the glass transition is attributed to changes in the molecular weight distribution of these irradiated polymers.

Although the exact form of its dependence on radiation level has not been unambiguously determined, it appears that the temperature of the glass transition increased with dosage for lightly irradiated "Perspex" polymers. This is difficult to reconcile with the above-mentioned observations [10-17, 28-30] that polymethylmethacrylate molecules were degraded by a process of chain scission when bombarded by high-energy electrons or gamma rays, and that no evidence existed for cross-linking such as occurred with polyethylene, polystyrene and many other polymers.

One possible explanation for the initial increase in T_g is that some cross-linking occurred, additives present in the commercial "Perspex" material acting as cross-linking agents, by a mechanism similar to that described by Pinner and Wycherley [15] for polymethylmethacrylate

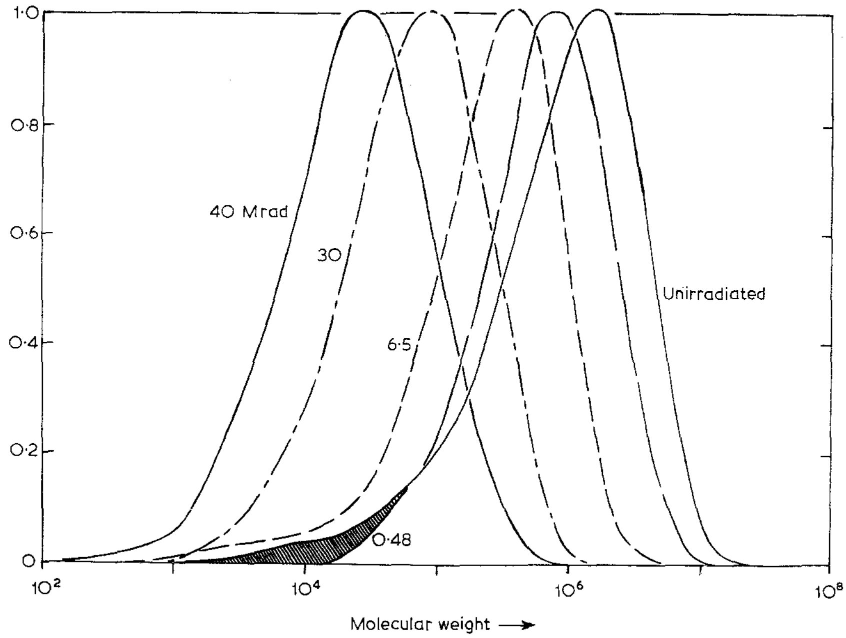

Figure 3 Gel permeation chromatograms for irradiated "Perspex" samples.

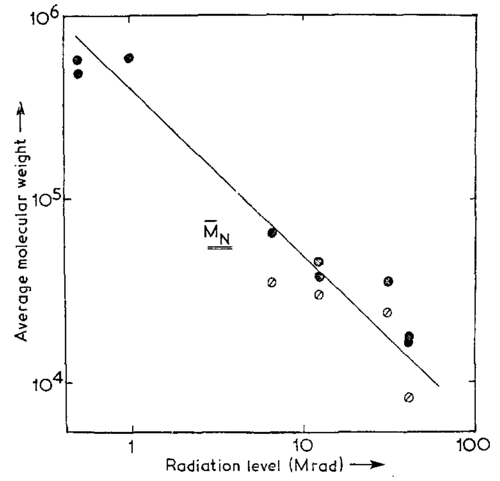

Figure 4 Variation of average molecular weight of irradiated "Perspex" samples.

compositions containing diallyl sebacate. The presence of oxygen may also have affected the chemical changes which occurred during irradiation. For such cross-linking a linear dependence of glass temperature on radiation level might be expected, since Charlesby [20] has reported that for cross-linking systems the density of cross-links is a linear function of dose, and Loshaek [31] has reported that glass temperature is a linear function of cross-link density. However, any such additives should have reacted during the free radical polymerization which produced the cast sheet.

Another possible explanation relies on progressive removal of residual monomer from the bulk polymer. Fydelor [29] has reported rapid reduction in the concentration of residual monomer in bulk PMMA specimens irradiated in air at ambient temperatures. The plasticization effect of such residual monomer would lower the glass temperature. The anomalous increase in T_g observed at low radiation levels (Fig. 2) could be explained by progressive removal of MMA monomer as irradiation proceeds.

Fig. 2b also indicates that for substantial radiation doses (4 to 40 Mrad) the temperature of the transition region decreased with increased incident radiation. For these irradiated "Perspex" samples a brown discolouration was noted, the intensity increasing with dosage; no colour or loss of clarity was detected in samples which had absorbed less than 0.5 Mrad. In addition, at higher radiation levels these polymers became increasingly more brittle.

Representative gel permeation chromatograms of irradiated and unirradiated "Perspex" samples are shown in Fig. 3.

The shifts observed in these chromatograms are consistent with preferential addition or end-linking of the "reacted monomer" to low molecular weight PMMA molecules. Residual monomer is rapidly removed [29], allowing the normal degradation process in PMMA to cause progressive reduction in average molecular weight.

Variation of number average molecular weight with radiation level is shown in Fig. 4: solid circles represent values obtained by gel permeation chromatography, and open circles represent values determined by vapour pressure osmometry.

Fig. 5 shows a typical plot of glass temperature as a function of reciprocal average molecular weight. The straight lines represent the relations $T_g = 132 - 1.55 \times 10^5 (1/\overline{M}_n)$ and $T' = 118.5 - 1.25 \times 10^5 (1/\overline{M}_n)$. These relations are in agreement with that reported by Bueche [32] and others, namely

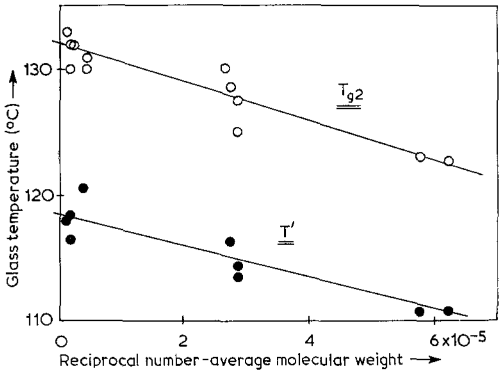

Figure 5 Dependence of glass temperature on reciprocal average molecular weight for irradiated "Perspex".

$$T_g = T_{g\infty} - \left(\frac{2\rho N\theta}{\alpha}\right) \cdot \left(\frac{1}{M}\right)$$

where T_g = glass temperature of polymer of finite average molecular weight; $T_{g\infty}$ = glass temperature of infinite polymer; ρ = density of polymer; N = Avagadro's number; θ = free volume per polymer chain end; $\alpha = \alpha_1 - \alpha_g$ is the difference in thermal expansion coefficients above and below the glass transition.

Substitution of the appropriate values gave 50×10^{-30} m^3 (i.e. 50 Å^3) as the order of magnitude of the free volume associated with each chain end in the polymethylmethacrylate polymer. This is in precise agreement with the value reported by Beevers and White [9] for atactic polymethylmethacrylate.

Plotted as a function of number-average molecular weight, the upper temperature limit T_{g2} of the glass transition region asymptotically approached 134° C as molecular weight increased beyond 3×10^5. Although this appears to be somewhat higher than the figure of 4 to 7×10^4 reported by Beevers and White [9], this difference represents a small increment in temperature, namely 3° C.

In addition, the width of the transition region for irradiated "Perspex" initially decreases with decrease in molecular weight. Lightly irradiated samples also display an initial narrowing of molecular weight distribution, as seen in the chromatograms for the two highest molecular weight polymers in Fig. 3 (and in the intervening chromatogram which has been omitted from the figure in the interests of clarity). It is suggested that the glass temperatures of these "Perspex" samples are dependent on average molecular weight and on molecular weight distribution.

In particular, for the samples with radiation doses in the range 0.0 to 0.5 Mrad T_{g2} changes little and the other estimates of glass temperature increase with increased radiation level, as in Fig. 2b. In addition, their gel permeation chromatograms indicate a lowering of average molecular weight, but also a noticeable reduction in the proportion of low molecular weight material in the range 10^3 to 10^5. This is evident, for instance, in the shaded area of Fig. 3, which represents that proportion of low molecular weight material in the unirradiated polymer which is not found in the polymer subjected to 0.48 Mrad gamma-radiation.

It is therefore postulated that, for low radiation levels, some addition of "reacted monomer" by end-linking to low molecular weight PMMA molecules occurs, although the dominant reaction is one of chain scission or depolymerization to produce polymer degradation, as evidenced by the overall reduction in molecular weight and in the reduced proportion of high molecular weight material.

For higher radiation doses there was no evidence of cross-linking or end-linking. As radiation level increased the average molecular weight and glass temperature both decreased.

The asymptotic limit for T_g, also reported elsewhere, indicates that the molecular weight dependence of glass temperature is marked at low values of molecular weight and negligible for very high molecular weights. A change in the proportion of low molecular weight molecules would, therefore, have a greater effect on T_g than would the same change in the proportion of high molecular weight molecules. For the lightly irradiated "Perspex" samples it is suggested that the increase in T_g in consequence of the removal of residual monomer and PMMA molecules with molecular weights of 10^3 to 10^5 outweighs the slight reduction caused by removal of an even larger proportion of molecules with molecular weights of 10^6 to 10^7. At higher radiation levels the reduction in the proportion of high molecular weight molecules and the increase in the proportion of low molecular weight both contribute to the lowering of glass temperature T_g.

3. Conclusion

The molecular weight dependence of the glass temperature has been established by observations for a series of irradiated polymethylmethacrylates. It has been confirmed that T_g is a linear function of reciprocal average molecular weight.

Apparently anomalous behaviour has been observed in "Perspex" exposed to γ-radiation: T_g initially rises with increase in radiation level, goes through a maximum, then falls with further radiation. GPC measurements provide evidence for simultaneous removal of low molecular weight material and degradation of high molecular weight molecules, with consequent narrowing of molecular weight distribution. The initial rise in glass temperature is attributed to the operation of these factors and it is suggested that residual monomer in the commercial polymer may be responsible for the apparent anomaly.

References

1. J. HEIJBOER, P. DEKKING and A. J. STAVERMAN, in "Proceedings of the 2nd International Congress on Rheology", edited by V. G. W. Harrison (Academic Press, New York, 1954) p. 123.
2. A. V. TOBOLSKY, D. CARLSON and N. INDICTOR, *J. Appl. Polymer Sci.* **7** (1963) 393.
3. R. B. TAYLOR and A. V. TOBOLSKY, *ibid* **8** (1963) 1563.
4. A. V. TOBOLSKY and M. TAKAHASHI, *ibid* **7** (1963) 1341.
5. B. R. SMITH, private communication (1973).
6. T. G. FOX and P. J. FLORY, *J. Appl. Phys.* **21** (1950) 581.
7. K. UEBERREITER and G. KANIG, *J. Colloid Sci.* **7** (1952) 569.
8. R. BUCHDAHL and L. E. NIELSEN, *J. Appl. Phys.* **21** (1950) 482.
9. R. B. BEEVERS and E. F. WHITE, *Trans. Faraday Soc.* **56** (1960) 744.
10. P. ALEXANDER, A. CHARLESBY and M. ROSS, *Proc. Roy. Soc. Lond.* **A223** (1954) 392.
11. A. CHARLESBY, "Atomic Radiation and Polymers" (Pergamon, London, 1960).
12. A. CHARLESBY and N. MOORE, *Int. J. Appl. Radiation & Isotopes* **15** (1964) 703.
13. P. ALEXANDER and D. TOMS, *J. Polymer Sci.* **22** (1958) 343.
14. A. CHAPIRO, *J. Chim. Phys.* **53** (1956) 295.
15. S. H. PINNER and V. WYCHERLEY, *J. Appl. Polymer Sci.* **3** (1960) 338.
16. A. R. SCHULTZ, P. I. ROTH and G. B. RATHMANN, *J. Polymer Sci.* **22** (1956) 495.
17. A. R. SCHULTZ, P. I. ROTH and J. M. BERGE, *ibid* **A1** (1963) 1651.
18. O. SISMAN, W. PARKINSON and C. BOPP, in "Radiation Effects in Organic Materials", edited by R. Bolt and J. Carroll (Academic Press, New York, 1963) p. 127.
19. A. R. SCHULTZ, *J. Polymer Sci.* **35** (1959) 369.
20. A. CHARLESBY, *Proc. Roy. Soc. Lond.* **A215** (1952) 187.
21. *Idem*, *Nature* **171** (1953) 167.
22. K. MORIMOTO and S. SUZUKI, *J. Appl. Polymer Sci.* **16** (1972) 2947.
23. D. G. GARDNER and M. T. A. TOOSI, *ibid* **11** (1967) 1065.
24. J. P. ALLISON, *J. Polymer Sci. A-1* **4** (1966) 1209.
25. F. A. BOVEY, "The Effects of Ionizing Radiation on Natural and Synthetic High Polymers", Polymer Reviews, Vol. 1 (Interscience, New York, 1958).
26. E. E. SCHNEIDER, M. J. DAY and G. STEIN, *Nature* **168** (1951) 645.
27. M. J. DAY and G. STEIN, *ibid* **168** (1951) 644.
28. P. F. FENG and J. W. KENNEDY, *J. Amer. Chem. Soc.* **77** (1955) 847.
29. P. J. FYDELOR, *European Polymer J.* **7** (1971) 401.
30. E. J. LAWTON, A. M. BUECHE and J. S. BALWIT, *Nature* **172** (1953) 76.
31. S. LOSHAEK, *J. Polymer Sci.* **15** (1955) 391.
32. F. J. BUECHE, "Physical Properties of Polymers" (Interscience, New York, 1962).

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