

Degradation of Polystyrene by Gamma Irradiation: Effect of Air on the Radiation-Induced Changes in Mechanical and Molecular Properties

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Synopsis

Irradiation of 3 mm polystyrene sheet in air at 30°C with γ rays caused a rapid decrease in the tensile and flexural strengths and strains to fracture. These properties were decreased to 50% of their initial values after ca. 80 Mrads and to 25% after ca. 200 Mrads, beyond which dose the rate of change was relatively small. These results contrast with the negligible changes that are observed after 600 Mrads in vacuum. The effect of irradiation in air has been correlated with decreasing molecular weight at the surface, even though crosslinking predominated over the complete sample so that a gel point was reached at a dose slightly in excess of 100 Mrads. Scission and crosslinking yields, $G(S)$ and $G(X)$, were determined as a function of depth by gel permeation chromatography of layers removed progressively from the surface. $G(S)$ decreased and $G(X)$ increased with depth, in accord with the concepts of increased scission by reaction with oxygen and a diffusion effect. Unusual transverse cracking to a limited depth occurred during tensile measurements, a phenomenon that is attributed to the nonuniform molecular weight profile.

INTRODUCTION

The effects of high-energy (ionizing) radiation on a polymer material may result in an improvement in some physical properties and a deterioration in others, there frequently being a decrease in ultimate strength and/or elongation to fracture whereas the modulus may increase. The increasing use of polymer materials in various radiation environments requires greater knowledge of the quantitative relationships between changes in mechanical properties and irradiation conditions, such as dose rate, total dose, temperature, surrounding environment, and the chemical and morphological structure of the polymer.

Two important molecular effects of radiation on polymers are chain scission and crosslinking, whereby the molecular weight and physical properties can be altered significantly by a relatively small radiation dose. Whether a polymer undergoes predominantly crosslinking or scission on irradiation depends primarily on its chemical structure. The former is indicated by the formation of insoluble gel above the gel dose D_g , resulting from formation of an "infinite" molecular network that commences when there is one crosslink per weight-average molecule: this phenomenon occurs provided that $G(S) < 4G(X)$. Homopolymers of substituted ethene monomers can be classified according to the presence or absence of a disubstituted main-chain carbon atom, disubstitution leading to the predominance of scission on irradiation in vacuum or an inert atmosphere; otherwise crosslinking is predominant.

Polystyrene forms an insoluble gel on irradiation under vacuum in accord with this criterion, Parkinson and co-workers¹ having found $G(X) = 0.034$ and $G(S) = 0.009$ for γ irradiation of polystyrene at 22°C under vacuum. These are low values compared with scission and crosslinking yields for nonaromatic polymers but conform with the radiation resistance observed in low-molecular-weight aromatic compounds,² a phenomenon that has been attributed to energy transfer to the benzene ring with subsequent nondegradative dissipation of the energy.

Polystyrene has been reported³ to be very resistant to radiation; no significant decrease in tensile strength, elongation, modulus, shear strength, or impact strength was observed after irradiation in the ORNL reactor to approximately 1000 Mrads despite the occurrence of considerable darkening. Moreover, it was claimed that there was no difference in the effect of irradiation in air or helium on the mechanical strength, although there was an increase in weight and density on irradiation in air. Doses as high as 30,000 Mrads were reported to cause less than 50% decrease in the above properties.⁴ However, much lower radiation resistance in air than in vacuum has been observed with aromatic polysulfones,⁵ which are similar to polystyrene in the sense that they are amorphous, glassy plastics with a high aromatic content.

Because of this apparent conflict between results for polystyrene and polysulfones we have reexamined the effect of air on the radiation-induced changes in the mechanical properties of polystyrene. In addition, since the effect of air on scission and crosslinking yields remains equivocal⁶ because of the wide variation in literature values of $G(S)$ and $G(X)$, the present work examines the role of air in radiation-induced changes in the molecular characteristics of polystyrene.

EXPERIMENTAL

Polydisperse polystyrene (Type HR001; high-purity granules) was supplied by Shell Chemicals, U.K., and a narrow molecular weight distribution sample ($\bar{M}_w/\bar{M}_n \leq 1.06$) was obtained as a powder from Pressure Chemical Co., Pittsburgh, Pa.; the \bar{M}_v values were 240,000 and 184,000 for the polydisperse and "monodisperse" samples, respectively. Sheets of polystyrene with a thickness of 3.2 mm were made from powder or granules by compression molding between stainless-steel glazing plates at 185°C and a pressure of 50 kg/cm² for 5 min. Bars for measurements of flexural strength were cut from the sheet with a bandsaw and the edges polished on a water-cooled lapping wheel. Dogbone specimens for tensile strength measurements were cut using a router and stress relieved at 100°C for 5 hr. Samples for measurements of compressive strength were obtained from the ends of specimens that had been used for flexural strength tests using prisms with lengths such that the slenderness ratio, i.e., the ratio of length to radius of gyration (0.289 times the smaller cross-sectional dimension for a uniform rectangular bar), was in the range of 11:1 to 18:1. The dimensions of all specimens used for testing are given in Table I.

For irradiation polystyrene samples were placed individually in open glass tubes to allow free contact with air and subjected to ⁶⁰Co γ rays at dose rates in the range 0.1 to 4.0 Mrads/hr; facilities at either the Australian Atomic Energy Commission Research Establishment, Lucas Heights (Sydney), or the University

TABLE I
Specifications of Samples Used for Mechanical Strength Tests

Specimen	Test	Length, mm	Width, mm	Thickness, mm	Span, mm	Wt., g	Gauge length, mm	Fillet radius, mm
A	flexural strength	76.2	12.7	3.2	50.8	4.0		
B	flexural strength	50.8	6.4	3.2	38.1	1.3		
C	tensile strength	76.2	12.7/6.4 ^a	3.2			38.1	25.4
D	tensile strength	127	12.7/6.4 ^a	3.2			38.1	76.2
E	tensile strength	203	19.1/12.7 ^a	3.2			50.8	76.2
F	compressive strength	13	13	3.2				
G	compressive strength	10	6.5	3.2				

^a Widths of grip and test sections, respectively.

of Salford, U.K., were used. Air was circulated through the irradiation containers holding the tubes to prevent the depletion of oxygen.

Flexural strength measurements were made with an Instron 1026 at a cross-head speed of 2 mm/min and a span of 50.8 mm for large bars (type A in Table I) and at 1 mm/min and a span of 38.1 mm for small bars (type B). Tensile and compression measurements were made at 2 mm/min.

In order to measure the depth dependence of molecular weight, successive layers were removed from irradiated bars by wet grinding on a lapping wheel. Removed polymer was recovered by filtering the washing water, dissolving the grindings in chloroform, filtering to remove particles of the abrasive, evaporating the solution, and drying the polymer film under vacuum at 50°C for 5 hr.

Viscosities of polystyrene samples were measured in toluene at 30°C with an Ubbelohde viscometer, and limiting viscosity numbers $[\eta]$ were obtained by Huggins and Kraemer relationships. Gel permeation chromatography experiments were performed at 20°C on a Waters 201 liquid chromatograph using four 61-cm columns of Styragel in series: these contained gels with porosities that permitted molecular sieving in the molecular size ranges of 10^6 Å, 10^5 Å, 10^4 Å, and 10^3 Å. Solutions (2 ml) of polystyrene in toluene (0.25% w/v) were used routinely, and the system was calibrated with narrow molecular weight distribution polystyrene samples of known size. Corrections were made for chromatographic dispersion.⁷

Gel and soluble fraction measurements were made by repeated extraction using either a Soxhlet extractor or a stainless-steel mesh bag; toluene was used as the extracting solvent. Results were analyzed by standard procedures.

RESULTS

Mechanical Properties

Flexural Strength. Miniature bars (type B, $50.8 \times 6.4 \times 3.2$ mm³, ca. 1.3 g) were compared with the smallest ASTM D736 size (type A, $76.2 \times 12.7 \times 3.2$ mm³, ca. 4 g) in order to establish their equivalence for flexural strength testing. Reproducibility of flexural fracture strengths was excellent (A, $\pm 3\%$; B, $\pm 5\%$) for unirradiated bars from the same pressing, but slightly higher absolute values were obtained from B bars (+5%) for which a smaller span was used (A, 50.8 mm; B, 38.1 mm). Results for irradiated bars showed similar differences. No dependence of flexural strength on strain rate in the range 1 to 5 mm/min was observed. However, the presence of an atmospheric environment during compression molding caused a 10%–15% reduction in the flexural strength compared with that for bars that were molded in a nitrogen atmosphere.

On irradiation under vacuum, the flexural strength and modulus of specimens prepared from sheet which had been compression molded in nitrogen were unaffected by doses up to 500 Mrads, (\square) in Figure 1(a). However, samples molded in air but irradiated under vacuum showed a progressive increase in flexural strength with dose to a value similar to that of samples molded in nitrogen, (\circ) in Figure 1(a).

Irradiation in air caused a rapid and approximately exponential decrease in flexural strength with dose, (\blacksquare) in Figure 1(a), similar results being obtained with specimens prepared from polydisperse or narrow molecular weight distribution

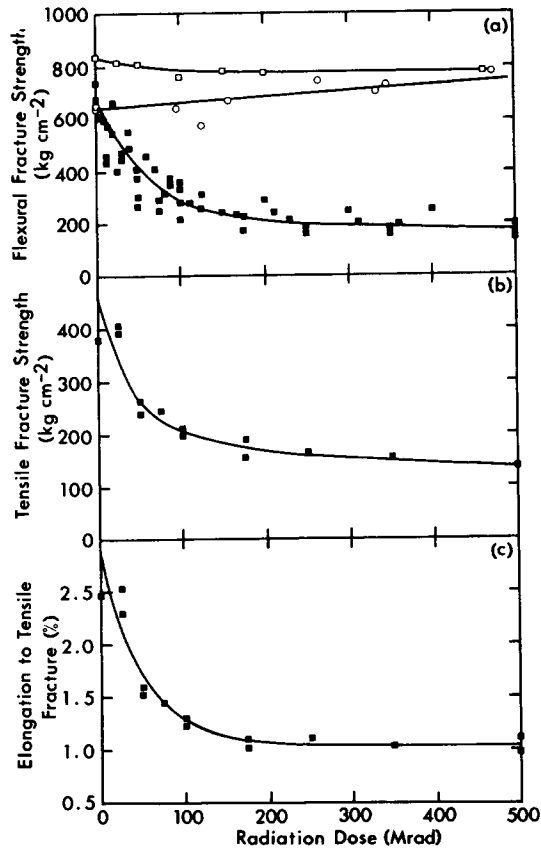


Fig. 1. Effect of radiation dose on mechanical strength of 3-mm polystyrene sheet: (a) flexural strength; (b) tensile strength; (c) elongation to tensile fracture; (■) sample molded and irradiated in air; (○) sample molded in air and irradiated under vacuum; (□) sample molded and irradiated in the absence of air (in part the data of Busfield and O'Donnell⁹).

polystyrene. The dose dependence of the flexural strength decreased markedly above 200 Mrads, by which stage the strength was about 25% of the unirradiated value. This retention of a finite flexural strength was not due to oxygen depletion in the environment of the irradiated specimens.

Tensile Strength. The use of miniature specimens was also investigated for tensile strength measurements. In this case a reduction in size compared with the ASTM recommendation was necessary because the radiation source provided a uniform dose rate only over a vertical distance of about 100 mm. Type C specimens (dimensions in Table I) gave similar results to the ASTM size (type E), but fracture frequently occurred at the end of the gauge length. This problem was overcome by using a larger fillet radius (type D), which also allowed an increased grip length. The reproducibility of tensile strength measurements was about $\pm 10\%$, which was inferior to the flexural strength tests.

The tensile strength was unaffected by irradiation under vacuum but showed an approximately exponential decrease with radiation dose in air, Figure 1(b), similar to the decay of flexural strength. The modulus was not changed significantly but the elongation to break decreased, Figure 1(c).

An unusual crack development phenomenon was observed in the tensile testing

of specimens irradiated in air. Samples subjected to doses greater than 100 Mrads exhibited hairline cracks on the surface. These cracks were of uniform depth (about 0.1 mm but seemingly a function of dose), perpendicular to the long, draw axis of the specimen and mostly parallel to each other. They passed completely around the cross section of the sample and tended to be equally spaced along the gauge length. Figure 2 shows cracks formed in specimens subjected to doses of 200, 350, and 500 Mrads; only a few cracks were formed in specimens with doses of 100 and 175 Mrads. The cracks started to form when the applied stress was approximately half the fracture stress and formed in succession along the sample until one crack (not necessarily the first one formed) propagated beyond the arrest depth and fracture occurred. Examination of the fracture surface showed that the crack surface was smooth and shiny, whereas the remainder was rough and exhibited a herring bone fracture pattern similar to that described by Bird and co-workers.⁸

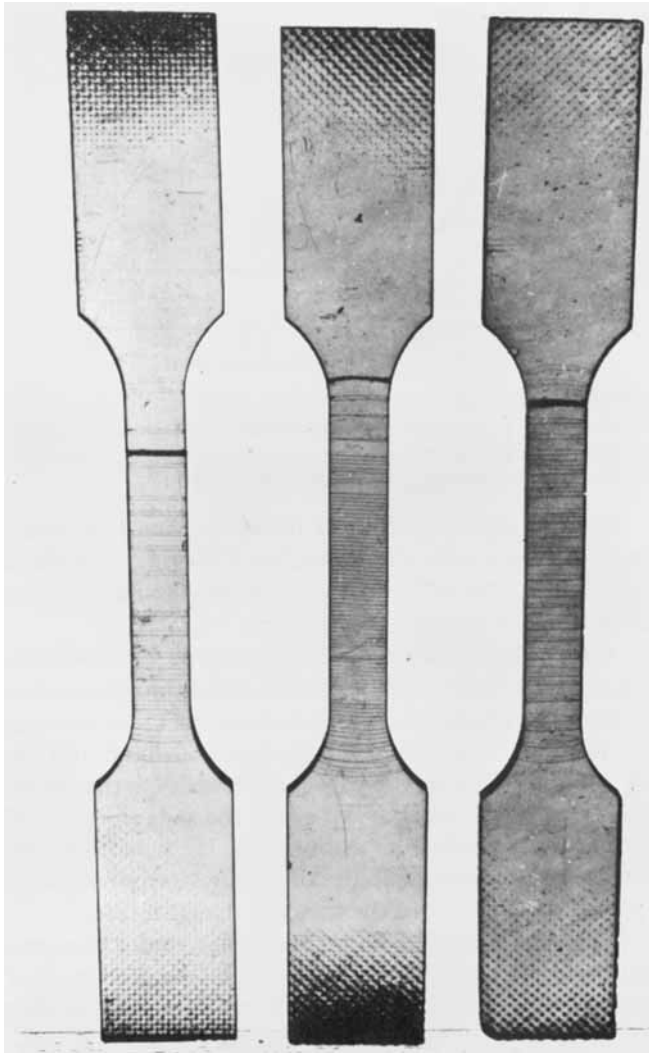


Fig. 2. Surface crack phenomenon in irradiated samples used for tensile testing.

Compressive Strength. The compressive strengths, measured on sections of type A flexural strength bars, gave high reproducibility (1060 ± 21 kg/cm²). Similar values were obtained for specimens with different dimensions (types F and G; dimensions in Table I). The unirradiated specimens underwent plastic deformation in compression, instead of the brittle fracture observed in flexural and tension tests, and formed raised crosses along the diagonals of the large sides. No significant variation in strength was observed with dose on irradiation under vacuum or in air up to 500 Mrads. However, after doses greater than 20 Mrads in air the specimens failed by brittle fracture, a phenomenon which had been observed with styrene-methyl methacrylate copolymers.⁹

Color Development

The UV spectrum of polystyrene bars showed a progressive shift of the aromatic absorption to longer wavelengths with increasing dose, Figure 3(a), the color development being much greater for samples irradiated in air than under vacuum. Further evidence for the involvement of air in this coloration process was the inverse depth dependence as measured by the absorption characteristics of solutions prepared by dissolving in chloroform successive layers of a polystyrene bar that had been subjected to 100 Mrads, Figure 3(b): absorbances have been normalized to those of 1% solutions in a cell with 1-cm path length.

Viscosimetric Studies of Irradiated Polystyrene

The limiting viscosity number of complete, polydisperse bars, measured at 30°C in toluene, was essentially unchanged in the dose range 0 to 80 Mrads but thereafter increased rapidly with dose (Fig. 4); a gel dose slightly in excess of 100

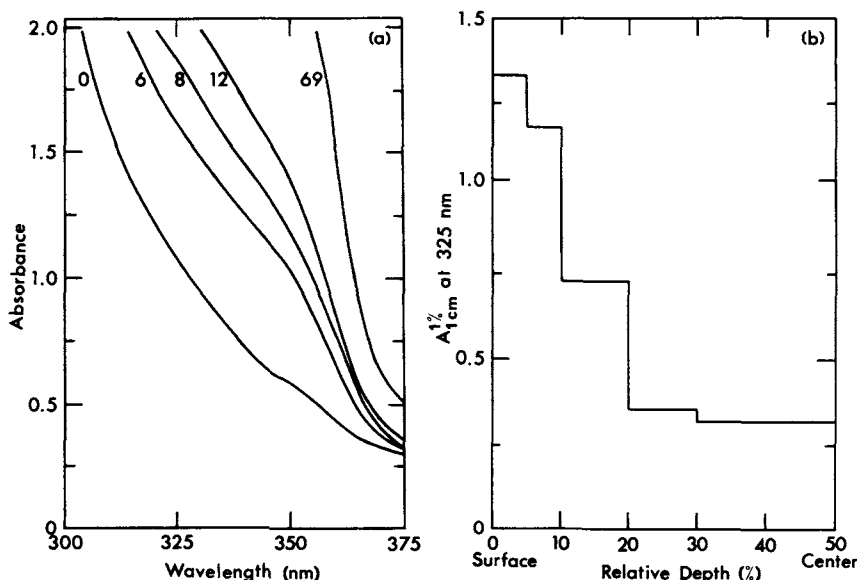


Fig. 3. Effect of irradiation in air on the color of 3-mm polystyrene sheet. (a) Demonstration of the red shift of aromatic absorption spectrum with increasing radiation dose; numbers adjacent to spectra indicate Mrads of γ irradiation. (b) Depth dependence of color development in a 3-mm sheet of polystyrene subjected to 100 Mrads γ irradiation.

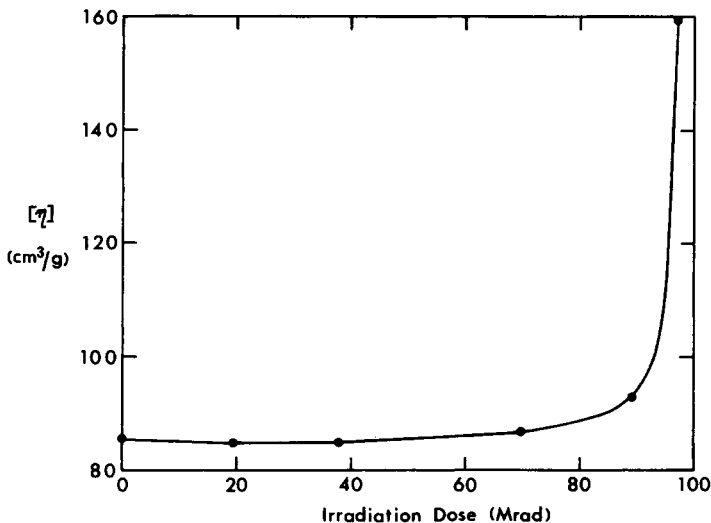


Fig. 4. Effect of radiation dose on limiting viscosity number of polydisperse polystyrene (whole bar of type A) irradiated in air.

Mrads is indicated for samples subjected to a dose rate of 0.2 to 0.4 Mrad/hr. These results reflect average sizes of polystyrene molecules comprising a whole bar and hence establish the overall predominance of crosslinking over scission. However, on the basis of the mechanical tests, Figure 1, and the depth dependence of color development, Figure 3(b), we have tested the postulate that the effects of irradiation on molecular weight are not homogeneous throughout the sample.

Irradiation of solid polymer samples in air results in competition between reactions of free radicals (produced by the radiation) with oxygen and without involvement of oxygen. The relative importance of the reaction with oxygen will be determined by factors such as the dose rate, the oxygen permeability of the polymer, and the distance of the radical from the surface. Since the reactions of free radicals with oxygen can be expected to cause degradation, scission of the polystyrene should be maximal at the surface and decrease progressively toward the center of the polymer bar.

Preliminary evidence that implicates the existence of such a phenomenon is shown in Figure 5(a), which presents the depth profile of the limiting viscosity number for a polystyrene bar that had been subjected to 50 Mrads; results are expressed relative to the magnitude of $[\eta]$ for unirradiated polystyrene. Since $[\eta] = k\bar{M}_v^a$, the fractional value of this ratio for the outside layer indicates predominance of scission at the expense of crosslinking in the surface layer, whereas the values greater than unity imply the predominance of crosslinking in the center of the bar, where the supply of oxygen would have been minimal if existent. The exponential decrease in the viscosity of the surface layer with increasing radiation dose, Figure 5(b), correlates reasonably well with the decline in mechanical properties of irradiated polystyrene bars, Figure 1. This concept of the decrease in mechanical strength of polystyrene bars being related to polymer degradation at the surface of the bar is substantiated further in the following section in which "monodisperse" polystyrene is used instead of the polydisperse sample to which Figure 5 refers. Moreover, because of the uncertainties that surround the in-

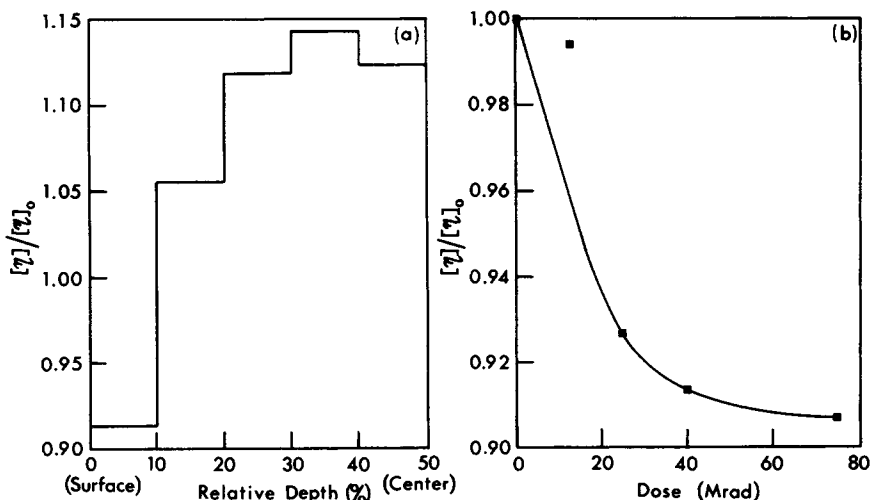


Fig. 5. Viscosimetric studies of (a) depth dependence of the molecular weight of a 3-mm sheet of polystyrene subjected to 50 Mrads γ irradiation in air, and (b) dose dependence of the surface molecular weight of such sheets.

terpretation of \bar{M}_v values for crosslinked polymers, the effects of γ irradiation on molecular size are followed by gel permeation chromatography.

Gel Permeation Chromatography of Irradiated Polystyrene

Depth Dependence of the Elution Profile. The results of gel permeation chromatography experiments are presented in Figure 6, about which the following points merit comment. (i) The solid line in Figure 6(a) represents the elution profile obtained with unirradiated narrow molecular weight distribution polystyrene powder, the pattern being consistent with the manufacturer's specification that $\bar{M}_w/\bar{M}_n \leq 1.06$. (ii) The broken line in Figure 6(a) describes the elution profile obtained with the same unirradiated polystyrene in sheet form,

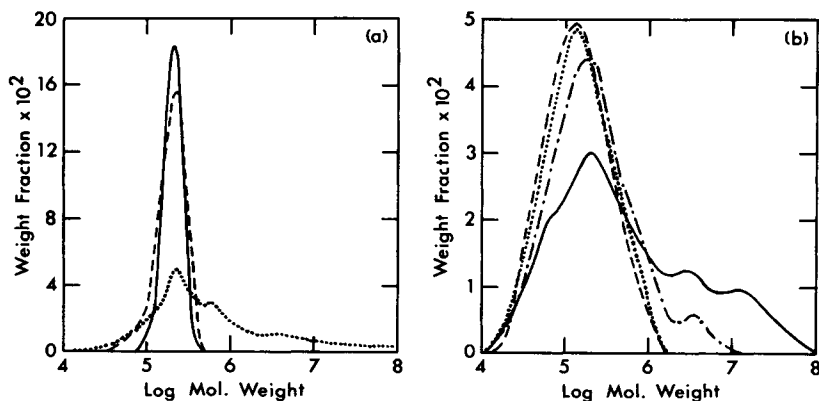


Fig. 6. Depth dependence of gel permeation chromatograms obtained with "monodisperse" polystyrene subjected to 100 Mrads γ irradiation in air: (a) --- unirradiated powder; (---) molded, unirradiated sheet; (.....) core of the irradiated sheet after removal of the outer 30% of the polystyrene from each side; (b) (---) surface layer (0%–5%); (.....) 5%–10%; (---) 10%–20%; (---) 20%–30%.

and the difference between this profile and that for the powder must reflect the effect of compression molding in the presence of air. In this connection, the presence of the low-molecular-weight tail in the molded sample correlates with the observation, Figure 1(a), that the flexural strength of polystyrene sheet molded in air is less than that of sheet molded in the absence of oxygen. (iii) The dotted line in Figure 6(a) denotes the elution profile for the core of a polystyrene bar that had been subjected to 100 Mrads of γ irradiation and subsequently had the outside 30% of its surface removed from each side. Although some scission has obviously occurred, the predominant effect of irradiation on the center of the bar is crosslinking. Indeed, the amount of lower-molecular-weight material is overemphasized in Figure 6(a) since the curves have all been normalized to unit area even though a significant but unmeasured amount of the core material did not dissolve. (iv) Figure 6(b) shows the chromatograms for the various layers removed from the same irradiated bar. Scission, not crosslinking, is clearly the predominant phenomenon occurring in the regions in greatest contact with air (oxygen). The relative decline of this degradation with the increasingly anoxic conditions encountered through the cross section of the bar is demonstrated even more convincingly in Figure 6 than in Figure 5(a).

Correlation Between Surface Molecular Weight and Mechanical Strength. The depth dependence of molecular weight, Figures 5(a) and 6, plus the exponential decrease in mechanical strength, Figure 1, and limiting viscosity number of the surface layer, Figure 5(b), with increasing dose indicates an interrelationship between strength and surface molecular weight. This hypothesis is tested in Figure 7, which presents the dependence of tensile and flexural strengths upon \bar{M}_n of the surface layer. The latter quantities have been calculated from gel permeation chromatograms for the surface layers of bars subjected to 0, 25, 50, 75 and 100 Mrads of γ rays. Mechanical strengths of the whole bars have been interpolated from Figures 1(a) and 1(b) and expressed relative to the values for unirradiated polystyrene sheet with $\bar{M}_n \approx \bar{M}_w \approx 200,000$. Expression

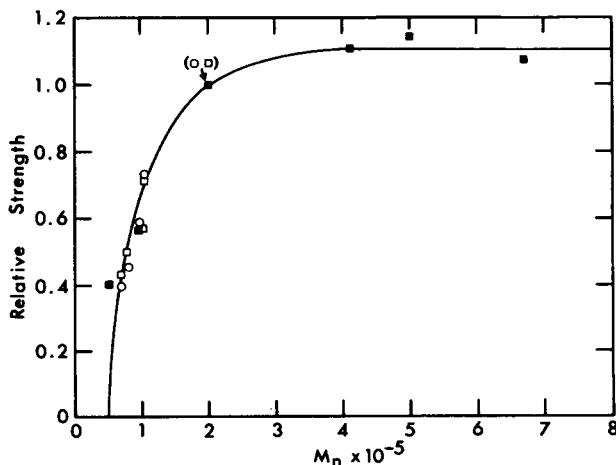


Fig. 7. Dependence of mechanical strength of irradiated polystyrene on surface molecular weight: (\square) tensile strength; (\circ) flexural strength; (\blacksquare) tensile strength of unirradiated polystyrene (data of Vlachopoulos et al.¹⁰). Results are expressed relative to values obtained for "monodisperse" polystyrene with a molecular weight of 200,000.

of strengths in this manner has permitted not only a direct comparison of the molecular weight dependence of tensile and flexural properties but also a comparison with the most recent tensile strength data for "monodisperse" polystyrene.¹⁰ The agreement between the present results for surface molecular weight and the literature data for unirradiated polystyrenes is most striking and also in accord with the conclusion that a molecular weight (\bar{M}_n) above about 50,000 is required for polystyrene sheet to possess significant mechanical strength.¹¹ We therefore conclude that a lower surface molecular weight is primarily responsible for the decrease in mechanical strength that accompanies irradiation of polystyrene sheet in air. The depth dependence of molecular weight also provides an explanation for the formation, during tensile testing, of transverse cracks which penetrate only partially through the specimen (Fig. 2). Beyond the surface layer, scission decreases markedly and the molecular weight of the polystyrene increases, thus providing a barrier to crack penetration at low stresses.

Evaluation of $G(S)$ and $G(X)$ from Gel Permeation Chromatograms.

In addition to providing values of $\bar{M}_n(D)$, elution profiles such as those shown in Figure 6 may also be analyzed to give the weight-average [$\bar{M}_w(D)$] and z -average [$\bar{M}_z(D)$] molecular weights of a sample subjected to radiation dose D , whereupon it is possible to determine the radiation chemical yields of scission and crosslinking from any pair of the following three expressions^{12,13}:

$$\bar{M}_n(D) = \bar{M}_n(0)/[1 + u\tau - u\chi] \quad (1)$$

$$\bar{M}_w(D) = 2\bar{M}_n(0)\phi_1(u\tau, \sigma)/[(u\tau)^2\{1 - (4\chi/u\tau^2)\phi_1(u\tau, \sigma)\}] \quad (2)$$

$$\bar{M}_z(D) = 3\bar{M}_n(0)\phi_2(u\tau, \sigma)/[\phi_1(u\tau, \sigma)\{1 - (4\chi/u\tau^2)\phi_1(u\tau, \sigma)\}^2] \quad (3)$$

where

$$\phi_1(u\tau, \sigma) = u\tau - 1 + (1 + u\tau/\sigma)^{-\sigma} \quad (4)$$

$$\phi_2(u\tau, \sigma) = 1 + (1 + u\tau/\sigma)^{-(\sigma+1)} - (2/u\tau)\{1 - [1 + u\tau/\sigma]^{-\sigma}\} \quad (5)$$

In these equations, τ is the probability that after a dose D (Mrads in this paper) a monomer unit in the polymer has undergone scission, and χ is the corresponding probability of formation of a crosslink per monomer unit. The width of the initial distribution, which is considered to be of the Schulz-Zimm type, is signified by σ , which is related to the initial number-average [$\bar{M}_n(0)$] and weight-average [$\bar{M}_w(0)$] molecular weights by the expression

$$\sigma = 1/\{[\bar{M}_w(0)/\bar{M}_n(0)] - 1\} \quad (6)$$

The number of monomer units u comprising an initial number-average molecule is obtained by dividing $\bar{M}_n(0)$ by the molecular weight of a monomer unit. $G(S)$ and $G(X)$ are then obtained from eq. (7):

$$G(S) = 9.65 \times 10^5 u\tau / D\bar{M}_n(0) \quad (7a)$$

$$G(X) = 9.65 \times 10^5 u\chi / D\bar{M}_n(0) \quad (7b)$$

Before applying eqs. (1) through (7) to the present data, values of the apparent molecular weights deduced from calibration curves for linear molecules have been corrected for crosslinking using the data of Shultz.¹⁴ Specifically, distribution-moment correction factors of 1.052 for $\bar{M}_n(D)$, 1.220 for $\bar{M}_w(D)$, and 1.466

for $\bar{M}_z(D)$ have been used, these values having been interpolated from Table I of Shultz¹⁴ for a system with a Mark-Houwink exponent of 0.72 and a Schulz-Zimm factor (σ) of 10 under conditions such that D is 0.6 of the gel dose. Figure 8(a) summarizes the depth dependence of the $G(S)/G(X)$ ratio obtained from elution profiles for samples subjected to 50 and 100 Mrads of γ -irradiation, the gel dose being 125 Mrads.⁶ Figure 8(b) presents the corresponding values of $G(X)$ and $G(S)$. Several points should be made in relation to Figure 8. (i) The value of σ obtained from a single pass in the GPC using eq. (6) is 13.7, which is considerably lower than our earlier and more reliable estimate⁶ of 33. However, variation of the value of σ over this range had no significant effect on the scission and crosslinking yields deduced from eqs. (1) to (3). (ii) Since the gel dose is 125 Mrads under the present conditions (Fig. 8 of Nichol and co-workers⁶), the value of 0.6 used for the fractional gel dose is clearly a compromise value. (iii) The results in Figure 8 represent the averages of the relevant parameters obtained by coupling $\bar{M}_n(D)$ with $\bar{M}_w(D)$ and with $\bar{M}_z(D)$. (iv) No marked differences were observed between the radiation chemical yields obtained for the two doses. (v) The $G(S)/G(X)$ ratio decreases at least threefold with increasing depth, Figure 8(a), there being a concomitant doubling of $G(X)$ to a value that approaches the crosslinking yield pertaining to irradiation of polystyrene under vacuum.¹

Effect of the Physical Form of Polystyrene on $G(S)/G(X)$ Ratios

Figures 5(a), 6, and 8 serve to emphasize that crosslinking and scission yields obtained from either gel or solution studies of the entire irradiated sample are average values that depend on the extent to which oxygen penetrates the sample. For example, irradiation of polystyrene in powder or film form should result in a much larger $G(S)/G(X)$ ratio for the whole sample because of the greater relative surface area of such systems compared with that of a sheet or bar. This

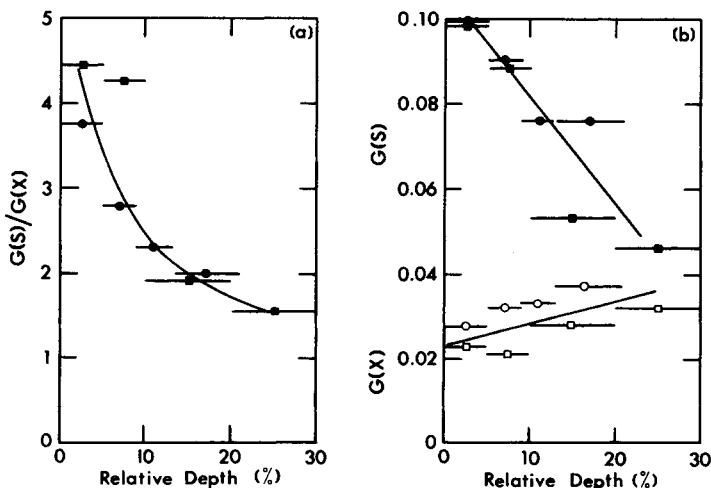


Fig. 8. Depth dependence of (a) the $G(S)/G(X)$ ratio and (b) the radiation chemical yields of scission (solid symbols) and crosslinking (open symbols) for "monodisperse" polystyrene subjected to 50 Mrads (circles) and 100 Mrads (squares) γ irradiation. The horizontal bar associated with each experimental point denotes the range of relative thickness pertaining to the measurement.

phenomenon is illustrated in Figure 9, which presents Charlesby–Pinner plots for polystyrene powder and sheet that had been irradiated in air. The much higher $G(S)/G(X)$ ratio for irradiated powder (3.7 compared with 1.0 for sheet) is in accord with the greater surface area-to-volume ratio for polystyrene in this form and correlates well with the value obtained for the surface layer of an irradiated bar, Figure 8(a). It might also be noted that the value of unity for $G(S)/G(X)$ of the irradiated sheet (bar) is in excellent agreement with our earlier conclusion⁶ that $G(S) = G(X)$ for polystyrene sheet with identical dimensions. An intermediate value of 1.9 obtained for the $G(S)/G(X)$ ratio for the granular form of polystyrene also conforms with the concept that the extents of scission and crosslinking depend primarily on the availability of oxygen within the polystyrene sample being irradiated in air.

DISCUSSION

The exposure time or dose required to reduce a given property to 50% of its initial value is frequently used as a measure of resistance of a polymer material to degradation in a particular environment. For 3-mm polystyrene sheet irradiated in air at 0.1 to 5.0 Mrads/hr, this is about 80 Mrads.

There have been various brief reports of increased scission when polystyrene has been irradiated in air. Thus, Feng and Kennedy¹⁵ found that the limiting viscosity number of 0.8-mm polystyrene sheet irradiated with ^{90}Sr – ^{90}Y β rays decreased in air but increased under vacuum. Gamma irradiation of polystyrene in air, or under vacuum followed by exposure to air, has been shown to increase the number of hydroxyl and carbonyl groups in the polymer.¹⁶ A marked difference in gel formation between polystyrene rod and film irradiated in air was observed by Alexander and Toms,¹⁷ presumably reflecting the increased sur-

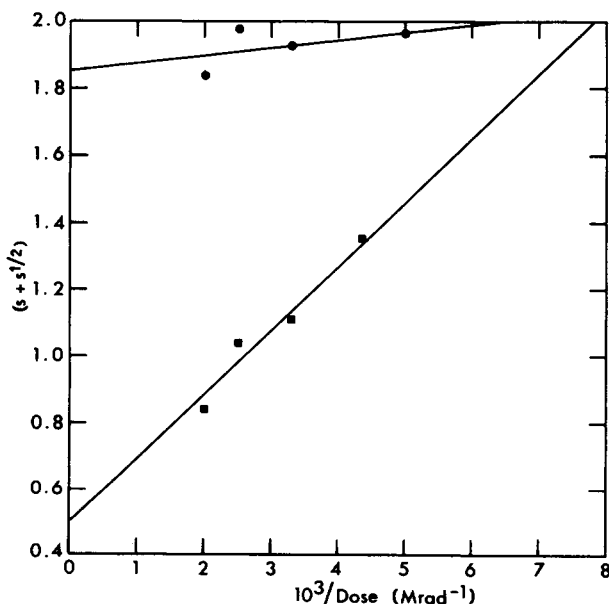


Fig. 9. Charlesby–Pinner plots of gel solubility data obtained with polystyrene in powder (●) and sheet (■) form.

face-to-volume ratio and hence facilitated diffusion into the film sample. Oxygen effects have also been observed with other polymers. For example, Dole and co-workers¹⁸ observed that the tensile strength of 0.076-mm, low-density polyethylene film was greatly decreased by irradiation in air but was relatively unaffected by irradiation under vacuum. A steady state between oxygen diffusion into polyethylene and reaction between oxygen and radicals has been demonstrated by Matsuo and Dole,¹⁹ the oxygen content being zero at depths greater than 0.5 mm for a dose rate of 0.2 Mrad/hr and an oxygen pressure of 7895 Pa.

In the present work we have shown that the mechanical properties of polystyrene deteriorate quite rapidly on irradiation in air, in contrast with the high resistance to irradiation under vacuum or in an inert atmosphere. Flexural strength has been found to be a particularly convenient means of following the deterioration in polystyrene, which is an amorphous, glassy plastic that exhibits failure by brittle fracture. Good reproducibility of the fracture strength was observed with small samples that were readily prepared from compression-molded 3-mm sheet and could be exposed in restricted test environments. Good correlation with the results of tensile tests was observed (Fig. 1).

The technique of removing successive layers from the surface has proved conclusively that whereas the molecular weight of the whole polystyrene specimen increases with radiation dose, the molecular weight of the surface decreases, Figures 5(a) and 6. There have been several reports of the variation in tensile strength with molecular weight which show that the strength increases rapidly from a zero threshold at $\bar{M}_n = 50,000$ to 60,000 and approaches a limiting maximum value above $\bar{M}_n \approx 100,000$. A similar dependence on surface molecular weight could reasonably be expected for flexural strength, since fracture is initiated by crack formation at the surface. Figure 7 provides convincing evidence for such dependence of mechanical strength (flexural and tensile) on the surface molecular weight of polystyrene. An analogous relationship between mechanical strength and molecular weight of irradiated polymer has been observed previously with styrene-methyl methacrylate copolymers irradiated under vacuum.⁹

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