Radiation degradation of poly(styrene-co-methylmethacrylate). 2. Protective effects of styrene on volatile products, chain scission and flexural strength

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The volatile products from γ-irradiation of poly(styrene-co-methylmethacrylate)s at 30°C are found to be the same as from PMMA. The *G* values are substantially below the values corresponding to linear relationships between the homopolymers. This is attributable to an intramolecular protective effect by the styrene units. Net *G*(scission) values have been derived from viscosity measurements on the irradiated copolymers after different doses. They also show a protective effect by styrene. The radiation dose (in vacuum) for a 50% reduction in flexural strength increased linearly with mole fraction of styrene from $(x_S)_p=0$ to 0.7, above which it increased more rapidly.

Keywords Degradation; radiation; poly(styrene-co-methyl methacrylate); styrene; chain scission; flexural strength

INTRODUCTION

The main features of the radiation degradation of a number of homopolymers have now been established, enabling prediction of the effects of radiation, under specified conditions, e.g. temperature and atmospheric environment, to be made on the basis of the structure of the polymer. The importance of copolymers in polymer materials science and engineering has been increasing rapidly, but few investigations have been made of the radiation degradation of copolymers and particularly of the structure–property degradation behaviour relationships.

We have previously reported[1] measurements of the flexural and compressive strengths of poly(styrene-co-methylmethacrylate)s after radiation doses in vacuum at 25°C up to 200 Mrad. There were consistent correlations between molecular weight and flexural strength for all the copolymers.

E.s.r. measurements of the concentrations of trapped free radicals in a 50:50 copolymer gave a value which was only 56% of the value interpolated linearly from the radical yields of the homopolymers[2]. This was apparently due to a protective effect by the aromatic component and is analogous to the reduced $G(H_2)$ values observed from liquid mixtures of benzene and cyclohexane[3].

Here, we have measured the yields of volatile products from the γ-irradiation of styrene–methylmethacrylate copolymers at 30°C as a function of copolymer composition and found a similar protective effect. A protective effect has also been inferred from the variation of *G*(scission) values, derived from the reduction in molecular weight measured by viscosity, with copolymer composition.

EXPERIMENTAL

Styrene and methylmethacrylate were distilled at 60°C under a low pressure of nitrogen. Random copolymers were prepared by free radical polymerization in bulk at 50°C using AIBN initiator, reprecipitating from toluene into methanol and drying under vacuum at 120°C.[1] Samples were sealed under vacuum after 50 h evacuation at 30°C and irradiated with ^{60}Co γ-rays at a dose rate of $\sim$2 Mrad h^{-1} to total doses up to 200 Mrad using the facilities of the Australian Atomic Energy Commission. Volatile products were determined by gas chromatography. Viscosities were measured in toluene at 30°C. Flexural strengths were determined on bars cut from compression moulded sheet.

RESULTS AND DISCUSSION

Volatile products

The volatile products from samples of each copolymer were analysed after several different radiation doses. Linear plots of product yield *versus* dose were obtained after low doses and the *G* value for each product was obtained from its yield/dose plot using $G(\text{product}) = \text{slope}(\text{mol g}^{-1}\ \text{Mrad}^{-1})/1.036$. The main volatile products were H_2, CO, CH_4 and CO_2, and the less-volatile products were Me_2O, HCO_2Me, MeOH, H_2O and $CH_3CO_2CH_3$. The *G* values for homopolymers are compared with previous reported measurements of Todd[4] and David *et al.*[5] in *Table 1*, and are in fair

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Table 1 G values for volatile products from the homopolymers: a comparison of experimental results with literature values

Poly(methylmethacrylate)

Product	H_2	CO	CH_4	CO_2	MeOH	DME	MeF	DMM	MeAc
This work	0.34	1.08	0.66	0.68	0.36	–	0.69	0.11	0.02
Todd[a] (1960)[4]	0.21	0.54	0.23	0.28	0.03	0.04	0.03	0.11	0.01
David *et al.* (1970)[5]	0.27	1.31	0.63	0.80	0.12	0.12	0.76	0.08	0.03

Polystyrene

Product	H_2
This work	0.033
Wall and Brown (1957)[6]	0.022
Burlant *et al.* (1962)[7]	0.039

[a] G values calculated from mol % of each component, total yield of volatile products and radiation dose given in ref 4
DME = dimethyl ether; MeF = methyl formate; DMM = dimethoxymethane

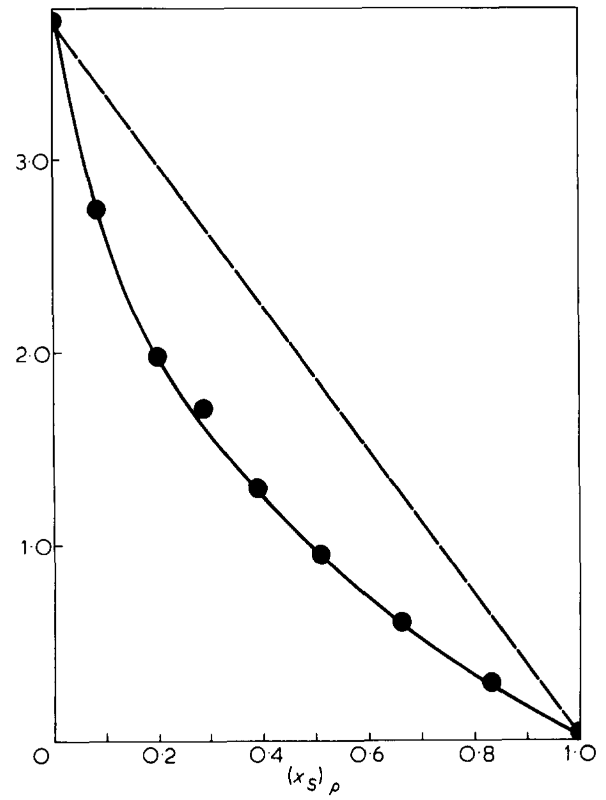

Figure 1 Variation of G(total volatile products) with copolymer composition for γ-irradiation at 30°C. $(x_S)_p$ = mole fraction of styrene in the copolymer

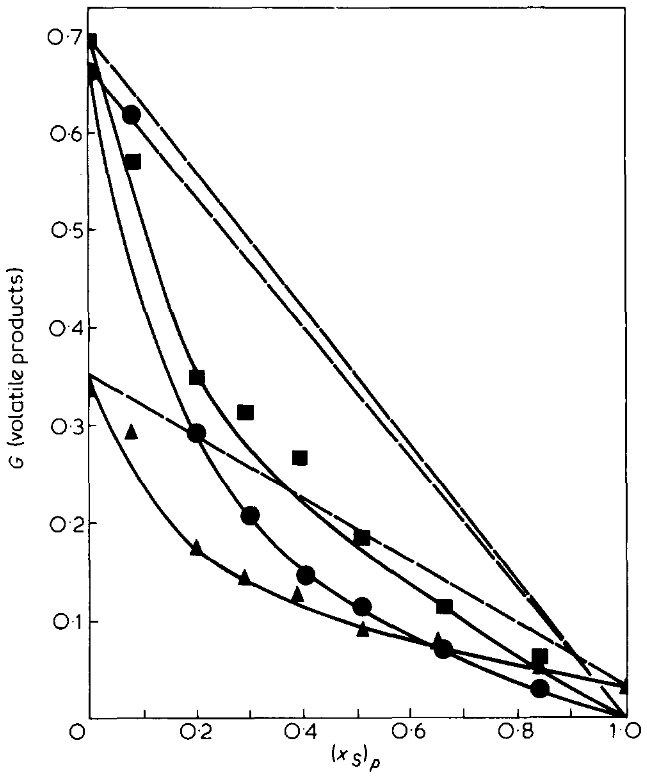

Figure 2 Variation of G (CH_4), G (CO_2) and G (H_2) with copolymer composition for γ-irradiation at 30°C. (●), CH_4; (■), CO_2; (▲), H_2. (——) experimental, (– – –) linear, relationship

agreement. The same distribution of products was observed for all the copolymers as from PMMA, indicating that these products result from fragmentation of MMA units in the copolymers, and particularly from the ester groups. This behaviour would be expected in view of the very low volatile product yield from polystyrene[6,7], which is mainly H_2. This low yield is attributable to intramolecular radiation protection by the aromatic phenyl group[8].

The yields of all products increased with MMA content of the copolymers as shown in *Figures 1* and *2*. Linear relationships between G(product) and copolymer composition would correspond to additivity of the radiation sensitivities of the two types of monomer unit in the copolymer. The experimental yields are clearly less than these predictions. Similar, but even greater deviations from linearity are well known for G(H_2) values from irradiation of liquid mixtures of benzene and cyclohexane[3]. This is the classic example of intermolecular radiation protection by an aromatic component of a mixture. In the copolymers, we are observing intramolecular protection in the solid state.

Molecular weight

The limiting viscosity numbers of the irradiated copolymers were converted to $\bar{M}_v$ values using literature data as described previously[1]. The molecular weights decreased upon irradiation for copolymers with $x_S \leqslant 0.66$, and more rapidly with increasing x_{MMA}, indicating that for $x_S \leqslant 0.66$ scission predominates over crosslinking. Assuming that the copolymers have the most probable molecular weight distribution, and that branching does not seriously affect the relationships between $[\eta]$ and $\bar{M}_v$, then $\bar{M}_v$ can be related to $\bar{M}_n$ by equation (1). Linear plots

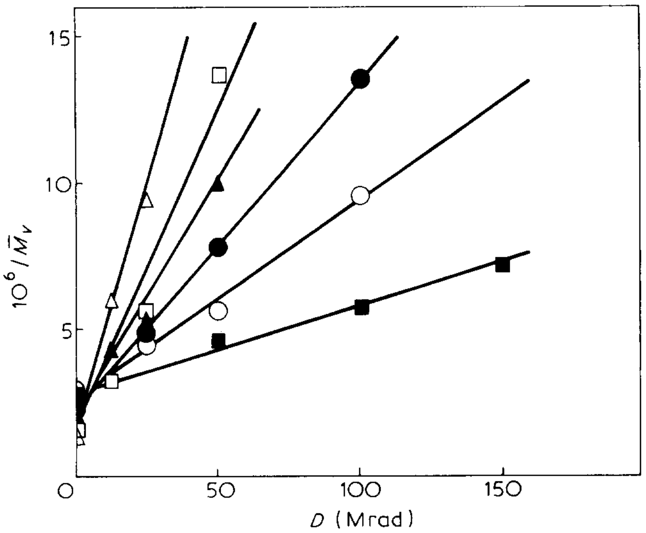

Figure 3 Variation of $1/\bar{M}_v$ with radiation dose (D) for irradiation of styrene–methylmethacrylate copolymers at 30°C. $(x_S)_p$: (■), 0.66; (○), 0.51; (●), 0.39; (▲), 0.29; (□), 0.20; (△), 0.08

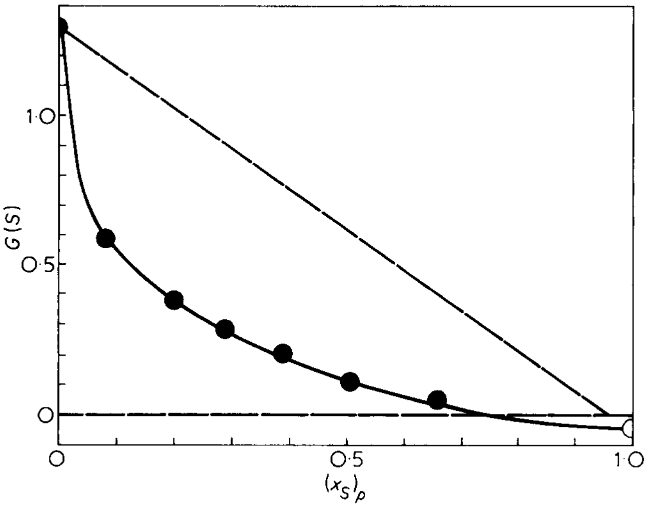

Figure 4 Variation of $G(S)$, derived from linear plots in *Figure 3* and equations (1) and (2) with copolymer composition. Value at $(x_S)_p$ = 1.0 taken from ref 9

of $1/\bar{M}_v$ *versus* dose D in Mrad were obtained, as shown in *Figure 3*, from which values of $G(S)$, the radiation chemical yield for net chain scission, were obtained using equation (2).

$$\bar{M}_n=\frac{\bar{M}_v}{[(a+1)\Gamma(a+1)]^{1/a}} \qquad (1)$$

$$1/\bar{M}_n=1/\bar{M}_n^0+G(S)D/9.65\times10^5 \qquad (2)$$

The relationship between $G(S)$ and copolymer composition is shown in *Figure 4*. There is a progressive decrease in $G(S)$ with increasing x_S. Moreover, there is a deviation from a linear relationship between PMMA and PS. It appears that the styrene units are causing a reduction in chain scission beyond their mole fractions in the copolymers. This relationship, shown in *Figure 4*, is quite similar to that for volatile products shown in *Figures 1* and *2*.

Flexural strength

A convenient expression for the rate of degradation of a polymer material in a particular environment is the exposure required for a property of interest to be reduced to one half of its initial value. For styrene–methylmethacrylate copolymers, flexural strength has been utilized to follow the deterioration in material properties[1]. The values of $D_{1/2}$ for irradiation of styrene–methylmethacrylate copolymers in vacuum can be obtained from plots of flexural strength *versus* dose. Alternatively, the relative flexural strengths gave quite good linear plots against log(dose), as shown in *Figure 5*, from which the $D_{1/2}$ values can be interpolated.

The vairation of $D_{1/2}$ with copolymer composition is shown in *Figure 6*. Perhaps surprisingly, no protective effect of styrene is evident. In fact, there is an approximately linear relationship of $D_{1/2}$ with x_S up to $x_S=0.67$, after which it rises rapidly. Polystyrene shows little change in flexural strength on irradiation in vacuum. The relationship in *Figure 6* can be explained by the increase in molecular weight with styrene content in this copolymer system necessary to achieve a given flexural strength. This negates the protective effect of the styrene units up to high x_S.

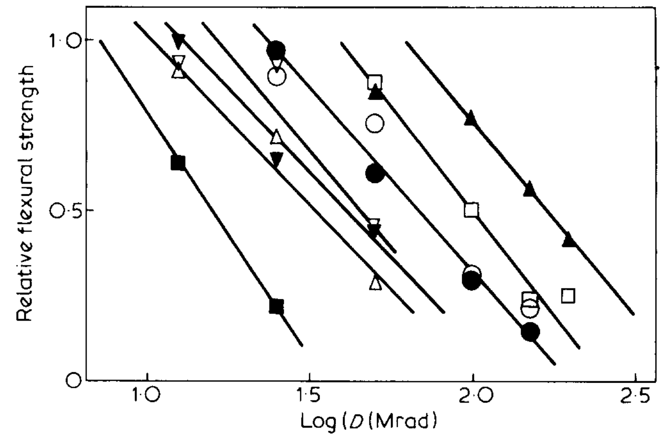

Figure 5 Variation of flexural strength of styrene–methylmethacrylate copolymers with log (radiation dose) for γ-irradiation at 30°C. $(x_S)_p$: (■), 0.00; (△), 0.08; (▼), 0.20; (▽), 0.29; (●), 0.39; (○), 0.51; (□), 0.66; (▲), 0.84

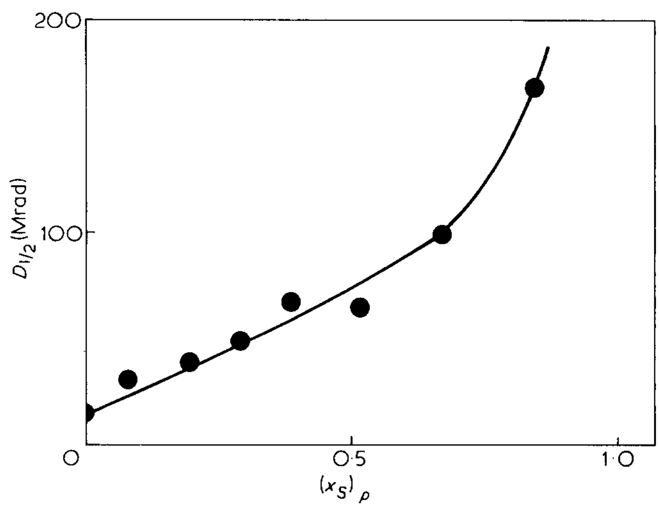

Figure 6 Variation of radiation dose, $D_{1/2}$, for flexural strength to decrease to one-half of its initial value, with copolymer composition

CONCLUSIONS

The volatile radiolysis products from the copolymers are attributable almost entirely to fragmentation of the methylmethacrylate units, and particularly of the ester groups. The deviation of G values from molar additivity of the homopolymer values indicates a protective effect by styrene units in the chains. Plots of $1/\bar{M}_v$ *versus* radiation dose are useful for obtaining estimates of $G(S)$, and the variation with copolymer composition also indicates a protective effect.

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