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Radiation Degradation of Copolymers. III. Poly(styrene-co-methyl Acrylate)

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ABSTRACT

The distribution of volatile products from γ-irradiation of copolymers of styrene and methyl acrylate is independent of the composition of the copolymer and the same as that obtained from poly(methyl acrylate). The yields are less than proportional to the methyl acrylate content, indicating a protective effect from the styrene units as observed previously in copolymers of styrene with methyl methacrylate. The flexural strengths of the copolymers, measured at 1°C, decrease with radiation dose for high styrene content, but increase for high methyl acrylate content. Samples irradiated in air have appreciably lower strengths than those irradiated in vacuum. Gel measurements show intermediate behavior for the copolymers between the homopolymers.

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INTRODUCTION

High energy irradiation causes the mechanical properties of polymer materials to deteriorate, and may be correlated with changes in molecular weight. These changes result from chain scission and cross-linking reactions. Extensive research has established guidelines for the relationships between radiation-induced changes and polymer structure for homopolymers. Thus polymers containing aromatic groups, e.g., polystyrene, are highly resistant to radiation whereas aliphatic, vinyl polymers with a disubstituted carbon atom in the main chain, e.g., poly(methyl methacrylate), readily undergo chain scission.

In contrast to homopolymers, remarkably little has been reported about the molecular and material property changes of copolymers under high-energy irradiation. Behavior intermediate between that of the homopolymers might be expected, but protective, or synergistic, effects could occur.

Previous studies on the γ-irradiation of copolymers of styrene and methyl methacrylate [1, 2] have illustrated a consistent correlation between flexural strength and molecular weight, with absolute values intermediate between those of the homopolymers.

The main objective in that work was to compare the relative influence in the copolymer chain of 1) a radiation-insensitive, cross-linking monomer unit with 2) a radiation-sensitive, chain scission monomer unit. In the present study we have examined the behavior of a copolymer system containing styrene, with a predominantly cross-linking, radiation-sensitive monomer unit, for which methyl acrylate was chosen. No work has apparently been reported on irradiation of copolymers of styrene with methyl acrylate.

EXPERIMENTAL

Styrene and methyl acrylate were distilled under a low pressure of nitrogen. The copolymers were prepared by bulk polymerization with AIBN initiator to low conversion at 60°C in an annular dilatometer. They were purified by precipitation into methanol from toluene and dried at 120°C in a vacuum oven. Compositions were determined by microanalysis and ^{1}H NMR. Variation of composition with conversion was calculated with a computer program for the integrated copolymer equation of the terminal model using reported reactivity ratios.

Polymer samples were sealed under vacuum or in air and irradiated in the ^{60}Co pond facility of the A.A.E.C. Volatile products were determined by gas chromatography using calibrations with pure compounds. Small sheets (3.2 mm thick) of the copolymers were compression molded in a nitrogen atmosphere. Bar specimens ($50 \times 6.4 \times 3.2$ mm for flexure; $12.0 \times 6.4 \times 3.2$ mm for compression) were cut with a bandsaw and edge-polished on a lapping wheel. Flexural and compressive strengths were measured with an Instron model 1026 tensometer using the small bars, as described previously [1]. For these mechanical strength measurements, the samples were irradiated at -78°C and measured at 1°C using a circulating water cooling system. Gel measurements were made on small sections of the bars by repeated extraction in boiling toluene under nitrogen using stainless-steel mesh bags. The extracted samples were dried in a vacuum oven above T_g, weighed and reextracted. Five extractions of ~8 h were necessary to obtain constant weight of gel.

RESULTS AND DISCUSSION

Gas Analyses

The yields of volatile radiolysis products were determined for each copolymer at several radiation doses at 30°C. Figure 1 shows some typical yield/dose plots; G values were determined from the slopes of these plots. Some measurements were also made after irradiation at -78 and +150°C.

The variation of G(total gas) with copolymer composition for irradiation at -78, +30, and 150°C is shown in Fig. 2. The G values for 150°C, which is well above the glass transition temperatures of all the copolymers, show a markedly concave relationship below the linear correlation with composition between the homopolymers. This is indicative of a protective effect of the styrene units in the copolymers and is analogous to the behavior observed previously in the irradiation of copolymers of styrene and methyl methacrylate [2, 3]. Deviation from linearity is less apparent at 30°C and not discernable within the experimental reproducibility at -78°C. There is no discontinuity evident between low styrene copolymers, which would be above T_g, and high styrene copolymers, which would be below T_g. At 30°C this transition should occur at $x_S \approx 0.25$.

The main volatile radiolysis products resulting from γ-irradiation were H_2, CO, CH_4, and CO_2, and there were minor amounts of Me_2O, HCO_2Me, and $MeCO_2Me$. The yields of the latter products are less reliable, both because of the small amounts and on account of their low volatility. G values at the three irradiation temperatures are shown in Table 1. It is notable that the temperature dependence of G(total volatile products) increases markedly with X_{MA}, as shown in Fig. 3. This is similar to the behavior observed previously in styrene-methyl methacrylate copolymers [2] and is therefore unlikely to be related to the lower T_g of PMA compared to PS. These volatile products are the same as those observed from the radiolysis

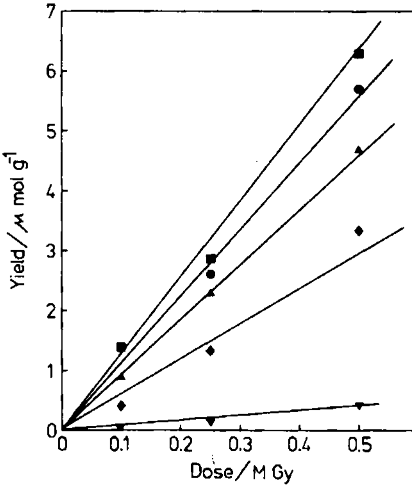

FIG. 1. Dose dependence of volatile product yields from γ-irradiaat 30°C of poly(styrene-co-methyl acrylate) containing 18 mol% styrene: (■) CH_4, (●) CO, (▲) CO_2, (◆) HCO_2Me, (▼) Me_2O.

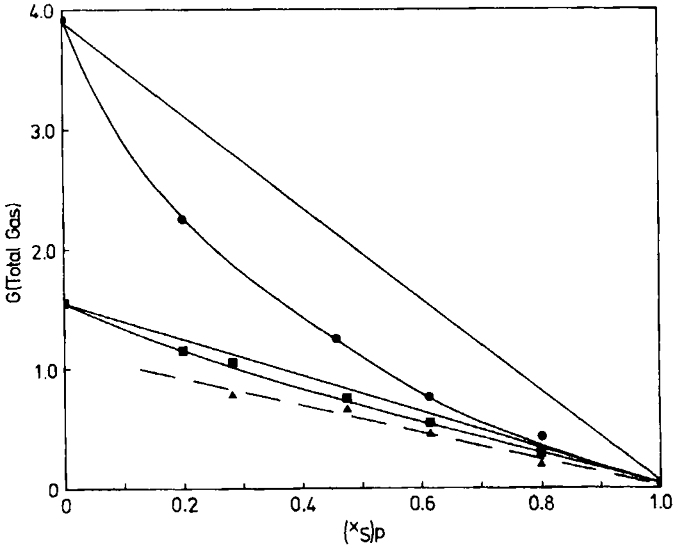

FIG. 2. Dependence of G(total volatile products) on the mole fraction of styrene, $(x_S)_p$, in poly(styrene-co-methyl acrylate). Irradiation at (●) 150°C, (■) 30°C, and (▲) -78°C.

TABLE 1. G Values for Volatile Products from γ-Irradiation of Poly(styrene-co-methyl acrylate)s at -78, 30, and 150°C

mol% STY	Mrd	H_2	CO	CH_4	CO_2	Me_2O	HCO_2Me	$MeCO_2Me$
-78°C								
29	25/50	0.15	0.20	0.16	0.15	0.009	0.065	0.005
43	25/50/100		0.18	0.11	0.11	0.008	0.08	0.004
60	50		0.12	0.072	0.065	0.002	0.032	0.002
80	50		0.048	0.036	0.039	0.001	0.018	0.002
30°C								
0	10/25/50	0.43	0.28	0.50	0.21	0.025	0.14	0.006
12	10/25/50	0.20	0.30	0.37	0.23	0.01	0.08	0.003
18	10/25/50	0.17	0.23	0.25	0.18	0.01	0.11	0.006
29	100		0.29	0.34	0.15	0.04	0.15	0.05
60	200		0.25	0.076	0.10	0.009	0.053	0.014
80	200		0.11	0.043	0.078	0.002	0.016	0.016
150°C								
0	50		0.57	0.66	0.27	0.019	0.088	0.004
12	50		0.43	0.23	0.24	0.014	0.068	0.002
18	50		0.43	0.15	0.19	0.006	0.052	0.001
43	100		0.25	0.09	0.13	0.005	0.035	0.001
60	100		0.11	0.048	0.064	0.001	0.020	-
80	100		0.06	0.026	0.042	0.001	0.005	-

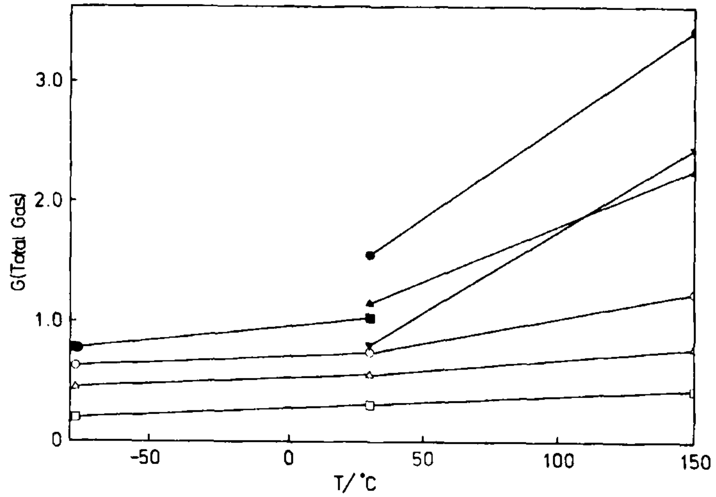

FIG. 3. Temperature dependence of the yields of volatile products from γ-irradiation of poly(styrene-co-methyl acrylate)s. $(x_S)_p$: (□) 0.80, (△) 0.60, (○) 0.43, (■) 0.29, (▼) 0.18, (▲) 0.12, (●) 0.00.

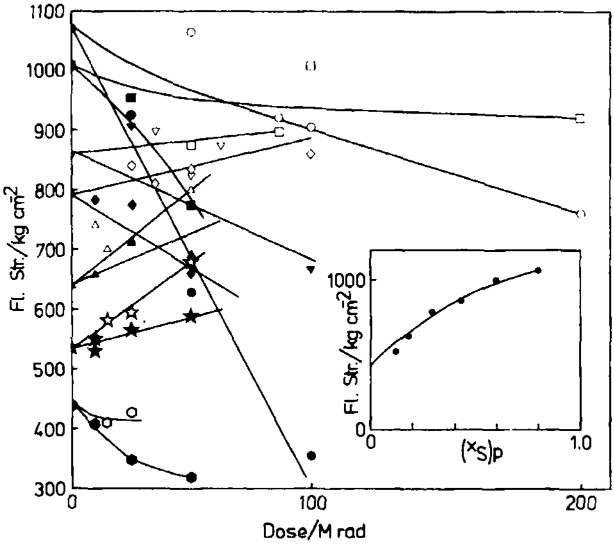

FIG. 4. Dose dependence of the flexural strength of poly(styrene-co-methyl acrylate) bars irradiated at -78°C in vacuum and air and measured at 1°C. $(x_S)_p$: (○) 0.00; (☆), 0.12, (△), 0.18; (◇), 0.29; (▽) 0.43; (□) 0.60; (○) 0.80. Irradiation in vacuum: open symbols. Irradiation in air: filled symbols. Insert: Variation of flexural strength of unirradiated samples with copolymer composition.

of poly(methyl methacrylate) by Todd [4] and by Geuskens [5] and of poly(methyl acrylate) by Todd [4], and can be attributed to the same sequence of reactions, involving mainly fragmentation of the ester group.

Flexural Strength

The variation in flexural strength of each copolymer with radiation dose, for irradiation in vacuum and in air, is shown in Fig. 4. It is more difficult to obtain measurements on the mechanical properties of copolymers of styrene and methyl acrylate, which can be compared as a function of copolymer composition, than for styrene-methyl methacrylate copolymers due to the substantial difference in T_g values in the former series (T_g = 8°C for PMA and 100°C for PS). For this reason the polymers were irradiated at -78°C and measured at 1°C, which was the lowest operational temperature available with the Instron. The results in Fig. 4 show some interesting effects. They may be summarized as 1) the flexural strength of the unirradiated samples increases with the styrene content: this is shown clearly in the insert and may be related to the magnitude of T_g - T (measurement). 2) The flexural strength after irradiation in air is always lower than after irradiation in vacuum. 3) Irradiation in vacuum of copolymers in the composition range 12-43 mol% styrene produces an increase in flexural strength. 4) The flexural strength decreases very rapidly for high styrene content copolymers upon irradiation in air.

Compressive Strength

The compressive strengths of the unirradiated bars were independent of copolymer composition except for $x_S = 0$ and 0.1, as shown in the insert in Fig. 5. The latter two compressive strengths are likely to reflect the low T_g values of these polymers. Irradiation had no significant effect on the compressive strengths, up to 100 Mrd for $x_S = 0.46$ and 200 Mrd for $x_S = 0.80$, as shown in Fig. 5.

Gel Measurements

The irradiated homopolymers and the copolymers all gave insoluble gel after minimum doses (D_g), which increased with an increase in styrene content. The dose dependence curves for the soluble fractions were similar, but were displaced to higher doses for higher styrene content as shown in Fig. 6. A comparison of irradiation at -78 and

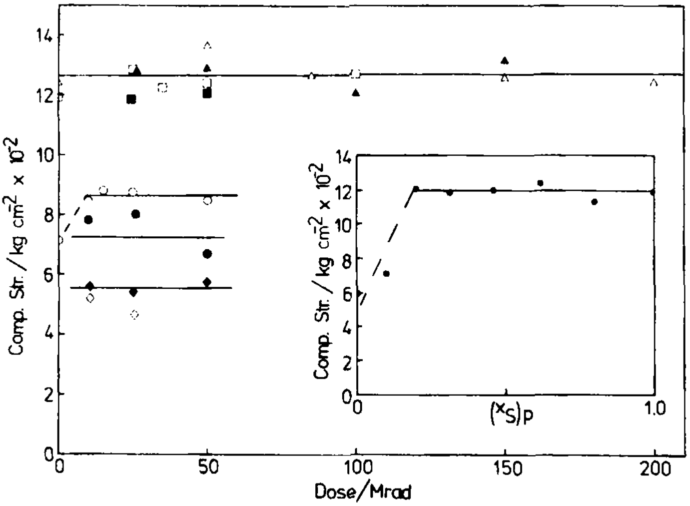

FIG. 5. Dose dependence of the compressive strength of poly(styrene-co-methyl acrylate) bars irradiated at -78°C and measured at 1°C. $(x_S)_p$: (◇), 0.00; (○), 0.12; (□), 0.43; (△) 0.80. Irradiation in vacuum: open symbols. Irradiation in air: filled symbols. Insert: Variation of compressive strength of unirradiated samples with copolymer composition.

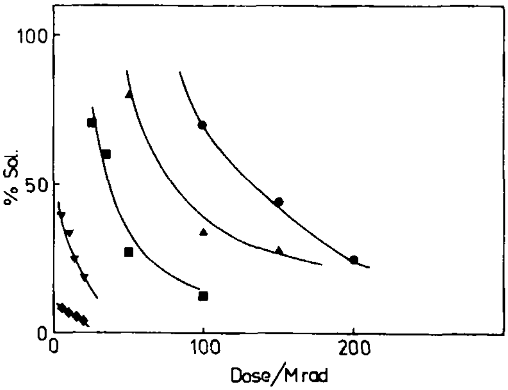

FIG. 6. Variation in soluble fraction of poly(styrene-co-methyl acrylate)s and the homopolymers with radiation dose at -78°C: (▼) PMA, (■) 32 mol% S, (▲) 62 mol% S, (●) PS, (◆) PMA at 30°C.

+ 30°C for PMA showed more rapid gel formation at the higher temperature. This positive temperature dependence of G(crosslink) through the T_g region is analogous to the behavior observed for aromatic polysulfones [6], but contrasts with that of polystyrene [7].

Burlant et al. [8] obtained no gel from the irradiation of PMA, below or above T_g, up to 25 Mrd, indicating that $G(S) > 4G(X)$, a result which is not in agreement with the present work. Our data for PMA are compatible with those of Schultz and Bovey [9] who derived $G(X) = 0.48$ and $G(S) = 0.17$ for irradiation at 25°C in air.

CONCLUSIONS

Irradiation of copolymers of styrene and methyl acrylate produces the volatile products H_2, CO, CH_4 and CO_2, and the less-volatile products Me_2O, HCO_2Me, and $MeCO_2Me$. These result from fragmentation of the methyl acrylate units in the copolymers (except for a small proportion of the H_2). Cross-linking and scission, as indicated by the variation in gel fractions with radiation dose, is intermediate between that of the homopolymers and shows a gradation with composition. Similarly, the effect of irradiation on the flexural strengths shows a gradation with copolymer composition. The effects of irradiation on flexural and compressive strengths are in accord with cross-linking being predominant, particularly with increasing methyl acrylate content and even in air for high x_{MA}. A protective effect is evident in the yields of volatile products.

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