γ-Irradiation of Styrene Copolymers

W. Burlant, D. Green, and C. Taylor

Chemistry Department, Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

While the effects of ionizing radiation on homopolymers are well described,[1-3] few studies of copolymer systems have been reported. The most serious effort in this area was by Alexander and Charlesby,[4] who noted that when styrene–isobutylene copolymers are irradiated in a pile, the system initially degrades to an extent proportional to the styrene concentration, then crosslinks; even copolymers containing 0.7 mole fraction styrene separated into a sol and gel fraction after doses of the order of 10 Mrep. A more recent note[5] reported that radiation protection occurs in emulsion copolymers of butadiene with styrene and acrylonitrile (dose range, 10 to 100 Mrep; probably irradiated in air). Survey experiments are reported for systems of the more common monomers.[6-12]

Experiments in this laboratory indicated that viscosity data were not a reliable index of radiation protection, and the large doses necessary to effect measurable solubility changes obscured truly initial effects. It appeared that mass analysis of the gases liberated as a function of copolymer composition would afford additional useful data; accordingly, styrene–methyl methacrylate (STY-MMA) and styrene–methyl acrylate (STY-MAC) copolymers were γ-irradiated in vacuo, and, in addition to viscosities, the decomposition gases were examined.

EXPERIMENTAL

Appropriate mixtures of redistilled monomers were degassed in 5-inch polymerization tubes and polymerized thermally to less than 5% conversion; the products were reprecipitated repeatedly from benzene solution with methyl alcohol, dried in vacuo for 4 hours at 100°, then analyzed for the elements to determine the composition. Intrinsic viscosities were determined in solvent benzene at 25°; the values for the starting materials were about 1.3 for the STY-MMA and 2.2 for the STY-MAC copolymers. A weighed amount of the dry polymer (about 0.1 gram) in an ampule was maintained at 80° for 1 hour at a pressure of about 10^{-5} mm.; the

tube was then sealed. Mass analysis prior to irradiation failed to reveal the presence of any gas.

A dose rate of 2.4×10^5 rep per hour (Co^{60} source; $FeSO_4$ dosimetry) was employed for all the experiments; doses ranged from 1.0 Mrep to 10.0 Mrep. It was assumed that one gram of polymer absorbed 58×10^{18} e.v. when given a dose of 1.0 Mrep.

About 1 day after irradiation, the ampules were sealed into a Consolidated Model No. 21-103 mass spectrometer, the conventional inlet system of which was modified to permit analysis of about 10^{-10} moles of gas.[13] The actual quantities measured were at least fifty times this value. Absolute quantities are believed to be within 10% of the true values; relative concentrations within a few per cent. Usually more than 90% of the gases in each tube were accounted for; in the case of PMMA, the analysis was about 98% complete. When the gas content of the low dose sample (1.0 Mrep) was too small for accurate analysis, these values were omitted from the average determinations. It is estimated that the mass data are reproducible to within ±10%, with the exception of the methyl formate and methyl alcohol determinations which are reproducible to within ±25%.

The molecular weight changes of PMMA were calculated as described previously:

$$M.W. = 2 \times 10^5 [\eta]^{1.46}$$

and $(1/M.W._{(final)} - 1/M.W._{(orig.)}) \times 6.02 \times 10^{23}$ gives the scissions per gram. Post irradiation effects were not considered. It is estimated that gel fractions (MAC polymers) were reliable to within ±10% at 10.0 Mrep; at lower doses, the physical characteristics of the gel precluded quantitative analysis.

RESULTS

STY-MMA Copolymers

A. Homopolymers

Crosslinking polystyrene by γ-rays has been described,[14] and the G-value for hydrogen atoms

TABLE I
Scissions Produced by γ-Irradiation of Polymethyl
Methacrylate

Energy absorbed, e.v./g., × 10^{-19}	Scissions/g. × 10^{-18}
5.8	1.20
11.6	1.94
29.0	3.99
58.0	8.91

$G(H)$ was reported as 0.045 (dose rates and doses of the same order of magnitude as those used in this study). In this laboratory, the viscosity data agreed with the literature values, but $G(H)$ was found to be 0.078 and constant over the dose range. The discrepancy may be significant in indicating the importance of sample preparation in radiation chemistry. Indeed, if radiation effects on polymeric systems can be explained by the zone theory of solids, as suggested,[15] the term "pure polymer" will bear scrutiny; thus, aside from foreign atoms, structural differences within the molecule (branching, for example) may alter electronic distributions about an atom, and act as impurity centers.

The well known degradation of PMMA by γ-rays was examined: G (scissions) was found to be 1.66 and constant over the dose range employed. The dependence of the number of scissions per gram of polymer on the energy absorbed is given in Table I and agrees well with the published values.[14]

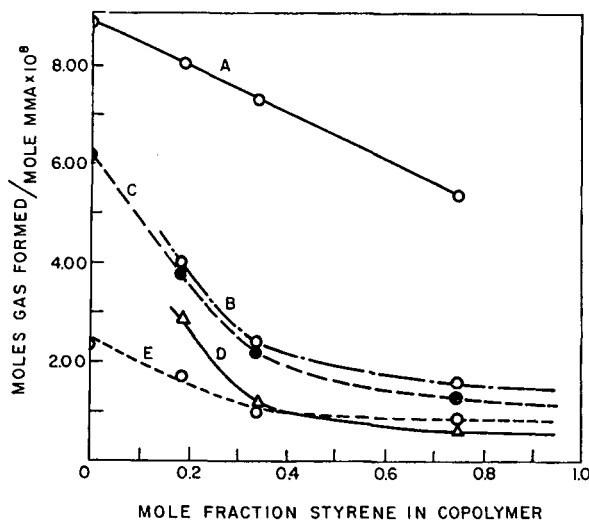Mass analyses of the radiation-produced gases are in general accord with the results of the latter workers, and are incorporated in Figure 1. The most apparent differences are the increases in CO and methyl formate found in this laboratory over the reported values (comparable doses); in addition Wall and Brown did not report methyl alcohol in the decomposition gases. $G(gas)$ for PMMA are given in Table II.

TABLE II
$G(gas)$ for γ-Irradiation of Polymethyl Methacrylate[a]

Gas	$G(gas)$
H_2	0.27
CO	0.89
CO_2	0.35
$HCOOCH_3$	0.5[b]
CH_3OH	0.2[b]
CH_4	1.21, 1.00, 0.72, 0.63[c]

[a] Average of values from doses of 2.0 to 10.0 Mrep.

[b] Constant to ±25%.

[c] In the order given are the $G(CH_4)$ for doses of 1.0, 2.0, 5.0, and 10.0 Mrep.

Within experimental error, all but the $G(CH_4)$ values are constant over the doses employed. No explanation is offered for the drift of $G(CH_4)$, although the site from which the H in the CH_4 comes might be a factor; experiments with appropriately deuterated molecules are in progress in this laboratory.

B. Copolymers

The change in viscosity of irradiated copolymers as a function of composition and dose are presented in Figure 2. The protective effect of styrene units

Fig. 1. Effects of γ-irradiation on gas yields of styrene-methyl methacrylate copolymers: (A) CO, (B) CO_2, (C) CH_4 and approximate $HCOOCH_3$, (D) CH_3OH, (E) H_2. Total dose, 10.0 Mrep.
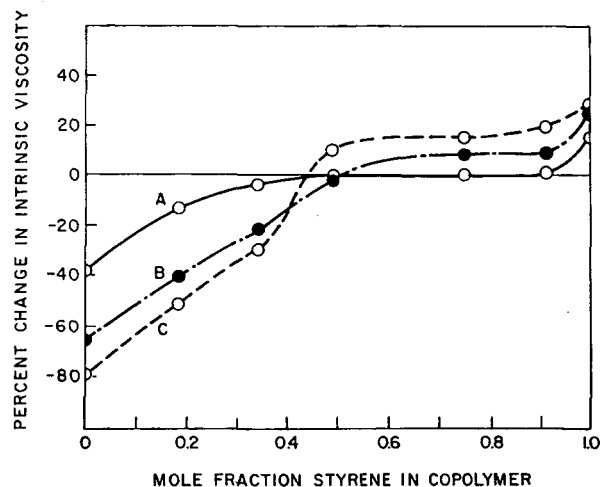

Fig. 2. Dependence of $[\eta]$ on copolymer composition and dose: (A) 2.0, (B) 5.0, (C) 10.0 Mrep.

are manifested in the change of $[\eta]$ with styrene content up to about 0.5 mole fraction of the latter; further addition of styrene does not result in increased protection. It is not apparent from these data whether true protection is offered in this composition range (that is, the absorption of energy by styrene molecules is complete enough so that no bonds are broken) or the rates of degradation and crosslinking are equal. The doses employed were too low to permit separation of sol and gel fractions.

Examination of the gases formed (Fig. 1) indicates that protection by styrene indeed occurs in copolymers made up essentially of MMA sequences, although above a styrene content of about 0.5 mole fraction gas yields are independent of concentration also. If the copolymer structure is considered in terms of the reactivity ratios of styrene and MMA (both equal to 0.5), it appears that protective effects are greatest in the polymer with the completely alternating configuration (0.5 mole fraction), and that these effects are not transmitted over more than one styrene unit.

Gas evolution was directly proportional to the dose given in the range studied. The yields of CO appear anomalous.

C. Temperature Effects

At $-80°$ and $-196°$, polystyrene, PMMA, and the 0.50 mole fraction copolymer were irradiated. The data for the homopolymers agreed with those reported and are discussed by Wall and Brown.[14] The viscosity of the copolymer was not changed appreciably by irradiation at these temperatures.

The gas yields of all these polymers remain essentially constant when the temperature of irradiation is lowered to $-196°$, and, while log K ($K =$ moles gas formed per mole MMA per hour) vs. $1/T_{abs}$ plots are straight lines with little slope, no fundamental significance attaches to the data, inasmuch as other rate factors are implicit in these measurements (gas diffusion, for example).

STY-MAC Copolymers

A. Homopolymer

Ionizing radiation is known to crosslink PMAC; in this laboratory, more than 80% gelation occurred at the lowest dose employed, 1.0 Mrep (10.0 Mrep produced no gel in polystyrene). The gas mixtures liberated (Fig. 3) were of the same composition as those from the MMA system, but were evolved in lesser amounts. It was noted that maximum gas evolution occurred while the PMAC was
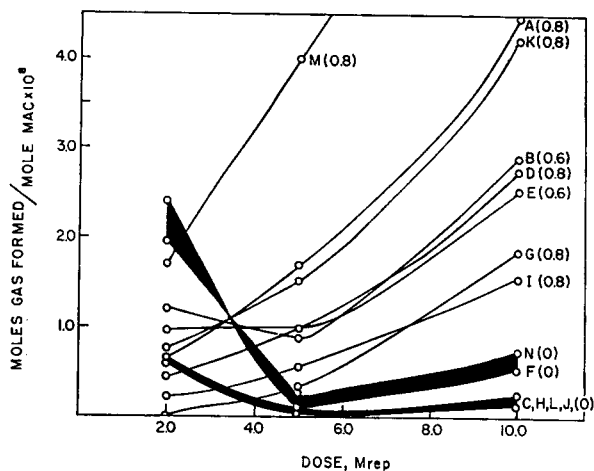

Fig. 3. Effects of γ-irradiation on gas yields of styrene–methyl acrylate copolymers: (A), (B), (C) H_2; (D), (E), (F) CH_4; (G), (H) CH_3OH; (I), (J) $HCOOCH_3$; (K), (L) CO_2; (M), (N) CO. The numbers in parentheses indicate the mole fraction of styrene in the copolymer.

crosslinking (2.0 Mrep); when gelation was complete (5.0 Mrep), gas formation decreased tenfold. It appears that the gelled polymer (all the susceptible atoms having been attacked during gelation) is more radiation resistant than the starting material. Upon continued irradiation of this insoluble fraction (10.0 Mrep), these gases are evolved at a slow rate.

B. Copolymer

It was found that, when styrene is incorporated in the copolymer, the amount of gelation is decreased (Table III), although gas evolution (per mole MAC) increases. At doses below those necessary for gelation (1.0 Mrep) gas concentrations were too low for reliable mass analyses, at higher doses (up to 10.0 Mrep) where gelation is occurring, quantitative study of gas yields is difficult because two variables must be considered: copolymer composition and degree of crosslinking. Nevertheless, it is of interest to examine the dependence of gas evolution on

TABLE III
Gel Formation in γ-Irradiated Styrene-Methyl Acrylate Copolymers[a]

Mole fraction styrene in copolymer	Gel formed, %
0	97
0.18	53
0.59	17
0.83	Trace
1.0	0

[a] Dose, 10.0 Mrep.

copolymer composition and dose. Figure 3 may be considered a qualitative summary of the effects of γ-irradiation on this system.

C. Temperature Effects

Decreased gelation was noted when PMAC and the 0.5 mole fraction copolymer were irradiated at −80° and −196°. Again, gas evolution was not appreciably temperature-dependent. Thus, the moles of gas formed per mole of MAC unit in the copolymer at −196° for H_2, CH_4, $HCOOCH_3$, CH_3OH, CO_2, and CO, were the following fractions of the values at 25°, respectively: 0.7, 0.4, 0.2, 0.3, 0.5, and 0.25; at −80°, the corresponding temperature coefficients were 0.8, 0.6, 0.3, 0.3, 0.5, and 0.4.

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Synopsis

Copolymers of styrene-methyl methacrylate were irradiated in vacuo with γ-rays; viscosity changes and gas yields (moles gas per mole methyl methacrylate in copolymer) for H_2, CO, CO_2, CH_4, $HCOOCH_3$, and CH_3OH were examined at doses of 1.0 Mrep to 10.0 Mrep. It was found that styrene molecules protect the copolymer from degrading while decreasing the gas yields up to a styrene concentration of about 0.5 mole fraction; above this concentration, these radiation effects are independent of composition. When styrene–methyl acrylate copolymers were irradiated, styrene offered protection against gelation but simultaneously increased the gas yields (gases liberated were identical with those from the first system).

Résumé

Des copolymères de styrène et de méthacrylate de méthyle ont été irradiés sous vide par des rayons-γ; les changements de viscosité et les rendements en gaz (moles de gaz par mole de méthacrylate de méthyle dans le copolymère) ont été déterminés pour H_2, CO, CO_2, CH_4, $HCOOCH_3$ et CH_3OH à des doses de 1.0 à 10.0 Mrep. On a trouvé que les molécules de styrène protègent le copolymère de la dégradation tandis qu'elles diminuent les rendements en gaz, ceci jusqu'à une concentration en styrène d'environ 0.5 comme fraction molaire; au dessus de cette concentration, les effets de radiation sont indépendants de la composition. Quand on irradie des copolymères de styrène-acrylate de méthyle, le styrène protège contre le gélification mais accroît simultanément les rendements en gaz (les gaz libérés sont les mêmes que ceux du 1ʳ système).

Zusammenfassung

Styrol-Methylmethacrylatocopolymere wurden im Vakuum mit γ-Strahlen bestrahlt. Viskositätsänderungen und Gasausbeuten (Mole Gas pro Mol Methylmethacrylat im Copolymeren) wurden bei Dosen von 1,0 bis 10,0 Mrep bestimmt. Es wurde gefunden, dass Styrolmoleküle bis zu einer Styrolkonzentration entsprechend einem Molenbruch 0,5 das Copolymere gegen Abbau schützen und die Gasausbeuten herabsetzen; oberhalb dieser Konzentration sind diese Strahlungswirkungen unabhängig von der Zusammensetzung. Bei der Bestrahlung von Styrol-Methylmethacrylatocopolymeren lieferte das Styrol einen Schutz gegen Gelierung, vergrösserte aber gleichzeitig die Gasausbeuten (die in Freiheit gesetzten Gase waren mit denen aus dem ersten System identisch).