Evaluation of scission and crosslinking yields in γ-irradiated poly(acrylic acid) and poly(methacrylic acid) from weight- and Z-average molecular weights determined by sedimentation equilibrium

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Weight- and Z-average molecular weights, $\bar{M}_w(D)$ and $\bar{M}_Z(D)$, of poly(methacrylic acid) (PMMA) and poly(acrylic acid) (PAA) have been determined by sedimentation equilibrium in the ultracentrifuge after various doses D of γ-radiation in vacuum. Relationships between $[M_i(0)/M_i(D)-1]/D$ and D ($i = w$ or Z), derived recently by O'Donnell and coworkers, have been used to determine radiation chemical yields for scission and crosslinking of $G(S) = 6.0$, $G(X) = 0$ for PMAA and $G(S) = 0$, $G(X) = 0.44$ for PAA. Allowance was necessary for the effects of COOH decomposition on the average values of the molecular weight and partial specific volume for irradiated PAA.

INTRODUCTION

Despite the importance of crosslinking and scission in modifying the physical and mechanical properties of irradiated polymers[1,2], relatively few procedures have been developed to determine their radiation chemical yields. Mathematical analysis of the soluble fractions after varying radiation doses according to a Charlesby–Pinner type relationship[3,4] provides estimates of these two parameters for systems in which crosslinking predominates. However, the values obtained for extensively crosslinked networks at high doses may differ significantly from those for linear polymer. It is clearly desirable to determine scission and crosslinking yields after low radiation doses, i.e. in the pre-gel region, so that the values are appropriate to the initial polymer being subjected to irradiation[5,6].

Quantitative expressions for the change in molecular-weight distribution and averages in terms of probabilities of scission ($\hat{t}$) and crosslinking ($\hat{\chi}$) per monomer unit per unit dose were formulated more than 25 years ago[7]. In our first consideration of this problem[5] the scission and crosslinking yields were determined for initial molecular-weight distributions other than the most probable by combining the dose dependences of the weight- and number-average molecular weights of the irradiated polymer. However, as we have noted recently[8], this procedure suffers from the disadvantage that the dose dependence of $1/\bar{M}_n(D)$ is often too insensitive for accurate estimation of the slope, which is related to the

difference in scission and crosslinking yields. An alternative procedure was therefore devised[8] which combines the dose dependences of weight- and Z-average molecular weights to yield $(\hat{t} - 4\hat{\chi})$ and $(\hat{t} - 8\hat{\chi})$ respectively for a polymer with a most probable initial distribution, and more complex relationships for other distributions. The practical application of this procedure remains largely untested.

In the present investigation, values of $\bar{M}_w(D)$ and $\bar{M}_Z(D)$ obtained by the low-speed sedimentation equilibrium technique[9] are used to determine the radiation chemical yields of crosslinking, $G(X)$, and scission, $G(S)$, for poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) subjected to γ-irradiation. On the basis of chemical structure, viz.:

Poly(acrylic acid)   Poly(methacrylic acid)
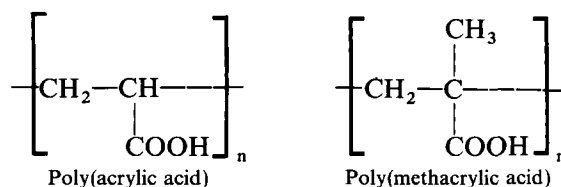
it is anticipated[10] that irradiation of poly(methacrylic acid) in the solid state would give rise to scission predominantly if not exclusively, whereas scission would occur to a much lesser extent than crosslinking during the corresponding irradiation of poly(acrylic acid). The solubility of these polymers in water but not in organic solvents has rendered their characterization difficult by conventional techniques, and thus prevented determination of the G values for scission and crosslinking. These

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two polymers therefore provide useful tests of the ability of sedimentation equilibrium to provide values of both G(S) and G(X) at the two extremes of the scission/crosslinking ratio.

EXPERIMENTAL

Materials

Redistilled methacrylic acid (7 g) was dissolved in 0.1 M HCl to which $K_2S_2O_8$ (0.1 g) and $K_2S_2O_5$ (0.1 g) were added as initiator and activator of the polymerization. The procedure used previously for the polymerization of itaconic acid[11] was also followed: the reaction mixture was deaerated by nitrogen bubbling, and was maintained at 25°C throughout the polymerization process (24 h). Poly(methacrylic acid) was isolated by dialysis against 0.1 M HCl and distilled water, which was then removed by freeze-drying.

Sodium polyacrylate with a nominal molecular weight of 5000 was obtained from Scientific Polymer Products, Ontario, NY. Conversion to poly(acrylic acid) entailed passage through a column of Amberlite CG120 in the acid form[12], after which the sample was freeze-dried to obtain the polymer in powder form.

Irradiation of polymers

Polymer (0.1 g) was evacuated in glass ampoules at 0.01 mPa for 24 h, and then heated to 80°C under vacuum for a further 24 h to remove any occluded water[13]. The evacuated ampoules were then placed in a Gammacell 200 facility and subjected to irradiation from the ^{60}Co source at ambient temperature ($\sim$30°C) and a dose rate of 4 kGy h^{-1}. Poly(methacrylic acid) was subjected to γ-radiation doses in the range 0–110 kGy, and poly(acrylic acid) to doses in the range 0–550 kGy.

Molecular-weight determination

The poly(methacrylic acid) and poly(acrylic acid) samples were dissolved in 2 mM HCl, a solvent in which the carboxyl groups of both polymers are fully protonated. Ionization of the carboxyl groups was avoided, so that the solution could be considered as a two-component system without prior dialysis against solvent[14], which could lead to loss of small scission products and hence invalidate the estimations of average molecular weights. Solutions with polymer concentrations of about 6–7, 4, 3 and 2 mg cm^{-3} were prepared for analysis by sedimentation equilibrium. The exact concentrations were determined refractometrically on the basis of a specific refractive increment of 0.140 cm^3 g^{-1} at 546 nm for both poly(methacrylic acid)[15] and poly(acrylic acid)[16].

Each solution was subjected to ultracentrifugation for 16–24 h at 20°C in the AN-D rotor of a Beckman model E ultracentrifuge fitted with electronic speed control. Rotor speeds of 6000–18 000 rpm for poly(methacrylic acid) and 24 000–34 000 rpm for poly(acrylic acid) were used in these sedimentation equilibrium experiments, which were of low-speed design[9] and conducted with 2 mm columns of polymer solution in a filled Epon double-sector cell: CCl_4 was added to both sectors to provide better definition of the bottom meniscus. The resulting equilibrium distributions were recorded as schlieren patterns as well as Rayleigh interferograms, both of which were measured with a two-dimensional comparator fitted with projection screen.

Apparent weight-average molecular weights were determined from the Rayleigh interferogram using the expression[9]:

$$\bar{M}_w^{app} = \frac{2RT(c_b - c_m)}{c_0(1 - \bar{v}\rho)\omega^2(r_b^2 - r_m^2)} \quad (1)$$

where c_0 is the initial concentration and $(c_b - c_m)$ the concentration difference (all in Rayleigh refractometric units) across the liquid column with radial extremities r_m and r_b in an experiment conducted at temperature T with angular velocity ω. Apparent Z-average molecular weights were obtained from the corresponding schlieren pattern using the relationship[9]:

$$\bar{M}_Z^{app} = \frac{[(1/r_b)(dc/dr)_b - (1/r_m)(dc/dr)_m]RT}{(c_b - c_m)(1 - \bar{v}\rho)\omega^2} \quad (2)$$

where r_b and r_m again denote the respective radial distances of the two menisci from the centre of rotation, and $(dc/dr)_b$ and $(dc/dr)_m$ are the corresponding concentration gradients at these two positions. In order to ensure that the concentration difference $(c_b - c_m)$ is in corresponding optical units, this quantity was obtained as the area under the schlieren pattern. A solvent density ρ of 1.000 g cm^{-3} was obtained from measurements in an Anton Paar precision density meter. The partial specific volume $\bar{v}$ of undissociated poly(methacrylic acid) was taken[17] as 0.71 cm^3 g^{-1}, and the corresponding value for poly(acrylic acid)[18,19] as 0.66 cm^3 g^{-1}. Since any concentration dependence of either $\bar{M}_w^{app}$ or $\bar{M}_Z^{app}$ was masked by the inherent experimental uncertainty of the estimates, the mean of values at the four concentrations was considered to define the average molecular weight ($\bar{M}_w$ or $\bar{M}_Z$).

Evaluation of G(S) and G(X) from the dose dependences of $\bar{M}_w$ and $\bar{M}_Z$

To determine radiation chemical yields of scission and crosslinking the dose dependences of $\bar{M}_w(D)$ and $\bar{M}_Z(D)$ were analysed by means of the expressions[8]:

$$\frac{\bar{M}_w(0)/\bar{M}_w(D) - 1}{D} = \left(\frac{(\sigma + 2)u\dot{t}}{3\sigma} - \frac{2(\sigma + 1)u\dot{\chi}}{\sigma} \right)$$
$$+ \left(\frac{(\sigma + 2)(\sigma - 1)(u\dot{t})^2}{36\sigma^2} \right)D \quad (3a)$$

and

$$\frac{\bar{M}_Z(0)/\bar{M}_Z(D) - 1}{D} = \left(\frac{(\sigma + 5)u\dot{t}}{6\sigma} - \frac{4(\sigma + 1)u\dot{\chi}}{\sigma} \right)$$
$$+ \left(\frac{4(\sigma + 1)^2(u\dot{\chi})^2}{\sigma^2} + \frac{2(\sigma + 1)(\sigma - 1)u\dot{\chi}u\dot{t}}{3\sigma^2} \right.$$
$$\left. - \frac{(\sigma + 3)(\sigma - 1)(u\dot{t})^2}{30\sigma^2} \right)D \quad (3b)$$

In these approximate linear transforms of the Inokuti and Dole expressions[3,8] for the dose dependences of weight- and Z-average molecular weights, u is the number-average degree of polymerization of the initial polymer ($\bar{M}_n(0)$ divided by the molecular weight of a monomer unit); $\dot{t}$ is the probability of scission per gray per monomer unit; and $\dot{\chi}$ is the corresponding probability of crosslinking. The breadth σ of the initial Schulz–Zimm molecular-weight distribution[20,21] is usually obtained

from $\bar{M}_n(0)$ and $\bar{M}_w(0)$, but in this investigation has been obtained from $\bar{M}_w(0)$ and $\bar{M}_Z(0)$ using:

$$\bar{M}_Z(0)/\bar{M}_w(0) = (\sigma+2)/(\sigma+1) \qquad (4)$$

By plotting the molecular-weight expressions on the left-hand side of equations (3a) and (3b) as functions of radiation dose D, estimates of $[(\sigma+2)u\dot{t}/3\sigma - 2(\sigma+1)u\dot{\chi}/\sigma]$ and $[(\sigma+5)u\dot{t}/6\sigma - 4(\sigma+1)u\dot{\chi}/\sigma]$ were derived from the respective ordinate intercepts. Solution of the resulting two simultaneous equations in $u\dot{t}$ and $u\dot{\chi}$ then yielded separate estimates of these two parameters. Radiation chemical yields of scission, $G(S)$, and crosslinking, $G(X)$, were then given by:

$$G(S) = 9.65 \times 10^9 u\dot{t}/\bar{M}_n(0) \qquad (5a)$$

$$G(X) = 9.65 \times 10^9 u\dot{\chi}/\bar{M}_n(0) \qquad (5b)$$

where $\bar{M}_n(0) = [\sigma/(\sigma+1)]\bar{M}_w(0)$.

RESULTS AND DISCUSSION

Poly(acrylic acid) should undergo predominantly cross-linking on irradiation because of the presence of at least one hydrogen atom on each carbon atom of the main chain, whereas the tetrasubstituted carbon in poly-(methacrylic acid) should result in scission[10]. Although the cause of this difference in behaviour on the basis of molecular structure is uncertain, there are numerous examples where it is applicable, provided that air is excluded during irradiation[7,22,23].

In the present investigation we have used sedimentation equilibrium to evaluate the dose dependence of $\bar{M}_w(D)$ and $\bar{M}_Z(D)$, and hence to determine $G(S)$ and $G(X)$. A particular objective has been to measure the G value for the lesser event, i.e. $G(S)$ for poly(acrylic acid) and $G(X)$ for poly(methacrylic acid).

Poly(methacrylic acid)

The decreases in the weight-average and Z-average molecular weights of poly(methacrylic acid) with dose, shown in *Figure 1*, show that substantial scission occurs. For unirradiated polymer $\bar{M}_w(0) = 132000 \pm 1700$ and $\bar{M}_Z(0) = 190000 \pm 3400$, from which $\sigma = 1.3 \pm 0.2$ (equation (4)). The initial molecular-weight distribution of the poly(methacrylic acid) sample is thus slightly narrower than a most probable distribution ($\sigma = 1$), presumably as the result of some low-molecular-weight polymer being
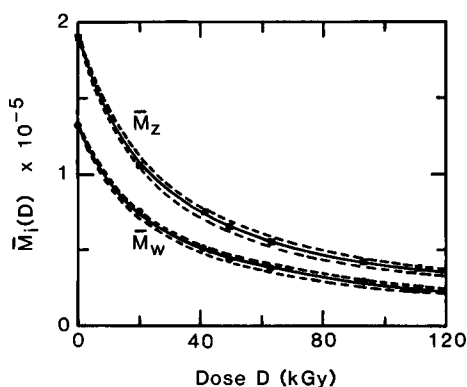
Figure 1 Dose dependences of the weight-average ($\bullet$) and Z-average ($\blacksquare$) molecular weights of poly(methacrylic acid) subjected to γ-irradiation *in vacuo* in the solid state at 30°C. (——) Exact theoretical relationships predicted (equations (1) and (9) of ref. 8) for $G(X)=0$ and $G(S)=6.0$. (– – – –) Range of uncertainty for $G(S)=6.0\pm0.5$
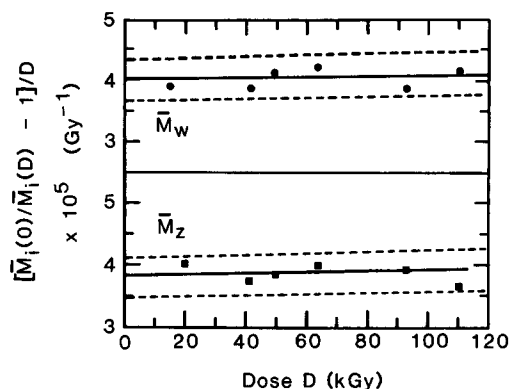
Figure 2 Plots of $\bar{M}_w$ and $\bar{M}_Z$ data for irradiated poly(methacrylic acid) according to equations (3a) and (3b). The full lines are the exact theoretical relationships calculated[8] for $G(X)=0$ and $G(S)=6.0$, and the broken lines for $G(S)=6.0\pm0.5$

removed during dialysis. In order to evaluate $G(S)$ and $G(X)$, the $\bar{M}_w$ and $\bar{M}_Z$ values are replotted (*Figure 2*) according to equations (3a) and (3b). Since both plots have zero slope, within experimental error, the ordinate intercepts have been taken as the means of the six experimental values in each case. Combination of these estimates of the ordinate intercepts with the theoretical expressions in equations (3a) and (3b) leads to the following two simultaneous equations:

$$0.85u\dot{t} - 3.54u\dot{\chi} = 0.401 \pm 0.036 \qquad (6a)$$
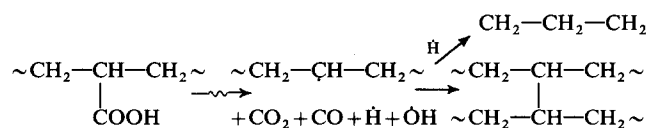
$$0.81u\dot{t} - 7.08u\dot{\chi} = 0.385 \pm 0.031 \qquad (6b)$$

Substitution of the resulting solution for $u\dot{\chi}$ into equation (5b) with $\bar{M}_n(0) = 75000$ yields $G(X) = -0.01 \pm 0.23$. Since the crosslinking yield cannot have a negative value, we can take $G(X) = 0.0 \pm 0.2$. Thus radiation degradation of poly(methacrylic acid) produces only scission. Substitution of $u\dot{\chi} = 0$ into equation (5a) then gives $u\dot{t} = 4.7(\pm0.4) \times 10^{-5}\,\text{Gy}^{-1}$, which leads to $G(S) = 6.0 \pm 0.5$. The exact theoretical dose dependences[3,8] for the expressions plotted in *Figures 1* and *2* are shown as full lines, and the broken lines indicate the range of values enveloped by the uncertainty in $G(S)$.
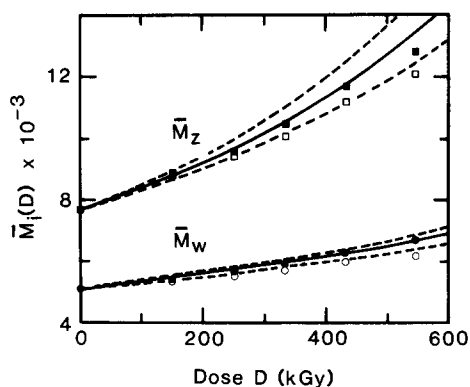
Poly(acrylic acid)

Because much smaller changes in molecular weight were observed during irradiation of the poly(acrylic acid) sample compared with the poly(methacrylic acid), higher radiation doses were required to effect substantial changes in molecular weight. From initial estimates of these changs in $\bar{M}_w(D)$ and $\bar{M}_Z(D)$ with dose (open symbols, *Figure 3*), crosslinking predominates. However, quantitative evaluation of crosslinking and scission yields requires correction of the measured molecular weights to take into account the large losses of CO_2 and CO that are associated with irradiation of poly(acrylic acid) to these doses[23].

The loss of CO_2 and CO from the carboxyl groups and the accompanying crosslinking are considered to occur by the reaction scheme:

$$\sim CH_2-CH-CH_2\sim \quad \sim CH_2-\underset{|}{C}H-CH_2\sim \xrightarrow{\;\overset{H}{\diagup}\;} \overset{\displaystyle CH_2-CH_2-CH_2}{\overset{\diagup}{\sim CH_2-CH-CH_2\sim}}$$

Consequently, when a monomer unit of poly(acrylic acid) loses the carboxyl group it becomes similar to an ethylene

Figure 3 Dose dependences of the weight-average ($\bigcirc$, $\bullet$) and Z-average ($\square$, $\blacksquare$) molecular weights of poly(acrylic acid) subjected to γ-irradiation *in vacuo* in the solid state. Open symbols refer to values calculated with $\bar{v} = 0.66\,\text{cm}^3\,\text{g}^{-1}$, the partial specific volume of unirradiated polymer, whereas full symbols are based on the calculated dose dependence of $\bar{v}$ (see *Figure 4*). (———) Exact theoretical relationships calculated[8] on the basis that $G(S) = 0$ and $G(X) = 0.44$. (– – – –) Range of dependences enveloped by the inherent uncertainty (± 0.05) in $G(X)$

unit, for which the partial specific volume ($\bar{v}$) is about $1.05\,\text{cm}^3\,\text{g}^{-1}$ (reciprocal of the density of linear polyethylene[24]), which differs markedly from the initial value[18,19] of $0.66\,\text{cm}^3\,\text{g}^{-1}$. Calculation of the molecular weight of an irradiated poly(acrylic acid) sample therefore requires account to be taken of the consequent dose-dependent change in $\bar{v}$ as the result of decarboxylation. The observation[23] that $G(\text{CO}) + G(\text{CO}_2) = 12$ gives an estimate of $8.95 \times 10^{-8}\,\text{Gy}^{-1}$ for ψ, the probability per gray that a monomer unit has been decarboxylated ($\psi = [G(\text{CO}) + G(\text{CO}_2)]M_1/(9.65 \times 10^9)$ where M_1 is the molecular weight of a monomer unit). If $\bar{v}$ and $\bar{v}'$ denote the respective partial specific volumes of monomer units in the normal and decarboxylated states, the average value ($\bar{v}_{av}$) for polymer subjected to a radiation dose D is then given by:

$$\bar{v}_{av} = \psi D \bar{v}' + (1 - \psi D)\bar{v} \qquad (7a)$$

The consequent dose dependence of the average partial specific volume is shown in *Figure 4*, and its effects on the calculated molecular weights are shown in *Figure 3*. Although γ-irradiation of poly(methacrylic acid) gives similar volatile product yields[23], the effect on $\bar{M}_w(D)$ and $\bar{M}_Z(D)$ was insignificant experimentally because of the lower doses needed for those samples.

Quantitative assessment of the effects of γ-irradiation on poly(acrylic acid) also requires a second consequence of COOH elimination to be taken into account. Loss of the carboxyl group decreases the molecular weight of a monomer unit from 72 to 28. By a similar procedure to that used for evaluating $\bar{v}_{av}$, the average molecular weight of a monomer unit after a dose D may be calculated from the expression:

$$\bar{M}_1(D) = 28\psi D + 72(1 - \psi D) \qquad (7b)$$

From the definitions of weight- and Z-average molecular weights, viz.:

$$\bar{M}_w = \sum [n_i(u_i M_1)^2] \Big/ \sum [n_i(u_i M_1)]$$

$$= M_1 \left[\sum (n_i u_i^2) \Big/ \sum (n_i u_i) \right] \qquad (8a)$$

and

$$\bar{M}_Z = \sum [n_i(u_i M_1)^3] \Big/ \sum [n_i(u_i M_1)^2]$$

$$= M_1 \left[\sum (n_i u_i^3) \Big/ \sum (n_i u_i^2) \right] \qquad (8b)$$

it follows that the corrected values of the initial molecular weights appropriate to polymer subjected to a radiation dose D are:

$$\bar{M}'_w(0) = [\bar{M}_1(D)/M_1]\bar{M}_w(0) \qquad (9a)$$

$$\bar{M}'_Z(0) = [\bar{M}_1(D)/M_1]\bar{M}_Z(0) \qquad (9b)$$

For the unirradiated sample of poly(acrylic acid) $\bar{M}_w(0) = 5100 \pm 400$ and $\bar{M}_Z(0) = 7700 \pm 600$, which indicate a most probable initial distribution ($\sigma = 1$) since $\bar{M}_Z(0)/\bar{M}_w(0) = 1.5 \pm 0.2$ (equation (4)); $\bar{M}_n(0)$ is therefore $\bar{M}_w(0)/2$ or 2550. Plots of the $\bar{M}_w(D)$ and $\bar{M}_Z(D)$ data in accordance with equations (3a) and (3b) respectively are shown in *Figure 5*. The zero slope for $[\bar{M}_w(0)/\bar{M}_w(D) - 1]/D$ is consistent with the theoretical prediction[1,8] that $1/\bar{M}_w(D)$ is linear in dose for a polymer with a most
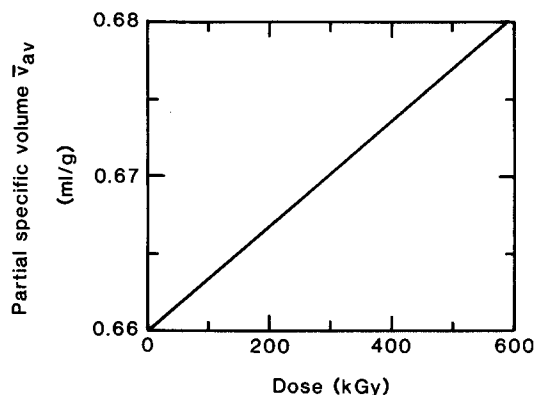
Figure 4 Dose dependence of the partial specific volume of poly(acrylic acid) subjected to γ-irradiation. This relationship is calculated from equation (7a) with values of $0.66\,\text{cm}^3\,\text{g}^{-1}$ and $1.05\,\text{cm}^3\,\text{g}^{-1}$ for $\bar{v}$ and $\bar{v}'$, the partial specific volumes of normal and decarboxylated monomer units respectively. The probability per gray of monomer decarboxylation (ψ) has been inferred from the finding[23] that $G(\text{CO}) + G(\text{CO}_2) = 12$
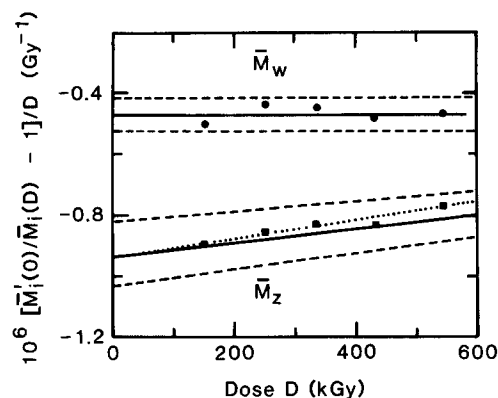
Figure 5 Plots of $\bar{M}_w$ ($\bullet$) and $\bar{M}_Z$ ($\blacksquare$) data for irradiated poly(acrylic acid) according to equations (3a) and (3b) for the evaluation of $G(S)$ and $G(X)$. (· · · · · ·) Relationship obtained by linear regression analysis of the $\bar{M}_Z(D)$ data to define the ordinate intercept. (———) Exact theoretical relationship calculated[8] on the basis that $G(S) = 0$ and $G(X) = 0.44$. (– – – –) Range of relationships enveloped by the experimental uncertainty (± 0.05) in $G(X)$

probable initial distribution. The mean of the five experimental values, -0.47 (± 0.06) $\times 10^{-6}\,\mathrm{Gy}^{-1}$, has therefore been taken as the ordinate intercept, which is $(u\hat{\imath} - 4u\hat{\chi})$ for a system with $\sigma = 1$ (equation (3a)). Linear regression analysis of the corresponding Z-average molecular-weight data yields the relationship shown by the dotted line in *Figure 5* and an ordinate intercept of -0.94 (± 0.04) $\times 10^{-6}\,\mathrm{Gy}^{-1}$, which gives $(u\hat{\imath} - 8u\hat{\chi})$ for a polymer with a most probable initial distribution (equation (3b)). These two simultaneous equations yield $G(X) = 0.44 \pm 0.09$ and $G(S) = -0.02 \pm 0.56$. In view of the large degree of uncertainty associated with the slightly negative and therefore physically unacceptable value of $G(S)$, it is considered that $G(S) = 0$; and that radiation degradation of poly(acrylic acid) leads solely to crosslinking. The full curves and lines in *Figures 3* and *5* are exact theoretical relationships calculated from equation (9) of ref. 8 on the basis that $G(S) = 0$ and $G(X) = 0.44$; and the broken curves and lines indicate the range of values enveloped by the uncertainty (± 0.05) in $G(X)$ that results from analysis of the experimental data solely in terms of crosslinking. We note that the consistent divergence of the predicted dose dependence (——) of $[\bar{M}_Z(0)/\bar{M}_Z(D) - 1]/D$ from the linear relationship used to evaluate the ordinate intercept could be taken to signify the need for slight upward revision of the $(u\hat{\imath} - 8u\hat{\chi})$ estimate. However, no such action is warranted because the amended ordinate intercept would still be within the uncertainty limits of the present analysis (– – – –).

CONCLUDING REMARKS

The evaluation of scission and crosslinking yields for poly(methacrylic acid) and poly(acrylic acid) samples subjected to γ-irradiation has confirmed the feasibility of determining $G(S)$ and $G(X)$ values for the radiation degradation of polymers from the dose dependences of weight- and Z-average molecular weights obtained by sedimentation equilibrium[8]. The analysis yielded no detectable crosslinking of poly(methacrylic acid) and no detectable scission of poly(acrylic acid). The $G(X)$ value of 0.44 for poly(acrylic acid) is lower than the estimate of 1.2 reported by Lawler and Charlesby[25], a discrepancy that may be due to several factors.

(i) A Charlesby–Pinner analysis[4] of soluble fractions at high radiation doses was used to evaluate $G(X)$, which may therefore differ from the crosslinking yield at low doses[3,7].

(ii) The assumption[25] that the commercial poly(acrylic acid) preparation had a most probable molecular-weight distribution ($\sigma = 1$) may not have been appropriate.

(iii) The viscosity-average molecular weight provided by the supplier was taken as $M_w(0)$.

There are no other published reports of crosslinking yields for poly(acrylic acid), and none of $G(S)$ for poly(methacrylic acid), subjected to γ-irradiation in the solid state. This scarcity of literature values emphasizes the importance of the present development of an experimental procedure for characterizing scission and cross-

linking during irradiation of polymers, particularly those soluble in water. Sedimentation equilibrium provides a rigorous method of evaluating these radiation chemical yields, for which no adequate procedure existed previously. It is hoped that this demonstration of the potential of sedimentation equilibrium for determining scission and crosslinking yields may result in greater use of this technique in studies of the radiation chemistry of polymers.

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