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Evaluation of Cross-Linking and Scission Yields in Irradiated Polymers from the Dose Dependence of the Weight- and *z*-Average Molecular Weights

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ABSTRACT: A procedure has been developed for the determination of scission and cross-linking yields, $G(S)$ and $G(X)$, in irradiated polymers by combination of the ordinate intercepts of plots of $([\bar{M}_w(0)/\bar{M}_w(D)] - 1)/D$ and $([\bar{M}_z(0)/\bar{M}_z(D)] - 1)/D$ versus dose (D). The required weight- and z-average molecular weight data for a given sample can be obtained by using the Rayleigh and schlieren optical systems, respectively, to record the solute distribution in a single sedimentation equilibrium experiment. The procedure has been tested by application to simulated data for a range of initial molecular weight distributions and values of $G(S)/G(X)$ and applied to previous sedimentation equilibrium results (Nichol, J. M.; O'Donnell, J. H.; Rahman, N. P.; Winzor, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1977,** *15,* 2919) for a polystyrene sample with $\bar{M}_w(0)/\bar{M}_n(0) = 1.03$ and $G(S)/G(X) = 1$.

Introduction

Irradiation of polymers produces cross-linking and scission, which have pronounced effects on the physical and mechanical properties of the polymer.[1,2] Determination of the radiation chemical yields of scission ($G(S)$) and cross-linking ($G(X)$) per 16.02 aJ (100 eV) of energy absorbed by the polymer is therefore important in characterizing the effects of irradiation. Traditionally, $G(S)$ and $G(X)$ for systems that predominantly cross-link ($G(S) < 4G(X)$) have been determined by a Charlesby–Pinner analysis[3,4] of soluble fractions after different doses. This method has the disadvantage that high irradiation doses are required to obtain the necessary extrapolation to infinite dose, especially for polymers that do not have the most probable molecular weight distribution ($\bar{M}_w/\bar{M}_n = 2$). Also, since scission and cross-linking yields may be different for linear and extensively cross-linked polymer, values of $G(S)$ and $G(X)$ appropriate to the initial polymer should be obtained from studies of samples subjected to low radiation doses. $G(S)$ and $G(X)$ may also be obtained from changes in the molecular weight distribution or in the two molecular weight averages $\bar{M}_w$ and $\bar{M}_n$.[5] Doses less than half of the gel dose (D_g) have been recommended to avoid significant errors in the measurement of average molecular weights.[5]

Although theoretical relationships have been derived[4,6] for the dose dependences of the average molecular weights $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ of samples with an initial Schulz–Zimm distribution,[7,8] convenient experimental procedures for analyzing such data in terms of $G(S)$ and $G(X)$ are confined to $\bar{M}_n(D)$[1,4] and $\bar{M}_w(D)$.[4,9] Combination of the relationships for both $\bar{M}_w(D)$ and $\bar{M}_n(D)$ is required to determine $G(S)$ and $G(X)$.[9] Osmometry is the conventional procedure for measuring $\bar{M}_n$, and light scattering has been used for evaluating $\bar{M}_w$. Gel permeation chromatography is widely used to determine $\bar{M}_n(D)$ and $\bar{M}_w(D)$ for irradiated polymers, but changes in relative hydrodynamic volume with cross-linking lead to serious errors, especially in weight-average molecular weight.

It is preferable to employ a single experimental technique for determination of the two molecular weight averages for the one sample. Sedimentation equilibrium in the analytical ultracentrifuge is an appropriate technique that has been largely ignored. It is the only thermodynamically rigorous procedure to yield more than one type of average molecular weight. The Chervenka[10] adaptation of the high-speed sedimentation equilibrium technique[11] has recently been recommended[12,13] for simultaneous evaluation of $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ for polydisperse polymers. However, $\bar{M}_n$ can only be determined if a rotor

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speed can be chosen that decreases the equilibrium concentration of solute at the air–liquid meniscus to effectively zero without rendering the concentration gradient too steep for experimental measurement of the concentration at the cell base. On the basis of our experience in the simulation of dose-dependent changes in molecular size distributions of irradiated polymers,[5] the increased polydispersity that results from radiation degradation of a polymer undergoing both scission and cross-linking would almost certainly preclude the measurement of $\bar{M}_n(D)$ over a sufficient range of doses. We have therefore examined the possibility of utilizing the combination of $\bar{M}_w$ and $\bar{M}_z$ obtained from sedimentation equilibrium to determine $G(S)$ and $G(X)$. This has entailed rearrangement of the expression for $\bar{M}_z(D)$[4,6] into a form that is convenient for experimental evaluation of a relationship between $G(S)$ and $G(X)$. In addition, we have assessed critically the linearity of the inverse dependence of $\bar{M}_w(D)$ upon dose that provides the second relationship between $G(S)$ and $G(X)$ to be used for evaluating both scission and cross-linking yields.

Theory

Dose Dependence of $\bar{M}_w$. For an initial Schulz–Zimm distribution the dose dependence of the weight-average molecular weight $\bar{M}_w(D)$ of a polymer undergoing random scission and cross-linking is given[4,6,9] by

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

$$\phi_1(u\dot{\tau}D,\sigma) = u\dot{\tau}D - 1 + [1 + (u\dot{\tau}D/\sigma)]^{-\sigma} \tag{1b}$$

where D denotes the radiation dose in grays, $\dot{\tau}$ is the probability per gray that a monomer unit will undergo scission, and $\dot{\chi}$ is the corresponding probability of forming a cross-link per monomer unit. The width of the initial distribution is signified by σ, determinable from the initial number-average ($\bar{M}_n(0)$) and weight-average ($\bar{M}_w(0)$) molecular weights by the expression

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

Division of $\bar{M}_n(0)$ by M_1, the molecular weight of a monomer unit, provides a vaue of u, the number-average degree of polymerization of the initial polymer. $G(S)$ and $G(X)$, the radiation chemical yields of scission and cross-linking, respectively, are related to $\dot{\tau}$ and $\dot{\chi}$ by the relationships

$$G(S) = 9.65 \times 10^9 \dot{\tau}/M_1 \tag{2a}$$

$$G(X) = 9.65 \times 10^9 \dot{\chi}/M_1 \tag{2b}$$

Although eq 1 thus provides a means of simulating the dose dependence of $\bar{M}_w(D)$ for any specified combination of $\dot{\tau}$ and $\dot{\chi}$ (or $G(S)$ and $G(X)$), it is clearly not a convenient form for evaluating $\dot{\tau}$ and $\dot{\chi}$ from an experimentally determined dose dependence of $M_w(D)$.

Simplification of eq 1 is achieved by using the binomial theorem to expand $[1 + (u\dot{\tau}D/\sigma)]^{-\sigma}$, whereupon eq 1b may be written as

$$\phi_1(u\dot{\tau}D,\sigma) = \frac{(\sigma + 1)(u\dot{\tau}D)^2}{2\sigma}\left[1 - \frac{(\sigma + 2)u\dot{\tau}D}{3\sigma} + \frac{(\sigma + 2)(\sigma + 3)(u\dot{\tau}D)^2}{12\sigma^2} + \ldots\right] \tag{3}$$

Combination of this expression for $\phi_1(u\dot{\tau}D,\sigma)$ with eq 1a and 1c then leads to the relationship

$$\frac{\bar{M}_w(0)}{\bar{M}_w(\mathrm{D})} = \{1 - \{2u\dot{\chi}D(\sigma + 1)/\sigma\}[1 - (\sigma + 2)(u\dot{\tau}D)/3\sigma + (\sigma + 2)(\sigma + 3)(u\dot{\tau}D)^2/12\sigma^2]\}/[1 - (\sigma + 2)(u\dot{\tau}D)/3\sigma + (\sigma + 2)(\sigma + 3)(u\dot{\tau}D)^2/12\sigma^2] \tag{4}$$

By use of the binomial theorem again to transfer the denominator to the numerator, eq 4 becomes

$$\frac{\bar{M}_w(0)}{\bar{M}_w(D)} = 1 + \left[\frac{(\sigma + 2)\lambda}{3\sigma} - \frac{2(\sigma + 1)}{\sigma}\right]u\dot{\chi}D + \left[\frac{(\sigma + 2)(\sigma - 1)\lambda^2}{36\sigma^2}\right](u\dot{\chi}D)^2 + \ldots \tag{5}$$

where $\lambda = \dot{\tau}/\dot{\chi} = G(S)/G(X)$.

This expression confirms an earlier counterpart[9] in regard to the term in D, which was then of prime interest because it accounted for the empirical observation[6] that $1/\bar{M}_w(D)$ is essentially linear with D for many systems but differs in regard to the term in D^2. The source of the discrepancy between eq 4 of that earlier study[9] and eq 5, which is now equivalent to eq 49 of Saito,[4] was the truncation of eq 3 after the second term in square brackets.

Although a plot of $1/\bar{M}_w(D)$ versus D is usually considered to be linear, it is evident from eq 5 that neglect of the D^2 term becomes questionable for a polymer that mainly undergoes scission (λ large). It is therefore suggested that eq 5 be reformulated as

$$\frac{[\bar{M}_w(0)/\bar{M}_w(D)] - 1}{D} = \left[\frac{(\sigma + 2)\lambda}{3\sigma} - \frac{2(\sigma + 1)}{\sigma}\right]u\dot{\chi} + \left[\frac{(\sigma + 2)(\sigma - 1)\lambda^2}{36\sigma^2}\right](u\dot{\chi})^2 D + \ldots \tag{6}$$

which allows $[\{(\sigma + 2)\lambda/3\sigma\} - \{2(\sigma + 1)/\sigma\}]u\dot{\chi}$ to be evaluated from the ordinate intercept of a plot of the left-hand side against D. The slope of the suggested plot seemingly provides the value of $[(\sigma + 2)(\sigma - 1)\lambda^2/36\sigma^2](u\dot{\chi})^2$ and hence a second simultaneous equation for evaluation of $\dot{\chi}$ and λ from weight-average molecular weight data alone, but this possibility needs further examination because of the presumed negligibility of higher order terms in eq 5. For a polymer with a most probable initial distribution, the adequacy of this approximation is readily demonstrated. Substitution of $\sigma = 1$ into eq 1b yields the expression

$$\phi_1(u\dot{\tau}D,\sigma) = (u\dot{\tau}D)^2/(1 + u\dot{\tau}D) \tag{7}$$

whereupon the relationship obtained by its substitution into eq 1a, namely

$$\bar{M}_w(0)/\bar{M}_w(D) = 1 + (\lambda - 4)u\dot{\chi}D \tag{8}$$

is an exact expression for the dose dependence of the weight-average molecular weight.[3] This expression is also obtained on substituting $\sigma = 1$ into eq 5.

Our reason for suggesting the reformulation of eq 5 as eq 6 is not to obtain additional information but rather to avoid the necessity of obtaining the coefficient of the term in D (eq 5) by estimation of the limiting tangent (as $D \rightarrow 0$) of the plot of $\bar{M}_w(0)/\bar{M}_w(D)$ versus D that is suggested by eq 5. We now investigate the possibility that a second simultaneous equation for evaluating $\dot{\tau}$ and $\dot{\chi}$ might be obtained from the dose dependence of the z-average molecular weight obtained by recording the sedimentation equilibrium distributions as schlieren rather than Rayleigh patterns.

Dose Dependence of $\bar{M}_z$. For an initial Schulz–Zimm distribution the dose dependence of the *z*-average molecular weight is given[4,6,9,14] by

$$\bar{M}_z(D) = \frac{3\bar{M}_n(0)[\phi_2(u\dot{\tau}D,\sigma)/\phi_1(u\dot{\tau}D,\sigma)]}{[1 - (4\dot{\chi}/u\dot{\tau}^2D)\phi_1(u\dot{\tau}D,\sigma)]^2} \tag{9a}$$

where $\phi_1(u\dot{\tau}D,\sigma)$ has already been defined (eq 1b) and

$$\phi_2(u\dot{\tau}D,\sigma) = 1 + [1 + (u\dot{\tau}D/\sigma)]^{-(\sigma+1)} - (2/u\dot{\tau}D)[1 - \{1 + (u\dot{\tau}D/\sigma)\}^{-\sigma}] \tag{9b}$$

From the above comparison of exact and approximate expressions for weight-average data, it is clearly informative to consider the simplest situation ($\sigma = 1$) first, so that any effects of series truncations in the polynomial formulations can be assessed.

With $\sigma = 1$, eq 9b becomes $\phi_2(u\dot{\tau}D,\sigma) = (u\dot{\tau}D)^2/(1 + u\dot{\tau}D)^2$, and eq 9a simplifies to

$$\bar{M}_z(0)/\bar{M}_z(D) = (1 + u\dot{\tau}D - 4u\dot{\chi}D)^2/(1 + u\dot{\tau}D) \tag{10a}$$

or, on the basis that $(1 + u\dot{\tau}D)^{-1} \simeq 1 - u\dot{\tau}D + (u\dot{\tau}D)$

$$\bar{M}_z(0)/\bar{M}_z(D) = 1 + (\lambda - 8)u\dot{\chi}D + 16(u\dot{\chi})^2D^2 + \ldots \tag{10b}$$

Since the D^2 term does not terminate the series, we recommend that eq 10b be rewritten, by analogy with eq 6, as

$$([\bar{M}_z(0)/\bar{M}_z(D)] - 1)/D = (\lambda - 8)u\dot{\chi} + 16(u\dot{\chi})^2D + \ldots \tag{11}$$

whereupon $(\lambda - 8)u\dot{\chi}$ may be obtained as the ordinate intercept of the plot suggested by eq 11. Since analysis of the dose dependence of the *z*-average molecular weight yields a value of $(\lambda - 8)u\dot{\chi}$ for a system with a most probable initial distribution, whereas analysis of the corresponding weight-average data gives an estimate of $(\lambda - 4)u\dot{\chi}$, values of λ ($=\dot{\tau}/\dot{\chi}$) and $\dot{\chi}$ (and hence $G(S)$ and $G(X)$) can be obtained by solving these two simultaneous equations. There now remains the problem of finding the general counterpart of eq 11 for systems deviating from the most probable initial distribution ($\sigma \neq 1$).

On the basis of the binomial theorem, the expression for $\phi_2(u\dot{\tau}D,\sigma)$, eq 9b, is again written as a power series. By retaining all terms in D^4 and lower, the result is

$$\phi_2(u\dot{\tau}D,\sigma) = \frac{(\sigma + 1)(\sigma + 2)(u\dot{\tau}D)^2}{6\sigma^2}\left[1 - \frac{(\sigma + 3)u\dot{\tau}D}{2\sigma} + \frac{3(\sigma + 3)(\sigma + 4)(u\dot{\tau}D)^2}{20\sigma^2}\right] \tag{12}$$

Combination of this expression with those for $\phi_1(u\dot{\tau}D,\sigma)$, eq 3, and $M_z(D)$, eq 9a, then yields, after substituting $\bar{M}_z(0)$ for $[(\sigma + 2)/\sigma]\bar{M}_n(0)$

$$\frac{\bar{M}_z(0)}{\bar{M}_z(D)} = \{[1 - \{2(\sigma + 1)u\dot{\tau}D/\sigma\}\{1 - (\sigma + 2)u\dot{\tau}D/3\sigma + (\sigma + 2)(\sigma + 3)(u\dot{\tau}D)^2/12\sigma^2\}]^2Y\}/[1 - (\sigma + 3)u\dot{\tau}D/2\sigma + 3(\sigma + 3)(\sigma + 4)(u\dot{\tau}D)^2/20\sigma^2] \tag{13a}$$

$$Y = 1 - (\sigma + 2)u\dot{\tau}D/3\sigma + (\sigma + 2)(\sigma + 3)(u\dot{\tau}D)^2/12\sigma^2 \tag{13b}$$

As in the derivation of the expression for $\bar{M}_w(0)/\bar{M}_w(D)$, the denominator is now eliminated by resort to binomial expansion. By neglecting all terms of higher order than D^2, the resultant expression for the molecular weight ratio becomes

$$\frac{\bar{M}_z(0)}{\bar{M}_z(D)} = 1 + \left[\frac{(\sigma + 5)\lambda}{6\sigma} - \frac{4(\sigma + 1)}{\sigma}\right]u\dot{\chi}D + \left[\frac{4(\sigma + 1)^2}{\sigma^2} + \frac{2(\sigma + 1)(\sigma - 1)\lambda}{3\sigma^2} - \frac{(\sigma + 3)(\sigma - 1)\lambda^2}{60\sigma^2}\right](u\dot{\chi}D)^2 + \ldots \tag{14}$$

To avoid the problem of estimating limiting tangents to determine the coefficient of the term in D, we rewrite eq 14 as

$$\frac{[\bar{M}_z(0)/\bar{M}_z(D)] - 1}{D} = \left[\frac{(\sigma + 5)\lambda}{6\sigma} - \frac{4(\sigma + 1)}{\sigma}\right]u\dot{\chi} + \left[\frac{4(\sigma + 1)^2}{\sigma^2} + \frac{2(\sigma + 1)(\sigma - 1)\lambda}{3\sigma^2} - \frac{(\sigma + 3)(\sigma - 1)\lambda^2}{30\sigma^2}\right](u\dot{\chi})^2D \tag{15}$$

For $\sigma = 1$ this expression simplifies to eq 11, as required. The value of $[(\sigma + 5)\lambda/6\sigma - 4(\sigma + 1)/\sigma]u\dot{\chi}$ may thus be obtaind as the ordinate intercept of the plot of $([\bar{M}_z(0)/\bar{M}_z(D)] - 1)/D$ versus D, whereupon its combination with the ordinate intercept of $[(\sigma + 2)\lambda/3\sigma - 2(\sigma + 1)/\sigma]u\dot{\chi}$ obtained from the corresponding analysis of weight-average data (eq 6) provides values of $\dot{\chi}$ and $\dot{\tau}$.

Evaluation of Simulated Data

The feasibility of evaluating $\dot{\tau}$ and $\dot{\chi}$, or $G(S)$ and $G(X)$, from the dose dependence of $\bar{M}_w(D)$ and $\bar{M}_z(D)$ depends to a great extent upon the accuracy with which either limiting tangents or ordinate intercepts can be determined. To provide an indication of any difficulties that might be encountered in the estimation of these parameters, eq 1 and 9 have been used to generate $\bar{M}_w(D)$ and $\bar{M}_z(D)$ data for systems with $\bar{M}_n(0) = 104\,000$, $u = 1000$, and a range of values of σ, the width of the initial Schulz–Zimm distribution: $G(X)$ was fixed at 0.02, and λ, the ratio G(S)/G(X), was assigned a series of values between 0.1 and 20.

Systems with a Most Probable Initial Distribution ($\sigma = 1$). These systems provide the simplest situation in that the plot of $1/\bar{M}_w(D)$ versus D is strictly linear (eq 8), whereupon there is no difficulty in obtaining the value of $(\lambda - 4)u\dot{\chi}$ from the slope of such a plot or as the ordinate intercept of the horizontal plot of $([\bar{M}_w(0)/\bar{M}_w(D)] - 1)/D$ versus D (eq 6). The extent to which the corresponding treatments of *z*-average molecular weight data can reasonably be expected to provide the value of $(\lambda - 8)u\dot{\chi}$ (eq 14 and 15) may be gauged from Figure 1.

(i) From Figure 1a it is evident that the plots of $M_z(0)/\bar{M}_z(D)$ versus D are curvilinear, a factor that mitigates against accurate assessment of the limiting tangents (– – –), which have been constructed on the basis of a slope of $(\lambda - 8)u\dot{\chi}$.

(ii) For $\lambda = 6$ the plotted curve seemingly predicts gel formation at high irradiation dose, a phenomenon that can only occur if $\lambda < 4$ (eq 10a). The possibility is therefore examined that the dose dependence of $\bar{M}_z(0)/\bar{M}_z(D)$ may exhibit a minimum for certain $G(S)/G(X)$ ratios. To test for the existence of a minimum, the first derivative of eq 10a with respect to D has been set equal to zero, the required condition being that

$$(u\dot{\tau} - u\dot{\chi}) + 2(u\dot{\tau} - 8u\dot{\chi})^2D - 8u\dot{\tau}u\dot{\chi}(u\dot{\tau} - 2u\dot{\chi})D^2 = 0 \tag{16}$$

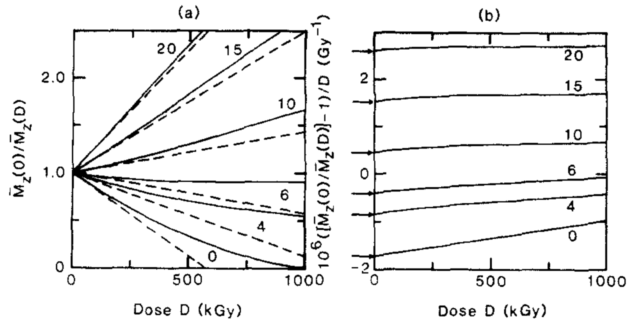

Figure 1. Determination of the parameter $(\lambda - 8)u\dot{\chi}$ from simulated data (eq 9) for the dose dependence of the *z*-average molecular weight, $\bar{M}_z(D)$, for a polymer with a most probable initial distribution ($\sigma = 1$) and the indicated values of $\lambda = \tau/\chi$ (the ratio of scission to crosslinking yields). (a) Plots of data (—) in accordance with eq 10 and the corresponding limiting tangents (- - -) with the theoretical slope of $(\lambda - 8)u\dot{\chi}$. (b) Plot of the same data in accordance with eq 11 to demonstrate the feasibility of extrapolation to obtain the theoretical ordinate intercept of $(\lambda - 8)u\dot{\chi}$ (horizontal arrow).

where $u\dot{\tau}$, $u\dot{\chi}$, and D are necessarily positive. In the solution to this quadratic, namely

$$D = \{-2(u\dot{\tau} - 8u\dot{\chi})^2 + [4(u\dot{\tau} - 8u\dot{\chi})^4 + 32u\dot{\tau}u\dot{\chi}(u\dot{\tau} - 8u\dot{\chi})(u\dot{\tau} - 2u\dot{\chi})]^{1/2}\}/[-16u\dot{\tau}u\dot{\chi}(u\dot{\tau} - 2u\dot{\chi})] \tag{17}$$

the denominator is negative for any system that does not undergo gelation at high radiation dose ($\lambda > 4$) and the first term of the numerator is clearly also negative because of the power to which it is raised. For the numerator to be negative (and hence D to be positive) the square root of the discriminant must be smaller than $2(u\dot{\tau} - 8u\dot{\chi})^2$, a requirement fulfilled by the condition

$$32u\dot{\tau}u\dot{\chi}(u\dot{\tau} - 2u\dot{\chi})(u\dot{\tau} - 8u\dot{\chi}) < 0 \tag{18}$$

Since $(u\dot{\tau} - 2u\dot{\chi})$ is positive for any system with $\lambda > 4$, this condition can only be met in the event that $u\dot{\tau} - 8u\dot{\chi} < 0$, i.e., that $u\dot{\tau} < 8u\dot{\chi}$. Dose-dependent increases in $\bar{M}_z(D)$ and subsequent decreases are thus confined to $4 < \lambda < 8$ for systems with $\sigma = 1$, a prediction borne out by the theoretical curves (—) in Figure 1a.

(iii) The difficulties inherent in determining the limiting tangents to the plots in Figure 1a may be overcome by analyzing the data in the alternative format (eq 11), which gives $(\lambda - 8)u\dot{\chi}$ as the ordinate intercept (Figure 1b): theoretical values are denoted by horizontal arrows. However, it should be noted that although eq 11 provides an accurate description of the ordinate intercept, its prediction of a λ-independent slope is clearly incorrect—an indication that the truncated polynomial expansion used in the derivation of eq 10b from eq 10a is inadequate from the viewpoint of defining the term in D^2. This inadequacy does not extend to definition of the term in D, which is the required parameter. For systems with a most probable initial distribution, use of the suggested analyses of $\bar{M}_w(D)$ and $\bar{M}_z(D)$ data for evaluating $G(S)$ and $G(X)$ thus seems appropriate.

Systems with Any Initial Schulz-Zimm Distribution. It is important to determine whether the same approach also applies to polymers with other initial distributions, since the irradiation of samples with very narrow initial distributions (σ large) has been recommended[14] for quantitative evaluation of cross-linking by sedimentation velocity. To establish that the procedure retains validity irrespective of the magnitude of σ and λ, simulated data for the dose dependence of $\bar{M}_w(D)$ and $\bar{M}_z(D)$ for a range of systems have been analyzed.

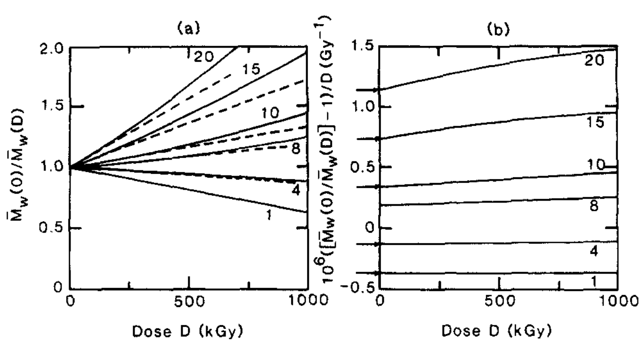

Figure 2. Quantitative evaluation of simulated data (eq 1) for the dose dependence of the weight-average molecular weight, $\bar{M}_w(D)$, of a polymer with a narrow initial distribution ($\sigma = 20$) and the indicated values of λ. Plots of data in accordance with (a) eq 5 and (b) eq 6, from which $[(\sigma + 2)\lambda/3\sigma - 2(\sigma + 1)/\sigma]u\dot{\chi}$ is obtaind from the limiting slope (- - -) and ordinate intercept (horizontal arrow), respectively.

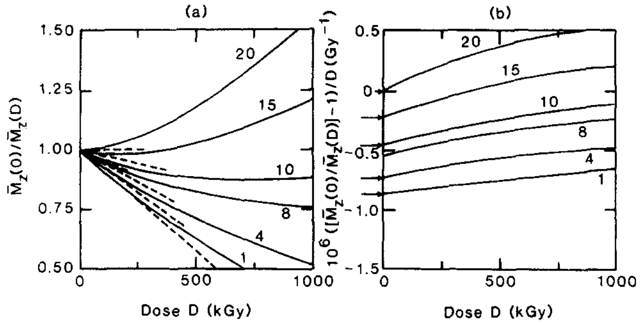

Figure 3. Quantitative evaluation of simulated data (eq 9) for the dose dependence of (a) $\bar{M}_z(0)/\bar{M}_z(D)$ and (b) $([\bar{M}_z(0)/\bar{M}_z(D)] - 1)/D$ for a polymer with a narrow initial distribution ($\sigma = 20$). Broken lines in (a) denote the limiting tangents with theoretical slopes of $[(\sigma + 5)\lambda/6\sigma - 4(\sigma + 1)/\sigma]u\dot{\chi}$, and horizontal arrows in (b) the ordinate intercepts corresponding to the same parameter.

Whereas irradiation of polymers with a most probable initial distribution ($\sigma = 1$) leads to a linear dose dependence of $\bar{M}_w(0)/\bar{M}_w(D)$ (eq 7), the corresponding dependence for systems with $\sigma \neq 1$ will exhibit curvature[9] when λ is large (eq 5). This may be gauged from Figure 2a, which refers to a very narrow initial distribution ($\bar{M}_w(0)/\bar{M}_n(0) = 1.05$; $\sigma = 20$). The extent of curvilinearity would be undetectable experimentally for systems with $\lambda < 4$ but would introduce uncertainty into estimations of the limiting tangents for systems characterized by higher λ values. On the other hand, the corresponding effect on the alternative form of analysis (eq 6) is merely a systematic dose-dependent increase in $([\bar{M}_w(0)/\bar{M}_w(D)] - 1)/D$ (Figure 2b). Regardless of whether the plot of $([\bar{M}_w(0)/\bar{M}_w(D)] - 1)/D$ versus D is horizontal (signifying essential linearity of the dose dependence of $\bar{M}_w(0)/\bar{M}_w(D)$) or is exhibiting upward curvature, the smooth form of the dependence allows the required extrapolation of experimental data to be made to obtain the ordinate intercept.

The corresponding analyses of simulated *z*-average molecular weight data are presented in Figure 3. From the dose dependence of $\bar{M}_z(0)/\bar{M}_z(D)$ (Figure 3a) the potential for the existence of minima in such plots is more obvious than it was in Figure 1b for systems with a most probable initial distribution. Whereas the upper limiting value of λ for the existence of a minimum for that initial distribution was 8 (eq 18), the corresponding limit for the present narrow initial distribution is at least 15 (Figure 3a). Attempts to obtain a more definitive estimate of this upper limit for the existence of a minimum

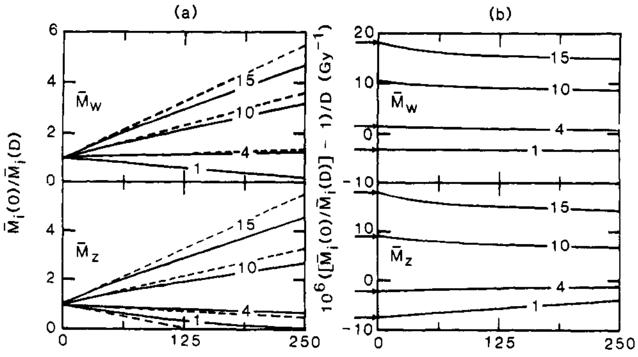

Figure 4. Quantitative evaluation of simulated data (eq 1 and 9) for the dose dependences of weight-average and *z*-average molecular weights for a polymer with a very broad initial distribution ($\sigma = 0.1$) and the indicated values of λ. (a) Plots of data in accordance with eq 5 (upper curve) and 14 (lower curve), together with the calculated limiting tangents (- - -) of $[\sigma + 2)\lambda/3\sigma - 2(\sigma + 1)/\sigma]u\chi$ and $[(\sigma + 5)\lambda/6\sigma - 4(\sigma + 1)/\sigma]u\chi$. (b) Plots of the same data in accordance with eq 6 and 15 and the theoretical ordinate intercepts (horizontal arrows) defining the same parameters.

by differentiating eq 9 with respect to D have been unsuccessful due to the inability to express the required condition (first derivative equal to zero) in a form amenable to a tractable solution. However, the only result would be a more precise definition of the values of λ for which it would not be possible to estimate limiting tangents from the dose dependence of $\bar{M}_z(0)/\bar{M}_z(D)$. As for the systems with $\sigma = 1$, this difficulty is readily circumvented by analysis of the data in the form $([\bar{M}_z(0)/\bar{M}_z(D)] - 1)/\mathrm{D}$ versus D (Figure 3b), where a minimum in the dose dependence of $1/\bar{M}_z(D)$ has no effect on the determination of the ordinate intercept. Evaluation of $G(S)$ and $G(X)$ by combining these ordinate intercepts from the dose dependences of weight- and *z*-average molecular weights thus appears to be equally valid for polymers with very narrow initial distributions as it is for polymers with a most probable initial distribution. Furthermore, we have shown that the various features of Figures 1–3 also apply to the radiation degradation of polymers with intermediate σ values.

Comparable analyses of the effect of radiation degradation on a polymer with a broad initial distribution ($\sigma = 0.1$) are summarized in Figure 4. For these systems the dependence of $\bar{M}_w(0)/\bar{M}_w(D)$ and $\bar{M}_z(0)/\bar{M}_z(D)$ (Figure 4a) differ from their counterparts for narrower initial distributions in that the sense of the curvilinearity is reversed: the magnitudes of slopes in Figures 1–3 are ever increasing with dose, but those in Figure 4 are mainly ever decreasing (see below). Another point of interest in Figure 4a is the divergent dose dependence of $\bar{M}_w(0)/\bar{M}_w(D)$ in comparison with that of $\bar{M}_z(0)/\bar{M}_z(D)$ for $\lambda = 4$. Whereas the decrease of $\bar{M}_w(D)$ with dose might be construed as evidence of scission, the increase of $\bar{M}_z(D)$ with dose signifies the occurrence of cross-linking: $\lambda = 4$ is, of course, the value of $G(S)/G(X)$ associated with the changeover in predominance of cross-linking and scission. The advantages of using eq 6 and 15 rather than eq 5 and 14 for evaluating the respective relationships between $G(S)$ and $G(X)$ also apply to polymers with this broad initial distribution (Figure 4b). Extrapolation of $([\bar{M}_w(0)/\bar{M}_w(D) - 1)/D$ to obtain the ordinate intercept should pose no difficulty in that the function exhibits a systematic decrease with increasing dose. For $\lambda > 4$ a similar situation applies to the corresponding plot for $\bar{M}_z(D)$, but for $\lambda \leq 4$ the value systematically increases with dose. Irrespective of the sense of the dose dependence of the $M_z(D)$ function, the ordinate intercept should be readily determined experimentally. The proposed procedure for determining $G(S)$ and $G(X)$ thus seems likely to be applicable throughout the range of possible initial distributions and $G(S)/G(X)$ ratios.

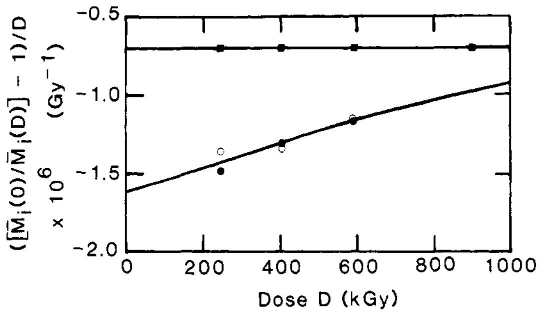

Figure 5. Analysis of weight-average (■) and *z*-average (●, ○) molecular weight data for γ-irradiated polystyrene with a narrow initial distribution ($\sigma = 33$). Open symbols denote published $\bar{M}_z(D)$ data,[14] whereas closed symbols refer to data obtained by remeasurement of those same sedimentation equilibrium distributions. Solid lines indicate the theoretical dose dependence for a polymer with $\sigma = 33$ and $G(S) = G(X) = 0.02$, the parameters deduced previously.[14]

Application to the γ-Irradiation of Polystyrene

Analyses of simulated radiation degradation data have failed to detect any theoretical deficiencies in the proposed procedure for evaluating $G(S)$ and $G(X)$ by combining information from the dose dependence of weight- and *z*-average molecular weights. To test whether limitations are likely to arise from inherent uncertainty in experimental results, we have reappraised the results of an earlier investigation into the effect of γ-irradiation on a polystyrene sample with $\sigma = 33$:[14] this is the only system for which a dose dependence of $\bar{M}_z(D)$ seems to have been reported. Access to the photographic records of the sedimentation equilibrium distributions has allowed corresponding calculations of $\bar{M}_w(D)$ for the samples to which the published $\bar{M}_z(D)$ results refer. The resultant plots (Figure 5) derived from the dose dependences of $\bar{M}_w(D)$ (squares) and $\bar{M}_z(D)$ (circles) show that the proposed procedure can give satisfactory values for $G(S)$ and $G(X)$. The plot for $\bar{M}_w(D)$ (■) gives $[(\sigma + 2)\lambda/3\sigma + 2(\sigma + 1)/\sigma]u\chi = -7.0(\pm 0.1) \times 10^{-6}$ Gy^{-1}, and its horizontal nature is in accord with prediction for $\lambda < 4$ (Figure 2b): a value of $\lambda = 1$ has been determined from the effect of radiation dose on sedimentation velocity patterns for these samples.[14] Uncertainty in the value of $\bar{M}_z(D)$ at the lowest radiation dose prevents an accurate estimate of the ordinate intercept of the $\bar{M}_z(D)$ plot (circles) in Figure 5. Nevertheless, the three experimental points are adequately described by the theoretical relationship (—) for a polymer with $u = 1894$ ($\bar{M}_n(0)/M_1$) and $G(S) = G(X) = 0.02$, which are the radiation yields derived from the ordinate intercept of -7.0×10^{-6} Gy^{-1} for the $\bar{M}_w(D)$ plot on the basis that $\lambda = 1$. The excellent delineation of the ordinate intercept of the $\bar{M}_w(D)$ plot and the agreement between the theoretical $\bar{M}_z(D)$ relationship and the experimental points suffice to indicate that the proposed procedure should generally provide a unique determination of $G(S)$ and $G(X)$ without recourse to any assumption about the value of the ratio $G(S)/G(X)$.

Concluding Remarks

The demonstration that cross-linking and scission yields can be determined from the dose dependences of weight-

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and z-average molecular weights is of particular relevance to the study of radiation degradation by ultracentrifugation, where $\bar{M}_w(D)$ and $\bar{M}_z(D)$ for an irradiated sample may be obtained from the same sedimentation equilibrium experiment. Although gel permeation chromatography is also used for that purpose, sedimentation equilibrium is the technique of choice for determining $\bar{M}_w(D)$ and $\bar{M}_z(D)$ because it avoids the errors inherent in chromatographically estimated molecular weight averages unless account is taken of differences in the elution volumes of linear and cross-linked polymer chains with the same molecular weight. An advantage of the proposed procedure is the sensitivity of $\bar{M}_z(D)$ to cross-linking, which enables $G(S)$ and $G(X)$ to be obtained from studies of samples subjected to low radiation doses. On the basis of analyses of simulated radiation degradation data, the present procedure of evaluating $G(S)$ and $G(X)$ from the ordinate intercepts of plots of $([\bar{M}_i(0)/\bar{M}_i(D)] - 1)/D$ versus D (i = w, z) applies to a wide range of initial molecular weight distributions and $G(S)/G(X)$ ratios. Finally, an experimental verification of the theoretical treatment is provided by an examination of results for the γ-irradiation of polystyrene.

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Registry No. Polystyrene, 9003-53-6.

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Volume Effects of Amylose–Water Interactions[†]

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ABSTRACT: Volume changes resulting from the sorption of water by amylose have been determined by a newly developed dilatometric procedure involving the dissolution in potassium hydroxide of samples previously equilibrated to a range of desired water contents. The data are represented by an empirical equation containing two exponentials. A theoretical expression including parameters obtainable from sorption isotherms was developed by which the volume changes could be resolved into contributions arising from contact adsorption and from adsorption in more distant layers. The contribution from the latter was very small amounting to a volume decrease of less than 0.04 mL/g of sorbed water. The contact adsorption, in contrast, produced very large volume decreases ranging from 0.47 mL in nearly dry samples to 0.32 mL/g of water for samples containing 0.14–0.29 g of water/g of dry amylose. The change in these values suggests more than one type of sorption site. Their large magnitude points to a mutual filling of molecular cavities by the participating species.

Introduction

It has been well established that the physical and chemical properties of starch are critically affected by its interactions with water.[1-4] These interactions have been studied by a variety of experimental methods.[5] Perhaps the most exhaustively applied of these methods has been the determination of vapor pressure–sorption isotherms which, in addition to their practical applications, give useful thermodynamic information.[3,6,7] An originally empirical expression, known as the GAB (Guggenheim, Anderson, De Boer) equation,[8-11] has been found to give a satisfactory representation of such isotherms over nearly the whole range of water activities.[6,12] The equation may be derived by means of a multilayer adsorption model in which the sorbed water molecules are divided into two classes: one consisting of strongly adsorbed molecules in contact with the surface and the other of weakly adsorbed molecules in the remaining layers.[10]

It is important to realize that the same model also allows the calculation of the distribution of sorbed water between the two classes. Knowledge of this distribution makes it possible to test the two-class model by means of other experimental methods.

We present here the results of dilatometric measurements aimed at obtaining the volume changes accompanying the interactions of water with amylose, one of the two major components of starch. Since on the molecu-

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