macroradical. As in all similar photochemical reactions, the more mobile alkyl or aryl radicals could in principle participate in hydrogen abstraction, recombination with other radicals, reaction with molecular oxygen, or elimination of a hydrogen radical to form an alkene. The reactions discussed here are extremely *low yield* processes that can best be explained by the interaction of radicals with nearby units within a polymer "cage". Radical–radical recombinations appear to be unlikely outside the polymer matrix. This interpretation explains the absence of propane or hexane from $[NP(OCH_2CH_3)_2]_{n \text{ or } 4}$, or hexafluoropropane from $[NP(OCH_2CF_3)_2]_{n \text{ or } 4}$, and the formation of butane from $[NP(OCH_2CH_3)_2]_n$ and biphenyl from $[NP(OC_6H_5)_2]_n$.

It should be noted that, with the sole exception of carbon dioxide generation, the cyclic model compounds behave on irradiation in a virtually identical manner to the high polymers. Thus, in future work, photolysis experiments on other cyclic phosphazenes may offer an excellent method for the preliminary screening of phosphazene high-polymer systems.

Based on this study, it appears that polyphosphazenes as a class have the capability to withstand appreciable exposure to near-ultraviolet radiation without sustaining appreciable skeletal cleavage or depolymerization to cyclic oligomers, *provided that phosphorus–chlorine bonds are absent*. Because the C–O bonds in alkoxy- and aryloxyphosphazenes constitute one of the weakest linkages in the system (Table IV), the recently synthesized polyphosphazenes that contain direct P–C bonds to the side group[32] are of considerable interest for future photolysis work.

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Chain Scission and Cross-Linking in the Radiation Degradation of Polymers: Limitations on the Utilization of Theoretical Expressions and Experimental Results in the Pregel Region

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ABSTRACT: An appraisal is made of current methods of determining radiation–chemical yields for main-chain scission and cross-linking of a polymer from measurements of molecular size distributions and average molar masses after high-energy radiation doses D below the gel dose D_g. Calculation of molecular size distributions by a single cycle of successive scission and cross-linking is shown to give significant errors. A multicycle procedure that uses iterative, numerical solutions of the fundamental scission and cross-linking equations is developed and shown to be superior. On the basis of theoretical calculations of likely experimental errors in measurements of $\bar{M}_w$ and $\bar{M}_z$ it is recommended that radiation doses be restricted to the region $D < 0.4D_g$ for evaluation of scission and cross-linking yields from the dose dependence of average molar masses.

High-energy (ionizing) radiation causes a variety of chemical reactions to occur in polymers and results in permanent molecular changes including scission and cross-linking of backbone chains.[2,3] These two effects are of particular importance because of resultant changes in the physical and mechanical properties of the irradiated

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polymer. Consequently much research has entailed evaluation of the radiation chemical yields of scission $G(S)$ and cross-linking $G(X)$ per 16.02 aJ (100 eV) of energy absorbed by various polymers.

Scission and cross-linking may occur simultaneously and either may predominate, depending on the molecular structure, the physical state of the polymer (crystalline or amorphous solid, melt, or solution), and the irradiation conditions (temperature, availability of oxygen). If $G(S) < 4G(X)$ an insoluble gel forms at irradiation doses greater than a critical gel dose D_g,[4] which decreases with increasing molar mass of the initial polymer; the gel fraction increases with dose to a limiting proportion determined by the ratio $G(S):G(X)$. Quantitative evaluation of $G(S)$ and $G(X)$ for such systems has usually involved analysis of solubility data by a Charlesby–Pinner type plot[5] of $(s + s^{1/2})$, where s is the soluble fraction, against the reciprocal of the radiation dose D, the theoretical relationship having been derived for various initial molecular size distributions.[6]

The use of gel fractions and/or the gel dose to determine $G(S)$ and $G(X)$ has several disadvantages. First, the method is clearly inapplicable to systems with $G(S) > 4G(X)$, since gel does not form. Second, effects of intramolecular cross-linking (cyclization) and end-linking are greater at higher doses and consequently their assumed absence may become an unacceptable approximation. Third, modifications of the chemical structure and physical state of the polymer may occur at high radiation doses and consequently the measured chemical yields may differ significantly from those of the initial polymer. Determination of $G(S)$ and $G(X)$ values that are appropriate to the initial polymer requires the interpretation of results obtained with samples subjected to low radiation doses, i.e., to doses in the pregel region; and solution properties should provide the necessary information.

Theoretical relationships for changes in the average molar masses $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ with radiation dose have been derived for various initial molecular size distributions, e.g., uniform, Poisson (or random), Schulz–Zimm, and Wesslau distributions, and also for an arbitrary initial distribution.[6] Consequently, experimental measurements of $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ after various radiation doses can be compared with the corresponding theoretical dependences for different $G(S)$ and $G(X)$ combinations. However, more information is available from the complete molecular size distribution after irradiation, particularly for narrow initial distributions.[7,8] These distributions have been obtained successfully by velocity sedimentation[7-9] and may also be determined by gel permeation chromatography.

Theoretical expressions have been derived for the change in molecular size distribution of a polymer after chain scission or cross-linking (reviewed, e.g., in ref 6). In the event that both processes occur simultaneously it has been assumed universally that the resultant molecular size distribution can be obtained by first calculating the effect of all the scission on the initial distribution and then calculating the effect of all the cross-linking on the resultant distribution. In this paper we compare this procedure with one involving successive increments of scission and cross-linking. We have also evaluated the magnitudes of errors in measured average molar masses that are likely to result from neglect of a portion of the high molecular size tail of the distribution after significant cross-linking has occurred. Various other limitations that may be encountered in the use of theoretical relationships pertaining to the pregel region are also considered.

Theory

A. Chain Scission. A general integro-differential equation describing the change in molecular size distribution of a polymer undergoing random chain scission may be written[10]

$$\frac{\partial w(p,\tau)}{\partial \tau} = -pw(p,\tau) + 2p\int_p^\infty w(l,\tau)\, dl/l \qquad (1)$$

where $w(p,\tau)$ is the weight fraction of molecules containing p structural (monomer) units after a radiation dose which produces, on average, τ chain scissions in each structural unit of the polymer: $w(l,\tau)$ is the corresponding fraction of molecules containing l structural units, where l takes all values greater than or equal to p in the integration. Equation 1 has been derived on the bases that (i) chain scission takes place at random, (ii) all polymers are linear, and (iii) the degree of polymerization is continuous. Because of greater relevance to experimental methods of recording molecular size distributions, equations are expressed in terms of weight fractions, $w(p,\tau)$ rather than $m(p,\tau)$, the corresponding number fraction, or $n(p,\tau)$, the number of molecules containing p structural units, which are the parameters used in numerical calculations of distributions. For 1 g of polymer the various molecular size distributions are related by

$$w(p,\tau) = pm(p,\tau) = pM_1 n(p,\tau) \qquad (2)$$

where M_1 is the molar mass of a structural (monomer) unit.

For dose-independent scission, the dose dependence of τ may be expressed as $\tau = \dot{\tau}D$, where $\dot{\tau}$ is the average number of chain scissions per structural unit per unit dose of radiation. The relationship between $G(S)$ and $\dot{\tau}$ depends on the unit of radiation dose chosen. In the past various units such as 1 eV/g, 1 eV/mol of structural unit, and 1 Mrad (≡10 J/g) have been used. On the basis of the SI unit of dose, viz., the gray (1 Gy ≡ 1 J/kg ≡ 100 rad), the relationship between $G(S)$ and $\dot{\tau}$ is

$$G(S) = 9.65 \times 10^9 \dot{\tau}/M_1 \qquad (3)$$

Note that $\dot{\tau}$ for unit dose of 1 Gy is 10^4 times smaller than $\dot{\tau}$ for unit dose of 1 Mrad.

Kimura[11] has derived an analytical solution to eq 1 for the particular case of an initial Schulz–Zimm molecular size distribution; the latter may be represented by

$$w(x,0) = uxm(x,0) = (1/u)[\sigma^{(\sigma+1)}/\Gamma(\sigma+1)]x^\sigma \exp(-\sigma x) \qquad (4)$$

where u is the number-average degree of polymerization of the initial polymer ($=\bar{M}_n(0)/M_1$) and $x = p/u$; σ denotes the breadth parameter ($\sigma = [\{\bar{M}_w(0)/\bar{M}_n(0)\} - 1]^{-1}$, $\bar{M}_w(0)$ being the initial weight-average molar mass), and Γ is the gamma function. For an initial Schulz–Zimm distribution with σ an integer, and hence $\Gamma(\sigma+1) = \sigma!$, Kimura[11] has shown that

$$w(x,\tau) = (x/u)[\sigma^{(\sigma+1)}/\sigma!]\left[x^{(\sigma-1)} + 2u\tau\sum_k\left\{\frac{\sigma! x^{(\sigma-k-1)}}{\sigma^{(k+2)}(\sigma-k-1)!}\right\} + u^2\tau^2\sum_k\sum_{k'}\left\{\frac{\sigma! x^{(\sigma-k-k'-1)}}{\sigma^{(k+k'+3)}(\sigma-k-k'-1)!}\right\}\right]\exp[-x(\sigma+u\tau)] \qquad (5)$$

In the summations k and k' cover all integers for which $0 \le k \le (\sigma-1)$ and $0 \le k' \le (\sigma-k-1)$.

However, if the initial distribution is not of the Schulz–Zimm type, a situation that can also result after some cross-linking of an initial Schulz–Zimm distribution has occurred, eq 5 is not appropriate. Saito[6] has deduced

Table I
Comparison of Average Molar Mass Ratios $\bar{M}_q(D)/\bar{M}_q(0)$[a] Determined from Calculated Molecular Size Distributions after Scission (eq 8 plus eq 6 or 7) with Theoretical Values Obtained from eq 9-11 for a System with $u = 1894$ and $M_1 = 104$[b]

	$\bar{M}_q(D)/\bar{M}_q(0)$[a]											
	Schulz-Zimm distribution, $\sigma = 33$						Poisson distribution ($\sigma = 1$)					
	$u\tau = 1.0$			$u\tau = 5.0$			$u\tau = 1.0$			$u\tau = 5.0$		
size of Δx in eq 6 and 7	$q = 1$	$q = 2$	$q = 3$	$q = 1$	$q = 2$	$q = 3$	$q = 1$	$q = 2$	$q = 3$	$q = 1$	$q = 2$	$q = 3$
0.10	0.5468	0.7356	0.8344	0.2206	0.3225	0.4368	0.5515	0.5014	0.4996	0.2216	0.1776	0.1668
0.05							0.5254	0.5008	0.5000	0.1929	0.1679	0.1666
0.01	0.5046	0.7257	0.8277	0.1716	0.3116	0.4323	0.5048	0.4998	0.4996	0.1717	0.1667	0.1666
0.0002	0.5009	0.7249	0.8271	0.1676	0.3113	0.4318						
theoretical value	0.5000	0.7248	0.8270	0.1667	0.3113	0.4318	0.5000	0.5000	0.5000	0.1666	0.1666	0.1666

[a] $\bar{M}_1 \equiv \bar{M}_n$; $\bar{M}_2 \equiv \bar{M}_w$; $\bar{M}_3 \equiv \bar{M}_z$. [b] This choice of u and M_1 values was governed by our previous considerations[8] of a polystyrene sample with $\bar{M}_n(0) = 197\,000$.

a general analytical expression which in present terminology may be written as

$$w(x,\tau) = [w(x,0) + ux\tau\sum_{z=x}^{\infty}\{(2 + uz\tau - ux\tau)/z\}w(z,0)\Delta z] \exp(-ux\tau) \quad (6)$$

where $z = l/u$ and Δz is a convenient constant increment in z.

The integro-differential expression for scission (eq 1) may also be solved numerically by a "marching" method using a computer. For this purpose eq 1 is written more conveniently in the form

$$w(x,\tau + \Delta\tau) = (w(x,\tau) + [2ux\sum_{z=x}^{\infty}\{w(z,\tau)\Delta x/z\} - uxw(x,\tau)]\Delta\tau) \quad (7)$$

We have compared the molecular size distributions calculated by means of eq 5, 6, and 7 after chain scission of an initial Schulz–Zimm distribution with $\sigma = 33$ and of a Poisson distribution ($\sigma = 1$) for different extents of scission in the range $0.1 \leq u\tau \leq 10$. The suitability of the "marching" solution (eq 7) was confirmed by the excellent agreement observed between the three distributions provided that the value of $\Delta\tau$ used in eq 7 was sufficiently small.

As a further test of the calculated distributions we have determined the values of $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ from these distributions by means of the accepted definitions

$$\bar{M}_q = \sum n_i M_i^q / \sum n_i M_i^{(q-1)} \quad (8)$$

where $q = 1$, 2, and 3 for $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$, respectively. These estimates were compared with values obtained from the analytical expressions derived[12] for the simultaneous scission and cross-linking of an initial Schulz–Zimm distribution (eq 9–11). A typographical error in the original publication[12] has been corrected in these expressions, which may be adapted to systems with scission only by setting χ, the average number of cross-links per structural unit after dose D, equal to zero.

$$\bar{M}_n(D) = uM_1/[1 + u\tau - u\chi] \quad (9)$$

$$\bar{M}_w(D) = 2M_1u\phi_1(u\tau,\sigma)/[(u\tau)^2\{1 - (4\chi/u\tau^2)\phi_1(u\tau,\sigma)\}] \quad (10)$$

$$\bar{M}_z(D) = 3M_1u\phi_2(u\tau,\sigma)/[\phi_1(u\tau,\sigma)\{1 - (4\chi/u\tau^2)\phi_1(u\tau,\sigma)\}^2] \quad (11)$$

where

$$\phi_1(u\tau,\sigma) = u\tau - 1 + (1 + u\tau/\sigma)^{-\sigma}$$

$$\phi_2(u\tau,\sigma) = 1 + (1 + u\tau/\sigma)^{-(\sigma+1)} - (2/u\tau)\{1 - [1 + (u\tau/\sigma)]^{-\sigma}\} \quad (12)$$

Table I compares the theoretical values of the ratio $\bar{M}_q(D)/\bar{M}_q(0)$ that was obtained from eq 9–11 with the corresponding estimates determined by means of eq 8 from the calculated molecular size distributions (eq 6 and 7). For both initial distributions ($\sigma = 33$ and $\sigma = 1$) and both extents of scission presented ($u\tau = 1$ and 5), very good agreement between the calculated and theoretical values of the three ratios is obtained provided that sufficiently small increments in x are used in the calculations.

B. Effect of Cross-Linking. An integro-differential equation describing the change in molecular size distribution of a polymer undergoing random cross-linking is[10]

$$\frac{\partial w(p,\chi)}{\partial\chi} = -2pw(p,\chi)\int_0^{\infty} w(l,\chi)\,dl + p\int_0^{p} w(l,\chi)w(p - l,\chi)\,dl \quad (13)$$

The average number of cross-links per structural unit after radiation dose D is again assumed to be dose independent ($\chi = \dot{\chi}D$), $G(X)$ and $\dot{\chi}$ being related by an expression analogous to eq 3. The following assumptions are inherent in the derivation of eq 13: (i) cross-linking is random; (ii) the number of cross-links is small compared with the number of monomer units available for cross-linking; (iii) no intramolecular cross-linking (cyclization) occurs; and (iv) the degree of polymerization can be treated as continuous.

Kells and Guillet[13] have shown that this equation can be solved by a numerical solution involving "marching" in increments of p and χ, the equation in a form suitable for computer use being

$$w(x,\chi + \Delta\chi) = w(x,\chi) + \Delta\chi[-2uxw(x,\chi) + (u^2/x)\sum_{i=0}^{x/\Delta x}\{i\Delta x(x - i\Delta x)w(i\Delta x,\chi)w(x - i\Delta x,\chi)\Delta\chi\}] \quad (14)$$

where $\Delta\chi = \chi/n$ and n is the chosen number of increments to comprise the total dose. The effect of varying this number of increments on a resultant molecular size distribution is shown in Table II. Significant differences in the apparent values of $uw(x,\chi)$ were observed with increasing n but were reasonably small above $n = 50$. Care is also required in selection of the magnitude of Δx, which should be less than 0.1 for reasonable accuracy to be maintained.

An analytical solution of eq 13 has been obtained[11,14] for an initial Schulz–Zimm molecular size distribution but not for an arbitrary initial distribution. Equation 15 presents this Kimura[11,14] solution, corrected for an error first detected by Kells and Guillet[13] and also for a typographical error in the latter paper.[13]

$$uxw(x,\chi) = [(\sigma^{(\sigma+1)}/\sigma!)x^{\sigma} + \{\sigma^{(2\sigma+4)}x^{(2\sigma+2)}u\chi\}/\{\sigma^2(2\sigma + 1)!\}] \exp\{-x(\sigma + 2u\chi)\} \quad (15)$$

Table II
Dependence of the Molecular Size Distribution Calculated from eq 14 upon the Number of Increments, n, Selected to Comprise the Total Radiation Dose for a System[a] Undergoing Cross-Linking Only ($u\chi = 0.245$)

	$uw(x,\chi)$				
x	$n = 5$	$n = 10$	$n = 20$	$n = 50$	$n = 100$
0.5	0.1821	0.1827	0.1929	0.1831	0.1831
1.0	1.2191	1.2347	1.2422	1.2466	1.2480
1.5	0.1245	0.1207	0.1189	0.1179	0.1176
2.0	0.2897	0.2712	0.2627	0.2579	0.2563
2.5	0.0946	0.0887	0.0860	0.0844	0.0839
3.0	0.1097	0.1014	0.0977	0.0956	0.0947
3.5	0.0576	0.0543	0.0527	0.0517	0.0514
4.0	0.0490	0.0475	0.0465	0.0459	0.0459
4.5	0.0317	0.0318	0.0315	0.0312	0.0311
5.0	0.0233	0.0251	0.0254	0.0254	0.0254

[a] The initial distribution used in these calculations was equivalent to that resulting from scission ($u\tau = 0.245$) of a Schulz-Zimm system with $u = 1894$, $\sigma = 33$.

Comparison of the molecular size distribution calculated from eq 15 with the result from eq 14 shows excellent agreement for $x < 2.5$, i.e., for molecular sizes up to 2.5 times that of the initial number-average polymer molecule (Figure 1). The poor agreement in the higher molecular size region is due to neglect of terms higher than the first power in χ and can be corrected[13] by including further terms in the series expansion. The complete analytical solution of eq 13 for an initial Schulz–Zimm distribution should therefore be written

$$uw(x,\chi) = \left\{\sum_{h=1}^{\infty} \frac{2^{(h-1)}\sigma^{h(h+1)}}{h!(h\sigma + h - 1)!}(u\chi)^{(h-1)}x^{(h\sigma+2h-2)}\right\} \times \exp\{-x(\sigma + 2u\chi)\} \quad (16)$$

The results of calculations using eq 16 are also included in Figure 1 for comparison; clearly the discrepancy between theory and calculation via eq 15 can be easily overcome.

Evaluation of the dose dependence of $\bar{M}_w(D)$ and $\bar{M}_z(D)$ for systems undergoing cross-linking only cannot be achieved by placing $\tau = 0$ in eq 10 and 11, which involve division by τ. Expressions applicable to systems with cross-linking in the absence of scission have therefore been derived. Saito[6,10] has provided a general method for solving eq 13 by noting that any required moment of the molecular size distribution is given by the expression

$$M_q(\chi)/M_1 = P_q(\chi) = f_q(\chi)/f_{(q-1)}(\chi) \quad (17a)$$

where

$$f_n(\chi) = \int_0^{\infty} p^{(n-1)}w(p,\chi)\,dp \quad (17b)$$

$$n = 0, 1, 2, \ldots$$

Nonzero values of the subscript j denote the appropriate derivatives with respect to χ. By this means he has shown[6,10] that

$$P_w(D) \equiv P_2(D) = f_2(\chi)f_1(\chi) \quad (18a)$$

where

$$f_2(\chi) = f_2(0)/[1 - 2\chi f_2(0)] \qquad f_1(\chi) = 1 \quad (18b)$$

$$f_2(0) = \int_0^{\infty} pw(p,0)\,dp \quad (18c)$$

Substitution of eq 3 for an initial Schulz–Zimm distribution into eq 18 yields $f_2(0) = (\sigma + 1)u/\sigma$, whereupon

$$\bar{M}_w(D) = M_1u(\sigma + 1)/[\sigma - 2u\chi(\sigma + 1)] \quad (19)$$

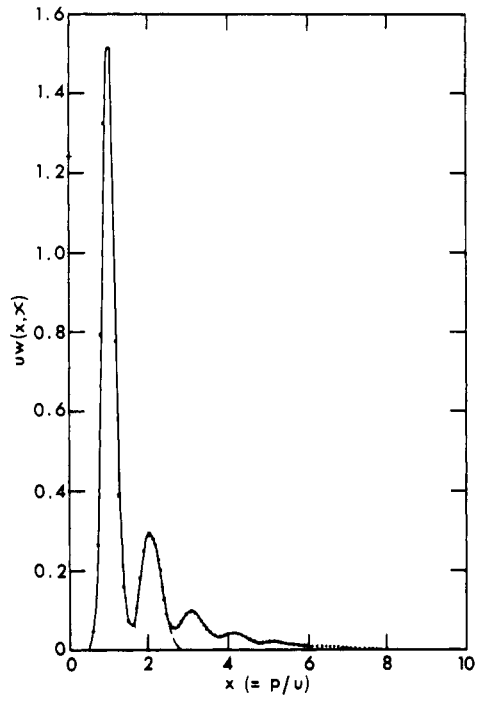

Figure 1. Comparison of weight distributions calculated from eq 14 (—), eq 15 (- - -), and eq 16 (···) for a Schulz–Zimm system undergoing cross-linking only. Parameters used were as follows: $\sigma = 33$, $u\chi = 0.204$.

The corresponding relationships for the z-average degree of polymerization are

$$P_z(D) \equiv P_3(D) = f_3(\chi)/f_2(\chi) \quad (20a)$$

$$f_3(\chi) = f_3(0)/[1 - 2\chi f_2(0)]^3 \quad (20b)$$

$$f_3(0) = \int_0^{\infty} p^2w(p,0)\,dp \quad (20c)$$

On substituting eq 3 (the initial Schulz–Zimm distribution) into eq 20c and integrating we obtain $f_3(0) = u^2(\sigma + 1)\cdot(\sigma + 2)/\sigma^2$ and hence

$$\bar{M}_z(D) = M_1u\sigma(\sigma + 2)/[\sigma - 2u\chi(\sigma + 1)]^2 \quad (21)$$

C. Simultaneous Scission and Cross-Linking. When chain scission and cross-linking occur simultaneously during the irradiation of a polymer the resultant molecular size distribution has previously been calculated by a two-stage procedure, assuming that all of the scission takes place first to produce a new distribution which is then subjected to the total amount of cross-linking. The assumptions given in the previous sections are assumed to apply to the appropriate stage. However, if $u\tau$ and $u\chi$ are sufficiently large this simple procedure could lead to serious errors in the final molecular size distribution. No analytical solution has yet been obtained for the simultaneous scission and cross-linking of an arbitrary initial molecular size distribution. Kimura[11,14] has derived an expression for an initial Schulz–Zimm distribution, but this is incorrect because of the above-mentioned error in his solution for cross-linking. By resort to a method similar to that of Kimura[11,14] the following analytical solution is obtained

$$w(x,\tau,\chi) = ux\left\{\sum_{h=1}^{\infty} \frac{a_h(\chi)}{(h-1)!}(ux)^{(h-1)} \exp[-x(u\tau + 2u\chi + \sigma)]\right\} \quad (22a)$$

where

$$\frac{da_h(\chi)}{d\chi} = 0; \qquad h = 1,2,3$$

$$\frac{da_h(\chi)}{d\chi} = \sum_{i=1}^{h-3} i(h-2-i)a_i(\chi)a_{(h-2-i)}(\chi); \qquad h \geq 4 \qquad (22b)$$

and

$$a_h(0) = \frac{\sigma^{(h-2)}}{u^{(h+1)}}[2u\tau\sigma + (\sigma - h + 1)u^2\tau^2];$$
$$h = 1, 2, \ldots, (\sigma - 1)$$
$$a_\sigma(0) = \frac{\sigma^{(\sigma-2)}}{u^{(\sigma+1)}}[u^2 + 2u\tau\sigma + u^2\tau^2]; \qquad h = \sigma \qquad (22c)$$
$$a_h(0) = 0; \qquad h > \sigma$$

Unfortunately, this solution for simultaneous scission and cross-linking of an initial Schulz–Zimm distribution has not proven useful for computer calculation of resultant molecular size distributions because of the complexity of the $a_h(\chi)$ terms.

We have therefore attempted to improve the calculated distribution for systems undergoing simultaneous scission and cross-linking by considering the dose to comprise a series of small increments and using the two-step procedure to determine the distribution after each dose increment. This calculated distribution was then considered to be the initial distribution for the following dose increment. The final molecular size distribution was obtained by performing the requisite number of cycles of successive scission and cross-linking.

Irrespective of the nature of the initial distribution, an arbitrary form pertains after the first increment or cycle of scission and cross-linking. The equations used for calculating changes in molecular size distributions must therefore be applicable to a distribution presented in tabular form. For this purpose either eq 6 or 7 for scission and eq 14 for cross-linking are entirely satisfactory. We have combined these two steps in a cycle in one computer program and compared the final distributions resulting from calculations made with different numbers of scission–cross-link cycles comprising the total radiation dose; the usual sequential procedure[13] is clearly a single cycle and thus represents the lower limit for the number of cycles.

Comparisons have been made for different breadths of initial Schulz–Zimm molecular size distribution and for different radiation doses, which have been normalized to values of $D/D_g = \chi/\chi_g$, where D_g is the dose for incipient gel formation and χ_g is the corresponding value of χ. Values of D_g for systems undergoing simultaneous scission and cross-linking have been calculated from eq 23, which was derived by Inokuti[15] for an initial Schultz–Zimm distribution; in this expression λ denotes the ratio τ/χ.

$$[4/(\lambda^2 u\chi_g)]\{\lambda u\chi_g - 1 + [1 + \lambda u\chi_g/\sigma]^{-\sigma}\} = 1 \qquad (23)$$

The effect of the number of cycles on the calculated weight-distribution parameter $uw(x,\tau,\chi)$ is shown in Figure 2 for $x = 1$, i.e., for molecules with the initial number-average molar mass. For comparative purposes values of $uw(1,\tau,\chi)$ are expressed relative to that obtained by the conventional single cycle procedure $[uw'(1,\tau,\chi)]$. The number of cycles used to generate the calculated molecular size distribution clearly has a significant effect on $uw(1,\tau,\chi)$, particularly at high radiation doses, but the extent of change per additional cycle becomes progressively less pronounced with increase in the number of cycles from 1 to 12. Selection of 12 as the maximum number of cycles tested should not be construed as an indication of our belief that we have necessarily obtained the required

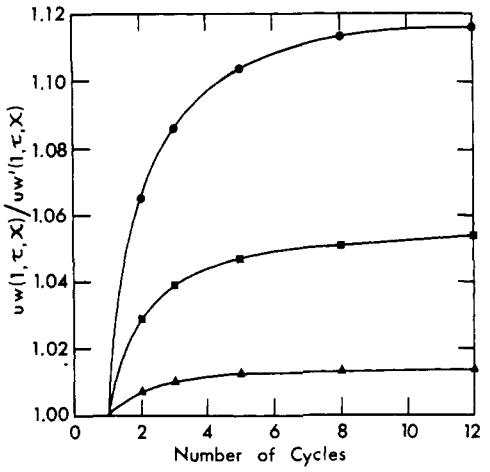

Figure 2. Dependence of the calculated weight distribution parameter $uw(1,\tau,\chi)$ upon the number of cycles of scission and cross-linking used in its computation for an initial Schulz–Zimm distribution with $u = 1894$, $M_1 = 104$, $\sigma = 33$, and $G(S) = G(X) = 0.02$: ▲, $D = 0.3D_g$; ■, $D = 0.6D_g$; ●, $D = 0.9D_g$.

Table III
Comparison of Weight Distributions Calculated by Multicycle (mc) and Single Cycle (sc) Procedures for a Schulz–Zimm System[a]

	$uw(x,\tau,\chi)$					
	$D = 0.3D_g$		$D = 0.6D_g$		$D = 0.9D_g$	
x	mc	sc	mc	sc	mc	sc
0.5	0.147	0.144	0.239	0.229	0.295	0.275
1.0	1.494	1.474	1.005	0.954	0.699	0.625
1.5	0.109	0.107	0.144	0.134	0.161	0.140
2.0	0.256	0.247	0.238	0.237	0.191	0.174
2.5	0.072	0.074	0.097	0.096	0.103	0.093
3.0	0.073	0.077	0.102	0.107	0.095	0.090
5.0	0.013	0.013	0.035	0.040	0.041	0.044

[a] $u = 1894$, $M_1 = 104$, $\sigma = 33$, and $G(S) = G(X) = 0.02$.

distribution (one indistinguishable from that pertaining to a calculation with an infinite number of cycles), but rather as an indication of our limited resources for computational expenditure. Qualitatively similar dependence upon the number of cycles used was observed for all values of x: the value $x = 1$ was singled out for presentation because solute with the molar mass of the initial number-average molecule comprised the major proportion of the distribution (~70%) and hence the large relative error implies a large absolute error as well.

Table III summarizes the effects of the magnitude of the dose (relative to D_g) on the actual distribution calculated by single and multicycle procedures, the result obtained with 12 cycles being used for the latter purpose. As may have been predicted intuitively, the discrepancies are greatest for high doses. Since the multicycle computation represents a better approximation to the actual system its use is recommended in preference to the single cycle procedure adopted earlier[8,13] for evaluating the effects of radiation on molecular size distributions.

Our application of multicycle calculations to changes in molecular size distribution after irradiation is based on the assumption that scission and cross-linking are effectively instantaneous phenomena on the time scale of the irradiation period. This assumption may not be valid for very short irradiation times such as those employed, for example, in pulse radiolysis, where the rates of the two processes need to be considered. Since chain scission would frequently be a unimolecular process and cross-linking a bimolecular reaction involving combination of

Table IV
Variation of Theoretical Average Molar Masses (Calculated from eq 9-11) with the Number of Significant Digits Used in the Calculations for a Schulz-Zimm Distribution[c]

	$G(S) = 0.02$, $G(X) = 0.02$ $D = 0.60$ MGy[a]			$G(S) = 0.001$, $G(X) = 0.05$ $D = 0.30$ MGy[b]		
no. of sig. digits	$\bar{M}_n(D) \times 10^{-5}$	$\bar{M}_w(D) \times 10^{-5}$	$\bar{M}_z(D) \times 10^{-5}$	$\bar{M}_n(D) \times 10^{-5}$	$\bar{M}_w(D) \times 10^{-5}$	$\bar{M}_z(D) \times 10^{-5}$
4	1.97	3.45	6.97	2.81	11.7	81000
5	1.97	3.48	6.94	2.81	10.8	6800
6	1.97	3.48	6.93	2.81	5.73	270
7	1.97	3.48	6.93	2.81	5.49	37.5
8	1.97	3.48	6.93	2.81	5.47	15.6
9	1.97	3.48	6.93	2.81	5.47	15.6
10	1.97	3.48	6.93	2.81	5.47	15.2

[a] $D_g = 1.43$ MGy. [b] $D_g = 0.48$ MGy. [c] $u = 1894$, $M_1 = 104$, and $\sigma = 33$.

Table V
Effect of Eliminating the Contributions of Higher Polymers to Average Molar Masses Calculated from Computed Distributions for a Schulz-Zimm System[c]

		$\bar{M}_n(D) \times 10^{-5}$		$\bar{M}_w(D) \times 10^{-5}$		$\bar{M}_z(D) \times 10^{-5}$	
D/D_g	x_{lim}	calcd[a]	theor[b]	calcd[a]	theor[b]	calcd[a]	theor[b]
0.3	5	1.99	1.97	2.71	2.90	3.72	4.66
	10	2.02		2.89		4.43	
	20	2.02		2.91		4.55	
0.6	5	1.89	1.97	3.14	5.05	4.64	15.4
	10	2.06		4.15		7.69	
	20	2.12		4.93		11.4	
0.9	5	1.67	1.97	3.19	19.2	4.93	241
	10	1.92		4.85		9.26	
	20	2.17		7.69		18.3	

[a] Value obtained by application of eq 8 to the computed distribution. [b] Value obtained from eq 9-11. [c] $u = 1894$, $M_1 = 104$, $\sigma = 33$, and $G(S) = G(X) = 0.02$.

free radicals or other active species, different kinetic parameters may well pertain. Indeed, Lindenau and co-workers[16] have deduced that scission occurs with $t_{1/2} \sim 20$ μs and cross-linking with $t_{1/2} \sim 0.4$ s in poly(methyl vinyl ketone) from experiments involving 2-μs pulses of 15-MeV electrons. Further development of pulse radiolysis methods to give molecular size distributions after irradiation should show small but significant differences between $G(S)$ and $G(X)$ values so determined and those obtained after longer irradiation periods unless single-cycle calculations are used for the former and multicycle calculations for the latter type of irradiation studies.

D. Potential Sources of Error in Evaluation of $G(S)$ and $G(X)$ from Average Molar Masses. An alternative experimental method of assessing the magnitudes of $G(S)$ and $G(X)$ (or $\dot{\tau}$ and $\dot{\chi}$) entails measurement of the dose dependences of $\bar{M}_n$, $\bar{M}_w$, and/or $\bar{M}_z$ and comparisons with the relationships predicted by eq 9-11. Use of these theoretical expressions for determining molar masses after scission and cross-linking must be carried out with great care for systems with low $\mu\tau$ and/or $u\chi$. From Table IV it is clear that serious errors in the predicted average molar masses can result from use of insufficiently high precision in the calculations; double precision specification may be necessary in the computer program.

Whereas such errors in the theoretical values of the molar mass averages may be overcome relatively readily, far more serious potential errors in experimental values are indicated by calculations of molar masses from molecular size distributions. Cross-linking causes the formation of species with molar masses that are multiples of that of the initial number-average molecule and a consequent high molecular size tail on the distribution; indeed, $\bar{M}_w \rightarrow \infty$ as $D \rightarrow D_g$. Consequently, the apparent values of $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ calculated from the final molecular size distribution by means of eq 8 depend on the maximum value of x used in the calculation. From the theoretical viewpoint this observation is trivial since eq 14 requires consideration of *all* finite values of x. However, calculations with a fixed upper limit (e.g., $x \leq 5$) serve a useful practical function because of experimental difficulties encountered in quantitative studies of average molar masses; three common experimental methods are considered for which such calculations may be relevant.

In sedimentation equilibrium the accuracy with which $\bar{M}_w$ and $\bar{M}_z$ can be determined decreases markedly as species with $x > 5$ contribute significantly to the pattern because of the difficulties encountered in defining the concentration gradient at the bottom of the liquid column. Although the required extrapolations may be improved by decreasing the speed used in the equilibrium sedimentation experiment, an optimal centrifugal speed is not readily selectable for systems exhibiting an extremely wide molecular size distribution. Measurements of $\bar{M}_w$ by light scattering for such systems are particularly prone to error since it is possible that some of the material corresponding to the high molecular size tail is lost during clarification procedures (centrifugation and/or ultrafiltration). GPC measurements are likely to be even more misleading due (a) to failure of the technique to resolve macromolecules larger than the exclusion limit of the column material and (b) to changes in relative hydrodynamic volume caused by branching.

Because of these deficiencies in experimental techniques for quantitative measurement of molar mass averages of systems exhibiting a high molecular size tail, eq 9-11 have been used in conjunction with molecular size distributions calculated by the multicycle procedure in order to evaluate the consequences of terminating the summations in eq 8 and 14 at various values of x. Table V illustrates the dependences of the apparent values of $\bar{M}_n(D)$, $\bar{M}_w(D)$, and $\bar{M}_z(D)$ on the maximum values of x used in the calcula-

tions; in considering these data it should be recalled that a value of 5–10 represents a reasonable likely maximum for x in experimental measurements. Clearly, relatively low radiation doses (D/D_g) need to be employed for reasonably accurate estimates to be made of molar mass averages and hence of radiation chemical yields. Measurements of molar size averages in the pregel region should therefore be confined to the region $D < 0.4D_g$, a restriction that necessitates high accuracy and/or the collection of adequate numbers of experimental measurements. If the data are being obtained by equilibrium sedimentation, particular care is required in the extrapolations used for determination of true average molar masses from measured values of $\bar{M}_w(D)^{app}$ and $\bar{M}_z(D)^{app}$, since their dependences on rotor speed become progressively more pronounced with increasing radiation dose D due to the greater polydispersity of the sample.[17]

Conclusions

1. Numerical solution of Saito's integro-differential equation for chain scission[10] by a "marching" method has been shown to give correct molecular size distributions.

2. Analytical expressions have been developed for the dose dependence of $\bar{M}_w$ and $\bar{M}_z$ for an initial Schulz–Zimm system undergoing cross-linking only.

3. An analytical solution for simultaneous scission and cross-linking of an initial Schulz–Zimm molecular size distribution is presented, but complexity of some of the terms seems likely to restrict its use.

4. Combination of "marching" solutions for scission and cross-linking has permitted evaluation of weight distributions by a multicycle procedure in which the total dose is considered to comprise a series of dose increments. This method of calculating distributions is shown to be superior to the single step procedure used previously.

5. Measurements of solution properties of irradiated polymers should be restricted to doses such that $D < 0.4D_g$ if values of $\bar{M}_w(D)$ and $\bar{M}_z(D)$ are to be compared with theoretical values calculated from analytical expressions.

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The Elastic Free Energy of Dilation of a Network

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ABSTRACT: The elastic contribution $(\mu_1 - \mu_1^0)_{el}$ to the chemical potential of the diluent in a swollen network is treated according to recent theory which takes account of constraints on junctions in real networks. The quantity $\lambda(\mu_1 - \mu_1^0)_{el}$, where λ is the linear expansion ratio, exhibits a maximum with increase in λ in qualitative agreement with experimental measurements, but contrary to previous theories. The premise that the free energy of a swollen network is additive in the contributions from mixing and elastic deformation is supported by the comparison of experiment with theory.

Recently Yen and Eichinger[1] reported experiments comparing the small difference between the activity of the diluent in a swollen network and in a solution of the linear polymer at the same concentration. They investigated poly(dimethylsiloxane) (PDMS) swollen with benzene and poly(styrene-*co*-butadiene) using benzene and *n*-heptane, respectively, as diluents in separate series of experiments. Similar experiments were carried out a number of years ago by Gee, Herbert, and Roberts[2] using natural rubber and benzene. Yen and Eichinger confirmed the earlier work of Gee et al. showing the contribution of the network to the chemical potential of the diluent to be at variance with conventional theories of rubber elasticity. Specifically, the product of this elastic contribution $(\mu_1 - \mu_1^0)_{el}$ to the chemical potential of the diluent and the linear dilation ratio λ passes through a maximum with concentration, according to the carefully executed investigations cited. Network theories examined by these authors predict either constancy of this product or increases that are essentially monotonic with concentration.

Yen and Eichinger[1] concurred with the opinion of Gee, Herbert, and Roberts[2] that the results cast doubt on a major premise of the theory of swelling of networks, namely the hypothesis that the elastic and mixing free energies are separable. Expression of the free energy of such a system as the sum of two terms, one arising from the intermolecular forces of short-range operating between neighboring species (chain units and solvent molecules, if the latter are present) and the other from deformation of the network, underlies theories of rubber elasticity as well as of swelling.

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