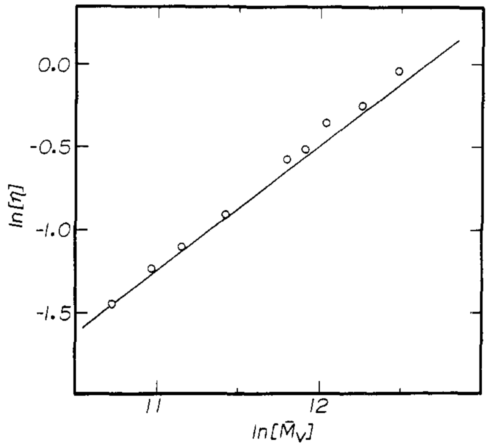

Figure 8. Double logarithmic plot of $[\eta]$ vs. $\bar{M}_v$ for PS-MVK-2: (●) experimental points adjusted to $\bar{M}_v$ basis; (—) line based on K, a values as determined for PS-MVK-1.

of vinyl ketone units in the polystyrene chain does not affect the Mark–Houwink parameters significantly, and leads to speculation that the procedure described has some general validity. Furthermore it is worth pointing out that it is not essential to use a mercury lamp to induce photodegradation. As has been well established in previous studies from these laboratories, nearly any polymer containing vinyl ketone groups will undergo random scission in solution when exposed to near-uv radiation.

The degradation could easily be carried out by simply exposing an oxygen-free solution to normal solar radiation in a Pyrex flask. Other chemical or physical processes leading to random scission of polymer chains could also be used, provided that they do not lead to extensive chemical changes in the system under study.

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References and Notes

(1) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 313.
(2) A. R. Schultz, *J. Chem. Phys.*, **29**, 200 (1958).
(3) R. W. Kilb, *J. Phys. Chem.*, **63**, 1838 (1959).
(4) D. I. C. Kells and J. E. Guillet, *J. Polym. Sci., Part A-2*, **7**, 1895 (1969).
(5) D. I. C. Kells, M. Koike, and J. E. Guillet, *J. Polym. Sci., Part A-1*, **6**, 595 (1968).
(6) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and W. J. Wenisch, *J. Am. Chem. Soc.*, **70**, 1527 (1948).
(7) J. E. Guillet, B. Houvenaghel-Defoort, T. Kilp, N. J. Turro, H.-C. Steinmetzer, and A. Schuster, *Macromolecules*, **7**, 942 (1974).
(8) O. F. Solomon and I. Z. Ciuta, *Bull. Inst. Polit. Gh. Gh. Dej. Buc.*, **30**, 3 (1968).
(9) W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.*, **9**, 503 (1952).
(10) J. R. Schaefgen and P. J. Flory, *J. Am. Chem. Soc.*, **70**, 2709 (1948).
(11) T. Oyama, K. Kawahara, and M. Ueda, *Nippon Kagaku Zasshi*, **70**, 727 (1958).

Calculation of Accuracy and Correction Factors in the Viscometric Determination of Chain Scission in Polymers

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ABSTRACT: A computer modeling study has been made of the degradation of polymer systems whose molecular weight distributions are given by either the Schulz distribution or by sums of Flory distributions. The calculations considered degradation by random scission only. The purpose of the study was to evaluate the applicability of equations for estimating the quantum yield of chain scission from changes in the weight average or viscosity average molecular weights. It was found that the error involved in using these equations could be greater than 20% if the initial dispersity, γ_0, did not fall in the range $1.5 < \gamma_0 < 2.5$ but could be estimated if the initial molecular weight distribution was known. Procedures are described for correcting viscometric data to provide accurate quantum yields and scission rates when the initial molecular weight distribution has been determined.

Viscometry is a convenient method for studying the random photodegradation of polymers in solution. The parameter of interest in such a study is the quantum yield of chain scission, ϕ_s, defined by

$$\phi_s = S_n/I_{abs}$$

$$S_n = \frac{W}{M_n(0)}\left(\frac{M_n(0)}{M_n(\tau)} - 1\right) \qquad (1)$$

where S_n is the number of moles of chain breaks, I_{abs} is the number of moles of photons absorbed, W is the total weight of polymer in solution, $M_n(0)$ is the initial number average molecular weight, and $M_n(\tau)$ is the number average molecular weight after an amount of irradiation such that the probability of rupture at a given monomer unit is equal to τ. Note that to determine ϕ_s one needs number average molecular weights as a function of irradiation, whereas viscosity measurements yield the viscosity average molecular weight, M_v, which lies between M_n and the weight average molecular weight, M_w, and is usually closer to the latter. Amerik and Guillet[1] degraded copolymers of methyl methacrylate and methyl vinyl ketone, as well as calculating molecular weight averages for the degradation of sums of Flory distributions. They concluded that, within experimental error, one could approximate S_n by S_w, where

$$S_w = \frac{2W}{M_w(0)}\left(\frac{M_w(0)}{M_w(\tau)} - 1\right) \qquad (2)$$

In order to apply this equation, one must first assume that the molecular weights determined from viscosity data are approximately equal to the weight average molecular weights.

The model degradation calculations of Amerik and Guillet were done for distributions whose initial dispersities, γ_0,

$$\gamma_0 = M_w(0)/M_n(0) \qquad (3)$$

were all greater than 2.0. Their values of S_n and S_w were all calculated at a value of ξ, the number of chain scissions per original average molecule, equal to 1.0. If we define U as the initial number average degree of polymerization, then $\xi = U\tau$, and also[2]

$$\xi = [M_n(0)/M_n(\tau)] - 1 \tag{4}$$

The development of automatic viscometry[3] has made possible the accurate and precise determination of very small changes in viscosity. It is thus possible to examine polymer degradation at values of ξ smaller than the value of 1.0 treated by Amerik and Guillet. It is therefore of interest to calculate how well S_w approximates S_n for small values of ξ. Initial dispersities both greater and less than 2.0 should be examined. In addition, one would prefer to have an equation, similar to eq 2, but which is a function of M_v rather than of M_w. Finally, one should determine the effect of the initial shape of the distribution on the approximation.

The theory of polymer degradation has been studied for many years and has been reviewed elsewhere.[2,4,5] The effect of random scission on polymer molecular weights and on polymer viscosity has also been examined.[5-10] The work of Cameron et al.[10] is especially useful because it gives $M_v(\tau)/M_n(\tau)$ ratios for both "coupling" and monodisperse distributions, and these values can be used to check the accuracy of the calculations to be described in this work.

The computations in this paper are based on the random scission equations developed by Saito[11] and on Kotliar's[6,7] sum of distributions approach. The central assumptions that are made are: (i) that the probability of main chain scission is independent of the position in the polymer chain; (ii) that the polymers are linear; and (iii) that the degree of polymerization is continuous, from zero to infinity, so that summations can be treated as integrals.[4]

For a polymer which is undergoing degradation by random scission, Saito has derived the equation[11]

$$n(P,\tau) = \left\{ n(P,0) + 2\tau \int_P^\infty n(l,\tau)\,\mathrm{d}l + \tau^2 \int_P^\infty \mathrm{d}l \int_l^\infty n(m,0)\,\mathrm{d}m \right\} e^{-P\tau} \tag{5}$$

where $n(P,0)$ is the number of polymer molecules having degree of polymerization P after zero irradiation and τ is, once again, the probability of scission per monomer unit. τ depends, of course, on the amount of radiation absorbed and on the quantum yield for chain scission. $n(P,\tau)$ is the number of polymer molecules having degree of polymerization P after irradiation sufficient to give a probability of monomer rupture equal to τ. The initial polymer molecular weight distribution, $n(P,0)$, is normalized so that

$$\int_0^\infty Pn(P,0)\,\mathrm{d}P = N \tag{6}$$

where N is the total number of monomer units in the system. Using eq 6 one can write the various molecular weight averages as

$$M_n(\tau) = m_0 N \Big/ \int_0^\infty n(P,\tau)\,\mathrm{d}P \tag{7}$$

$$M_w(\tau) = (m_0/N) \int_0^\infty P^2 n(P,\tau)\,\mathrm{d}P \tag{8}$$

$$M_v(\tau) = m_0 \left[(1/N) \int_0^\infty P^{1+a} n(P,\tau)\,\mathrm{d}P \right]^{1/a} \tag{9}$$

where m_0 is the monomer molecular weight and "a" is the Mark Houwink viscosity law exponent, which usually has a value between 0.5 and 1.0.

The molecular weight averages can thus be calculated, as a function of τ, for different initial distributions. A tabulation of commonly used distributions is given by Scott.[5] One such distribution is the Schulz distribution, defined by

$$n(P,0) = \left(\frac{b+1}{U}\right)^{b+2} \frac{N}{\Gamma(b+2)} P^b e^{-(P/U)(b+1)} \tag{10}$$

where $\Gamma(x)$ is the γ function and b is a parameter which determines the initial dispersity, γ_0. For the Schulz distribution, we have

$$\gamma_0 = \frac{b+2}{b+1},\ M_n^S(0) = m_0\mathrm{U},\ M_w^S(0) = m_0 U \left(\frac{b+2}{b+1}\right)$$
$$M_v^S(0) = \frac{m_0 U}{b+1}\left[\frac{\Gamma(b+a+2)}{\Gamma(b+2)}\right]^{1/a} \tag{11}$$

The superscript S refers to the Schulz distribution. The Schulz distribution was chosen as the model distribution on which to do degradation calculations, since it is less effected by high and low molecular weight cut-off values than are logarithmic-normal distributions.[12,13]

Applying Saito's degradation equation to the Schulz distribution, Inokuti[14] has obtained

$$M_w^S(\tau) = \frac{2m_0}{\tau}\left\{1 - \frac{1}{U\tau}\left[1 - \left(1 + \frac{U\tau}{b+1}\right)^{-(b+1)}\right]\right\} \tag{12}$$

One also has that

$$M_n^S(\tau) = M_n^S(0)/(1 + U\tau) \tag{13}$$

and one can derive the equation

$$\begin{aligned} M_v^S(\tau) = {} & M_v^S(0) \\ & \times \left\{ \left(\frac{1}{1 + U\tau/(b+1)}\right)^{b+a+2} \left[1 + \frac{2z(\beta-1)}{(\alpha-1)} F(1,\beta;\alpha;z) \right.\right. \\ & + \frac{\beta z^2(\beta-1)}{(\alpha-1)} F(1,\beta+1;\alpha;z) \\ & \left.\left. - \frac{\beta z^2(\beta-1)}{\alpha} F(1,\beta+1;\alpha+1;z) \right] \right\}^{1/a} \end{aligned} \tag{14}$$

where $F(1,\beta;\alpha;z)$ is the hypergeometric function, and

$$\alpha = a + 3$$

$$\beta = b + a + 3$$

$$z = \frac{U\tau}{U\tau + b + 1}$$

$$F(1,\beta;\alpha;z) = 1 + \frac{\beta}{\alpha^z} + \frac{\beta(\beta+1)}{\alpha(\alpha+1)} z^2 + \frac{\beta(\beta+1)(\beta+2)}{\alpha(\alpha+1)(\alpha+2)} z^3 + \ldots \tag{15}$$

The Schulz distribution is broad for negative b values and becomes monodisperse as b becomes large positively. When $b = 0$ one obtains the Flory distribution[15] (sometimes called the most probable, or Poisson-like[11] distribution) which has a dispersity of 2.0 and is defined by

$$n(P,0) = \frac{N}{U^2} e^{-P/U}$$

$$\begin{aligned} M_n^F(0) &= m_0 U & M_n^F(\tau) &= \frac{M_n^F(0)}{(1 + U\tau)} \\ M_w^F(0) &= 2m_0 U & M_w^F(\tau) &= \frac{M_w^F(0)}{1 + U\tau} \\ M_v^F(0) &= m_0 U[\Gamma(a+2)]^{1/a} & M_v^F(\tau) &= \frac{M_v^F(0)}{1 + U\tau} \end{aligned} \tag{16}$$

The superscript F refers to the Flory distribution. It is now well established that polymer distributions approach the Flory distribution as they undergo random scission.[2,5]

Kotliar[7] has pointed out that, rather than use the Schulz distribution, in many cases it may be preferable to use composite distributions made up of sums of Flory distributions. When summing k distributions in order to obtain the molecular weights of the total distribution, calculations are done on the individual distributions first, and these distributions are combined according to

$$\begin{aligned} N_{\mathrm{total}} &= \sum_{i=1}^{k} N_i \\ M_{\mathrm{n_{total}}}{}^{-1} &= \sum_{i=1}^{k} \frac{N_i}{N_{\mathrm{total}} M_{\mathrm{n}_i}} \\ &= \frac{N_1}{N_{\mathrm{total}} m_0 U_1 \tau} + \frac{N_2}{N_{\mathrm{total}} m_0 U_2 \tau} + \ldots \\ n_{\mathrm{total}}(P,\tau) &= \sum_{i=1}^{k} n_i(P,\tau) \\ M_{\mathrm{w_{total}}} &= \sum_{i=1}^{k} \frac{N_i}{N_{\mathrm{total}}} M_{\mathrm{w}_i} \\ M_{\mathrm{v_{total}}} &= \left[\sum_{i=1}^{k} \frac{N_i}{N_{\mathrm{total}}} M_{\mathrm{v}_i}{}^{a} \right]^{1/a} \end{aligned} \tag{17}$$

Kotliar[6,7] has examined the degradation of sums of two Flory distributions for the case where $N_1 = N_2$ and gives equations for calculating the ratio of molecular weights to obtain any desired γ_0. In the same manner as done by Kotliar, one can derive equations for obtaining these ratios for other cases. For example, for a sum of three Flory distributions with

$$\begin{aligned} N_1 &= N_2 = N_3 \\ M_{\mathrm{n}_2}(0) &= \theta M_{\mathrm{n}_1}(0) \qquad \gamma_0 = \frac{M_{\mathrm{w_{total}}}(0)}{M_{\mathrm{n_{total}}}(0)} \\ M_{\mathrm{n}_3}(0) &= 1.5\theta M_{\mathrm{n}_1}(0) \end{aligned} \tag{18}$$

we find that

$$\theta = \frac{(6.75\gamma_0 - 7.75) \pm \sqrt{(7.75 - 6.75\gamma_0)^2 - 37.5}}{7.75} \tag{19}$$

Since θ is the solution of a quadratic equation, there are two distributions which satisfy the conditions of eq 18.

In our studies we wished to degrade various Schulz distributions, and sums of Flory distributions, and to examine the effect on S_{n}, S_{w}, and the molecular weight averages. It is convenient at this point to define

$$\begin{aligned} S_{\mathrm{v}} &= \frac{\delta^{\mathrm{F}} W}{M_{\mathrm{v}}(0)} \left(\frac{M_{\mathrm{v}}(0)}{M_{\mathrm{v}}(\tau)} - 1 \right) \\ \delta^{\mathrm{F}} &= \frac{M_{\mathrm{v}}{}^{\mathrm{F}}(0)}{M_{\mathrm{n}}{}^{\mathrm{F}}(0)} = [\Gamma(a+2)]^{1/a} \\ R_{\mathrm{v}} &= \frac{S_{\mathrm{v}}}{S_{\mathrm{n}}} = \frac{\delta^{\mathrm{F}}}{\delta_0 U \tau} \left(\frac{M_{\mathrm{v}}(0)}{M_{\mathrm{v}}(\tau)} - 1 \right) \qquad \delta_0 = \frac{M_{\mathrm{v}}(0)}{M_{\mathrm{n}}(0)} \\ R_{\mathrm{w}} &= \frac{S_{\mathrm{w}}}{S_{\mathrm{n}}} = \frac{2}{\gamma_0 U \tau} \left(\frac{M_{\mathrm{w}}(0)}{M_{\mathrm{w}}(\tau)} - 1 \right) \end{aligned} \tag{20}$$

The superscript F indicates that the symbol refers to the Flory distribution. The factor of two in the equation for R_{w} occurs because two is the dispersity of a Flory distribution. R_{v} and R_{w} give the errors which occur due to approximating S_{n} by S_{v} or by S_{w}, respectively. R_{v} and R_{w} both tend toward unity as the value of the scissions per molecule, ξ, becomes large. The expressions for R_{v} and R_{w} in the limit as ξ tends toward zero will vary depending on the distribution used. For example, for the Schulz distribution

$$\begin{aligned} \lim_{\xi \to 0} R_{\mathrm{w}}{}^{\mathrm{S}} &= \frac{2}{3} \left(\frac{b+3}{b+2} \right) \\ \lim_{\xi \to 0} R_{\mathrm{v}}{}^{\mathrm{S}} &= \frac{\delta^{\mathrm{F}}}{\delta_0} \frac{(b+a+2)}{(b+1)(a+2)} \end{aligned} \tag{21}$$

When discussing the shapes of molecular weight distributions, it is convenient to examine plots of weight fractions, $W(P,\tau)$, as well as simulated gel permeation chromatograph (GPC) traces. The weight fraction is given by

$$W(P,\tau) = (P/N) n(P,\tau) \tag{22}$$

and its integral over all P is equal to unity. In an idealized GPC trace, the elution volume, V, is proportional to the logarithm of the molecular weight, $m_0 P$, for all values P. The integral of the GPC trace height with respect to V is proportional to the injected weight, W, of polymer. But since $\mathrm{d}V \propto (\mathrm{d}P/P)$ this integral can be written

$$\int_0^{\infty} G(P) \, (\mathrm{d}P/P) \propto W \tag{23}$$

where $G(P)$ is the height of the GPC trace at some value of P. Given our normalization condition, eq 6, we see that eq 23 is only valid if

$$G(P) \propto P^2 n(P,\tau) \tag{24}$$

Weight fraction plots are commonly used, and need no explanation. Simulated GPC traces are valuable because they relate a molecular weight distribution to what is observed experimentally. In addition, GPC traces accentuate the high molecular weight portions of distributions and thus complement weight fraction plots. The difference between $W(P,\tau)$ and $G(P)$ can be clearly seen in Figure 1 which shows these quantities for a 1:1 mixture by weight of two Schulz distributions, each distribution having $b = 10$ and $\gamma_0 = 1.09$. Note that in the GPC trace one can more clearly see behavior at high molecular weight. Note also that while the maxima in $W(P,\tau)$ occur at $P = 10^3$ and $P = 10^4$, the maxima in $G(P)$ occur at $P = 1.09 \times 10^3$ and 1.09×10^4. In general, for a single undegraded Schulz distribution the maximum in $W(P,\tau)$ occurs at $P = U$ while the maximum in $G(P)$ occurs at $P = \gamma_0 U$.

As a check on the accuracy of the computer programming, the calculations were done using three different computer programs. The first program calculated and combined molecular weights according to eq 12, 13, 14, and 17. This program was valid for all values of b greater than -1. The second program was based on a set of equations which were derived, using the Schulz distribution and eq 5, in such a way as to be valid only for $b = 0, 1, 2, \ldots$. These equations are

$$\begin{aligned} M_{\mathrm{n}}{}^{\mathrm{S}}(\tau) &= M_{\mathrm{n}}{}^{\mathrm{S}}(0)/(1 + U\tau) \\ M_{\mathrm{w}}{}^{\mathrm{S}}(\tau) &= \frac{2M_{\mathrm{w}}{}^{\mathrm{S}}(0)}{(b+2)(b+1)} (1+X)^{-(b+1)} \times \sum_{n=0}^{b} (1+n)(1+X)^n \\ M_{\mathrm{v}}{}^{\mathrm{S}}(\tau) &= M_{\mathrm{v}}{}^{\mathrm{S}}(0) \left\{ \frac{1}{(1+X)^{b+a+2}} \left[1 + b!X \times \sum_{n=0}^{b} \frac{\Gamma(b+a+2-n)}{\Gamma(b+a+2)} \frac{(1+X)^n}{(b-n)!} (2 + (n+1)X) \right] \right\}^{1/a} \\ X &= U\tau/b + 1 \end{aligned} \tag{25}$$

The program then used eq 17 and 25 to calculate and combine molecular weights.

The third program calculated $n(P,\tau)$ as a function of P. If a sum of distributions was being degraded, the various $n_i(P,\tau)$ were calculated and then summed. The resulting distribution was numerically integrated according to eq 7–9 in order to obtain the molecular weights. The program then calculated and plotted weight fractions and simulated GPC traces, $G(P)$. For this third program, the distributions were selected such that U was greater than 10^3 in order to avoid any significant number of molecules at $P = 0$.[16] As long as this precaution was

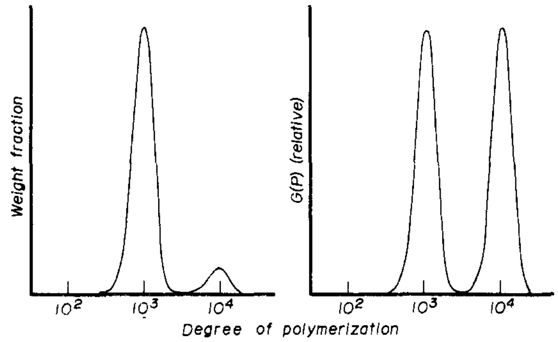

Figure 1. Sum of two undergraded Schulz distributions, each with $b = 10$ and $\gamma_0 = 1.09$: $U_1 = 10^3$, $U_2 = 10^4$, $N_1 = N_2$, $\gamma_{0_{\text{total}}} = 3.30$.

Table I
Composition of Distributions which are Sums of Flory Distributions

Distribution No.	Subdistributions			Total distribution	
	No.	Proportions	U_i	γ_0	U_{total}
D1	2	$N_1 = N_2$	$U_2 = 2.6180U_1$	2.50	$1.4472U_1$
D2	2	$N_1 = N_2$	$U_2 = 5.8284U_1$	4.00	$1.7071U_1$
D3	3	$N_1 = N_2 = N_3$	$U_2 = 2.1187U_1$ $U_3 = 1.5U_2$	2.50	$1.6791U_1$
D4	3	$N_1 = N_2 = N_3$	$U_2 = 5.0U_1$ $U_3 = 1.5U_2$	4.00	$2.2500U_1$
D5	3	$N_1 = N_2 = N_3$	$U_2 = 0.31466U_1$ $U_3 = 1.5U_2$	2.50	$0.4764U_1$
D6	3	$N_1 = N_2 = N_3$	$U_2 = 0.13333U_1$ $U_3 = 1.5U_2$	4.00	$0.2222U_1$
D7	3	$N_1 = N_2 = N_3$	$U_2 = 1.6052U_1$ $U_3 = 2U_2$	2.50	$1.5508U_1$
D8	3	$N_1 = N_2 = N_3$	$U_2 = 4.0430U_1$ $U_3 = 2U_2$	4.00	$2.1882U_1$

taken, the results of this third program were, as expected, independent of the initial molecular weight.

The results of all three programs were found to be the same when the programs were run at integer values of b. The programs gave the same results as did hand calculations using Kotliar's[6] equations for the degradation of 1:1 sums of Flory distributions. The degradation of the Schulz distribution with $b = 1$ (the "coupling distribution") gave the same values for $M_v(\tau)/M_n(\tau)$ as were obtained by Cameron et al.[10] Degradation of Schulz distributions gave the same results for $M_w(\tau)/M_w(0)$ as listed by Inokuti.[14] These tests were taken as evidence for the validity of the derived equations and the correctness of the computer programming.

Results

A variety of distributions were subjected to random scission, both individual Schulz distributions and sums of Flory distributions. For the sake of simplicity, m_0 was taken as 1.0 in all cases so that $M_n(0) = U$. Table I lists the components of some composite distributions. Table II lists computed R_w and R_v values for degraded distributions at several values of ξ, the number of scissions per original number average polymer molecule. It should again be noted that R_w and R_v are the errors in approximating S_n by S_w or by S_v. Thus if $R_w = 1.20$, this corresponds to 20% error. The values of R_w and R_v at $\xi = 0$ were hand calculated using formulas similar to eq 21. For example, for the 1:1:1 mixture of three Flory distributions defined by eq 18 and 10

$$\lim_{\xi \to 0} R_w = \left(\frac{2}{\gamma_0}\right)\left(\frac{1.5\theta + 2.5}{4.5\theta}\right)\left(\frac{1 + 3.25\theta^2}{1 + 2.5\theta}\right) \tag{26}$$

Table II
Degradation of Distributions which are Sums of Flory Distributions

Distribution No.	a	ξ	γ	δ	R_w	R_v
D1	0.50	0	2.500	2.092	1.200	1.173
		0.06	2.433	2.049	1.189	1.157
		0.2	2.323	1.978	1.167	1.137
		11.0	2.105	1.836	1.100	1.080
D1	0.75	0	2.500	2.294	1.200	1.186
		0.06	2.433	2.239	1.189	1.175
		0.2	2.323	2.149	1.167	1.153
		1.0	2.105	1.971	1.100	1.091
D2	0.75	0	4.000	3.499	1.500	1.518
		0.06	3.604	3.183	1.472	1.483
		0.2	3.064	2.750	1.417	1.419
		1.0	2.286	2.119	1.250	1.240
D3	0.75	0	2.500	2.299	1.180	1.168
		0.06	2.436	2.246	1.169	1.158
		0.2	2.330	2.158	1.150	1.139
		1.0	2.114	1.979	1.092	1.085
D4	0.75	0	4.000	3.557	1.354	1.372
		0.06	3.654	3.270	1.335	1.350
		0.2	3.157	2.856	1.301	1.311
		1.0	2.355	2.182	1.198	1.198
D5	0.75	0	2.500	2.288	1.242	1.217
		0.06	2.427	2.230	1.225	1.201
		0.2	2.311	2.137	1.193	1.172
		1.0	2.097	1.964	1.108	1.095
D6	0.75	0	4.000	3.424	1.785	1.775
		0.06	3.517	3.064	1.714	1.695
		0.2	2.934	2.621	1.591	1.562
		1.0	2.222	2.065	1.300	1.275
D7	0.75	0	2.500	2.289	1.231	1.209
		0.06	2.429	2.232	1.215	1.194
		0.2	2.314	2.141	1.185	1.166
		1.0	2.100	1.966	1.105	1.094
D8	0.75	0	4.000	3.532	1.440	1.447
		0.06	3.627	3.231	1.408	1.412
		0.2	3.114	2.811	1.353	1.354
		1.0	2.333	2.162	1.215	1.210

Table III lists computed R_w and R_v values for the degradation of individual Schulz distributions, with the $\xi = 0$ values being hand calculated using eq 21.

Amerik and Guillet[1] estimated how well S_w approximated S_n by doing calculations for 1:1 mixtures of Flory distributions degraded to an ξ value of 1.0. They calculated R_w values for a number of different initial dispersities. When $\xi = 1.0$, R_w is given by

$$R_w(\xi = 1) = \frac{2}{\gamma_0}\left(\frac{M_w(0)}{M_w(\tau)} - 1\right) \tag{27}$$

The computations of Amerik and Guillet were based on equations given by Kotliar and Eichenbaum.[7] One of these equations contained a misprint, which resulted in Amerik and Guillet's dispersities being in error. The correct equations are given by Kotliar.[6] Table IV presents corrected values for initial dispersities and for $R_w(\xi = 1)$.

An examination of Tables II and III reveals several features of interest. First, the tables do not specify the U values for the various distributions, since the results are independent of molecular weight as long as there is not a significant fraction of molecules at $P = 0$. Second, as ξ increases the distributions approach the Flory distribution with γ going toward 2.0 and δ going toward δ^F. For $a = 0.5$, $\delta^F = 1.767$ and for $a = 0.75$, $\delta^F = 1.884$. Note that initial distributions which are broad approach the Flory distribution more rapidly than do initial

Table III
Degradation of Schulz Distributions

b	a	ξ	γ	δ	R_W	R_V
10	0.50	0	1.091	1.068	0.7222	0.7518
		0.06	1.130	1.102	0.7255	0.7553
		0.2	1.212	1.174	0.7329	0.7633
		1.0	1.536	1.439	0.7709	0.8022
10	0.75	0	1.091	1.068	0.7222	0.7212
		0.06	1.130	1.116	0.7255	0.7390
		0.2	1.212	1.193	0.7329	0.7467
		1.0	1.536	1.489	0.7709	0.7853
2	0.75	0	1.333	1.293	0.8333	0.8390
		0.06	1.368	1.325	0.8361	0.8418
		0.02	1.439	1.390	0.8422	0.8480
		1.0	1.688	1.615	0.8704	0.8765
1	0.75	0	1.500	1.441	0.8889	0.8919
		0.06	1.529	1.467	0.8911	0.8942
		0.2	1.587	1.520	0.8958	0.8990
		1.0	1.778	1.692	0.9167	0.9199
$-\frac{1}{3}$	0.75	0	2.500	2.329	1.067	1.066
		10.06	2.454	2.289	1.064	1.064
		0.2	2.372	2.215	1.059	1.059
		1.0	2.172	2.037	1.042	1.042
$-\frac{2}{3}$	0.75	0	4.000	3.667	1.167	1.168
		0.06	3.724	3.425	1.156	1.157
		0.2	3.299	3.050	1.137	1.138
		1.0	2.520	2.354	1.087	1.087

Table IV
Dispersities and Correction Factors as Given by Amerik and Guillet Compared to Revised Values

Amerik and Guillet		Revised	
γ_0	$R_w(\xi = 1)$	γ_0	$R_w(\xi = 1)$
2.00	1.000	2.00	1.000
2.50	0.950	2.25	1.056
2.90	0.922	2.45	1.092
3.33	0.903	2.67	1.125
4.25	0.870	3.12	1.180
5.20	0.859	3.60	1.222
7.14	0.820	4.57	1.281
10.10	0.800	6.05	1.335

distributions which are narrow. Third, R_v is quite close to R_w and is dependent on the Mark Houwink exponent, a. When $a = 1.0$, R_v will be equal to R_w. R_v and R_w depend both on γ_0 and on which distribution is used. As γ_0 becomes farther from 2.0, the errors in approximating S_n by S_w or by S_v increase. R_v and R_w are in general much smaller for the degradation of individual Schulz distributions than for the degradation of sums of Flory distributions, reflecting the fact that these distributions have different shapes.

It is instructive to compare the shapes of different distributions, both initially and as a function of degradation, in order to see how the shape of the distribution affects R_w and R_v. Figures 2–5 show weight fractions and simulated GPC traces, $G(P)$, for initial distributions and for distributions undergoing degradation. In a given figure all the $G(P)$ traces have, of course, the same area. Note that a shoulder on a weight fraction plot can correspond to a separate peak in a GPC trace. This is clearly seen for distribution D2 in Figure 2. A comparison of Tables II and III with Figures 2, 3, and 4 shows that smaller values of R_w and R_v correspond to $G(P)$ traces that are unstructured or which, if structured, have a larger proportion of their mass at high molecular weight. Compare, for example, the R_w values and the shapes of distributions D2, D4, and D8. It is therefore apparent that substantial errors can occur when viscometry is used to follow the degradation of a polymer which has a large initial dispersity or a structured GPC trace.

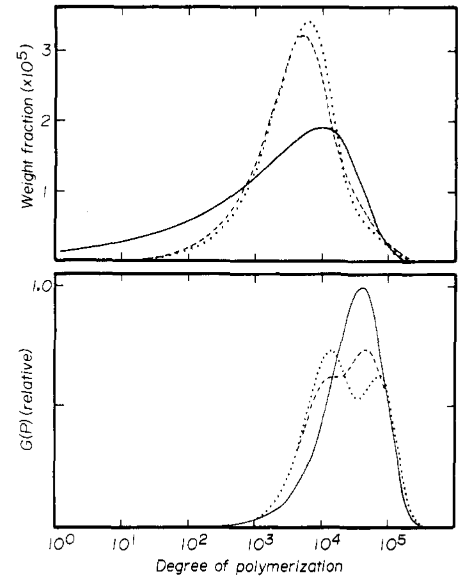

Figure 2. Three undegraded distributions, each with $\gamma_0 = 4.0$ and $M_n(0)_{\mathrm{total}} = 10^4$: (—) Schulz distribution with $b = -\frac{2}{3}$; (···) distribution D2; (- - -) distribution D8.

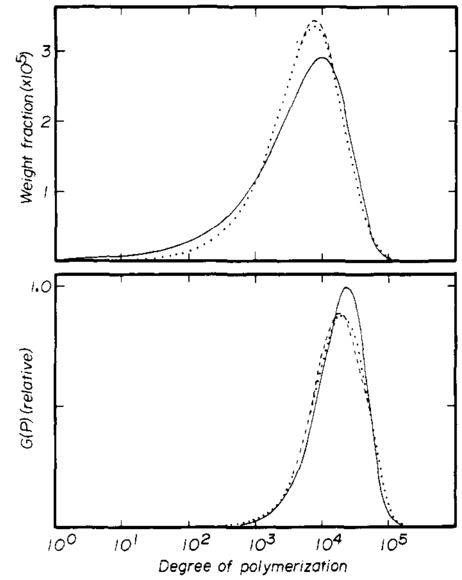

Figure 3. Three undegraded distributions, each with $\gamma_0 = 2.5$ and $M_n(0)_{\mathrm{total}} = 10^4$: (—) Schulz distribution with $b = -\frac{1}{3}$; (- - -) distribution D1; (···) distribution D3.

Figures 4 and 5 illustrate the changes in shape which occur when distributions undergo degradation. Both figures show the approach to a Flory distribution, with $\gamma = 2.0$, but the narrow distribution in Figure 5 approaches a Flory distribution more slowly than does a broad distribution.

Let us refer once again to Tables II and III. Since the value of R_v is close to that of R_w, one can examine R_w and S_w values only, rather than also discussing R_v and S_v values. Figures 6, 7, and 8 show the variations in S_n, S_w, and γ for three different initial distributions as a function of ξ. ξ is related to the experimental parameter I_{abs} by

$$\xi = ZUI_{\mathrm{abs}}\phi_s/N \tag{28}$$

where Z is Avogadro's number. Note that the difference between S_w/W and S_n/W increases as ξ increases but that the

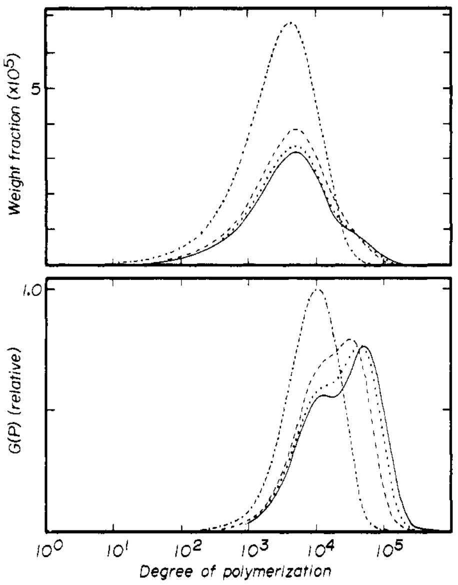

Figure 4. Distribution D4 at different levels of degradation: (—) $\xi = 0$, $\gamma = 4.0$; (···) $\xi = 0.06$, $\gamma = 3.65$; (- - -) $\xi = 0.2$, $\gamma = 3.16$; (- · -) $\xi = 1.0$, $\gamma = 2.36$.

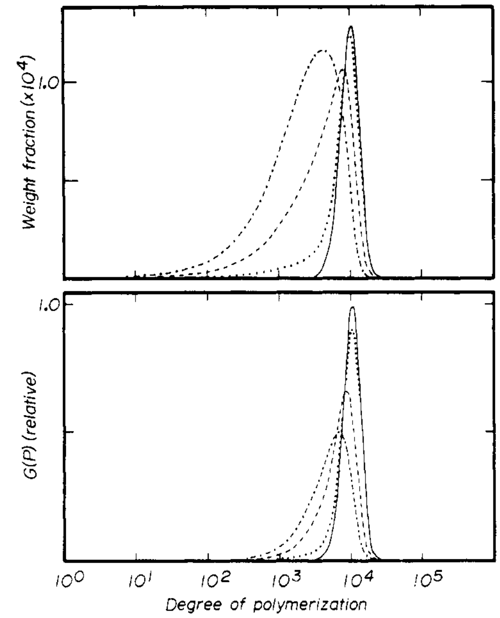

Figure 5. Schulz distribution with $b = 10$ at different levels of degradation: (—) $\xi = 0$, $\gamma = 1.09$; (···) $\xi = 0.2$, $\gamma = 1.21$; (- - -) $\xi = 1.0$, $\gamma = 1.54$; (- · -) $\xi = 2.0$, $\gamma = 1.74$.

curves become parallel at large ξ values. This can be verified by comparing

$$\lim_{\xi \to \infty} \left(\frac{\partial S_n/W}{\partial \xi} \right)$$

with

$$\lim_{\xi \to \infty} \left(\frac{\partial S_w/W}{\partial \xi} \right)$$

or by recalling that

$$\lim_{\xi \to \infty} R_w = 1.0$$

It is clear that if one irradiates a sample only once in order to obtain one S_w value, and if one then approximates S_n by

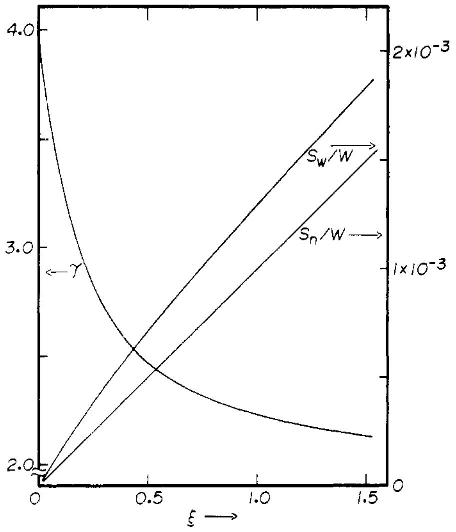

Figure 6. Variation of S_n/W, S_w/W, and γ for the degradation of distribution D6, with $M_n(0)_{total} = 10^3$.

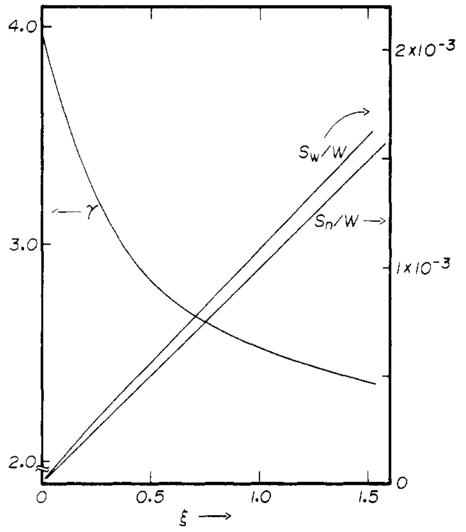

Figure 7. Variation of S_n/W, S_w/W, and γ for the degradation of a Schulz distribution with $b = -\frac{2}{3}$, $M_n(0) = 10^3$.

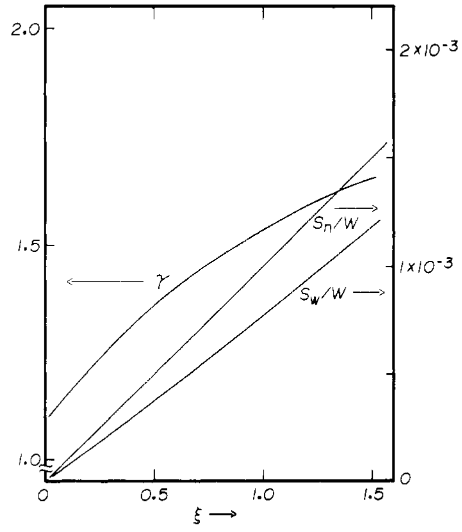

Figure 8. Variation of S_n/W, S_w/W, and γ for the degradation of a Schulz distribution with $b = 10$, $M_n(0) = 10^3$.

S_w, the calculation of ϕ_s according to eq 1 will lead to an error whose magnitude depends on ξ, γ_0, and on the shape of the initial distribution. However, one generally calculates ϕ_s by plotting a number of S_w values as a function of I_{abs} and taking the slope.[1,3] If only the slope is considered, and if one works at large values of ξ, where the slope of S_n is parallel to that of S_w, then one will obtain the correct value of ϕ_s from a plot of S_w vs. I_{abs}. This procedure is, of course, only valid when there are no side reactions to consider and when one has a linear S_w vs. I_{abs} plot. These plots are, however, generally curved and one must then work at small values of ξ.[17] In this region the error in the slope will be roughly equal to the difference between S_w and S_n at the largest ξ in the range studied. If one wishes to make use of data obtained when only a small amount of degradation has occurred, then one will have to apply corrections in order to obtain ϕ_s from viscosity data. This can be done by making a plot similar to those given in Figures 6–8.

For most purposes the value of S_v can be approximated to within 1 or 2% error by the value of S_w which is independent of the value assumed for a, the Mark Houwink exponent. A more accurate procedure would involve the calculation of S_v, but the additional computation is probably not justified for most work. If one has a plot of S_n and S_w as a function of ξ, one uses it to obtain S_n values corresponding to the experimental S_v (S_w) values. These S_n values are then plotted against I_{abs} in order to obtain ϕ_s. The key to this procedure is having a plot of S_v and S_n vs. ξ. If the initial distribution is a Schulz distribution, or if it can be represented by a sum of Flory distributions, a plot can be easily made. For initial distributions with γ_0 less than 2.0, one might reasonably assume that the distribution was a Schulz distribution. For initial distributions with γ_0 greater than 2.0, one would have to examine the shape of its GPC trace and match it either by a Schulz distribution or by a suitable sum of Flory distributions. By reference to Tables II and III, one can see that if the GPC trace is unstructured, and if the initial dispersity is between 1.5 and 2.5, then the correction factor when obtaining ϕ_s from viscosity data will be less than 20%. Larger corrections will be necessary when the initial dispersity is outside this range.

Conclusions

Based on these studies it can be concluded that the number of moles of chain breaks S_n in a polymer undergoing random degradation can be estimated with an accuracy of ±20% or better using the equation

$$S_v = \frac{W[\Gamma(a+2)]^{1/a}}{M_v(0)}\left(\frac{M_v(0)}{M_v(\tau)} - 1\right) \qquad (29)$$

provided that (1) the initial dispersity of the sample, γ_0, is between about 1.5 and 2.5, (i.e., that usually obtained by radical polymerization at low conversion); (2) that the distribution is of a form which can be approximated by a Schulz or sum of Flory distributions; and (3) that the initial degree of polymerization U is greater than about 100. Very little error is introduced by the assumption that $M_v = M_w$.

If greater accuracy is required, it is necessary to determine the initial molecular weight distribution, fit it to either a Schulz or sum of Flory distributions, and calculate the correction factor R_v as a function of ξ by the procedures described herein. A plot similar to Figures 6, 7, or 8 can then be used to convert the measured values of S_v to the desired value of S_n required for stoichiometric calculations. The errors should then be reduced to the order of a few percent.

It is perhaps worth reiterating that distributions which are nearly monodisperse, such as those obtained by anionic polymerization or by successive fractionation, will not approach the Flory distribution very rapidly, and hence quantum yields or reaction efficiencies measured by viscometry on such polymers can be seriously in error unless corrected by these procedures. The relations given in Figure 8 provide a useful first approximation for data obtained on approximately monodisperse polymers (i.e., $\gamma_0 \leq 1.09$), and we recommend this procedure where applicable.

As the number of chain scissions per molecule (ξ) increases, S_v becomes an increasingly better approximation to S_n, since the distribution approaches the Flory distribution.

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References and Notes

(1) Y. Amerik and J. E. Guillet, *Macromolecules*, **4**, 375 (1971).
(2) H. H. G. Jellinek, "Stereochemistry of Macromolecules", Vol. 3, A. D. Ketley, Ed., Marcel Dekker, New York, N.Y., 1968, p 371.
(3) J. E. Guillet, B. Houvenaghel-Defoort, T. Kilp, N. J. Turro, H.-C. Steinmetzer, and G. Schuster, *Macromolecules*, **7**, 942 (1974).
(4) O. Saito, "The Radiation Chemistry of Macromolecules", Vol. 1, M. Dole, Ed., Academic Press, New York, N.Y., 1972, p 223.
(5) K. W. Scott, *J. Polym. Sci., Part C*, **46**, 321 (1974).
(6) A. M. Kotliar, *J. Polym. Sci., Part A*, **2**, 1057 (1964).
(7) A. M. Kotliar and S. Eichenbaum, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **9**, 341 (1968).
(8) A. M. Kotliar, *J. Polym. Sci.*, **51**, S63 (1961).
(9) A. M. Kotliar, *J. Polym. Sci.*, **61**, S25 (1962).
(10) G. G. Cameron, G. P. Kerr, and A. R. Gourlay, *J. Macromol. Sci., Chem.*, **A2**, 761 (1968).
(11) O. Saito, *J. Phys. Soc. Jpn.*, **13**, 198 (1958).
(12) A. M. Kotliar, *J. Polym. Sci., Part A*, **2**, 4303 (1964).
(13) A. M. Kotliar, *J. Polym. Sci., Part A*, **2**, 4327 (1964).
(14) M. Inokuti, *J. Chem. Phys.*, **38**, 1174 (1963).
(15) G. Odian, "Principles of Polymerization", McGraw-Hill, New York, N.Y., 1970.
(16) G. J. Howard, *J. Polym. Sci.*, **59**, S4 (1962).
(17) J. E. Guillet and R. G. W. Norrish, *Proc. R. Soc. London, A*, **233**, 153 (1955).