

## Molecular Weight Distribution in a Polymer Film Degraded by Light

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### Synopsis

An explicit expression is derived for the weight distribution function of polymer molecules in a photodegraded film. A most probable weight distribution of linear molecules is assumed initially present; normally incident, monochromatic light obeying a single Beer-Lambert absorption relation is the photolyzing radiation. The dependence of the weight distribution upon the film's optical thickness and the integrated incident light flux is illustrated by curves computed according to the derived functions. Predicted gel permeation chromatograms are indicated.

In a previous paper<sup>1</sup> various molecular weight averages and functions thereof were derived for polymer films, having initially a most probable size distribution (MPD) of linear molecules, after subjecting them to chain scission and crosslinking by light. Solution viscosity data for poly(methyl methacrylate) films which had undergone scission by 2537 Å. wavelength light were analyzed by means of the derived viscosity function.<sup>2</sup> Number distributions have been computed, at low extents of degradation, for some light-degraded polymer films which were composed initially of a single (monosperse) molecular weight material.<sup>3</sup> Since the MPD more nearly represents many linear polymers encountered in practice and high extents of degradation may be of interest, it is deemed desirable to state explicitly the weight distribution function of such polymers scissioned in film form by light.

The system here considered is a polymer film of thickness  $L$  (in centimeters) subjected to normally incident monochromatic light irradiation for a period of  $t$  (in seconds). The polymer's absorption coefficient  $k$  (in reciprocal centimeters) is assumed constant throughout the irradiation period. The energy absorbed per gram of polymer at depth  $x$  (in centimeters) below the incident surface is assumed to obey a Beer-Lambert relation:

$$\begin{aligned} R_x &= t\bar{v}kI_0e^{-kx} \\ &= R_0e^{-kx} \end{aligned} \quad (1)$$

where  $\bar{v}$  is the polymer specific volume (in cubic centimeters per gram),  $I_0$  is the incident radiation intensity (in photons per square centimeter per

second), and  $R_0$  is the energy absorption (in photons per gram) in the incident surface.

If pure chain scission proportional to the energy absorbed results, the number of molecules per gram in a lamina at depth  $x$  is equal to the original number of molecules per gram,  $(N/\bar{M}_{n0})$ , plus the number of scissions per gram in the lamina:

$$N/(\bar{M}_n)_x = (N/\bar{M}_{n0}) + \phi_d R_0 e^{-kx} \quad (2)$$

$\bar{M}_{n0}$  is the original number-average molecular weight of the polymer,  $\phi_d$  (chain scissions/absorbed photon) is the quantum yield of scissions, and  $(\bar{M}_n)_x$  is the number-average molecular weight of the polymer at depth  $x$  when the accumulated energy absorption in the incident surface is  $R_0$ .  $N$  is Avogadro's number.

Random scission of molecules comprising a MPD of molecular weights perpetuates the MPD. Therefore, in each lamina the weight fraction of polymer having molecular weight  $M$  is given by

$$w_M(R_0, \phi_d, \bar{M}_{n0}, k, x) = [M/(\bar{M}_n)_x^2] e^{-M/(\bar{M}_n)_x} \quad (3)$$

The weight fraction of polymer having molecular weight  $M$  in the total irradiated film of thickness  $L$  is then obtained by integration

$$w_M(R_0, \phi_d, \bar{M}_{n0}, k, L) = L^{-1} \int_0^L w_M(R_0, \phi_d, \bar{M}_{n0}, k, x) dx \quad (4)$$

To simplify the result of the integration we introduce a reduced molecular weight,

$$z \equiv M/\bar{M}_{n0} \quad (5)$$

and a parameter  $B$  equal to the number of scissions in the incident surface per original surface molecule,

$$B \equiv \phi_d R_0 \bar{M}_{n0} N^{-1} \quad (6)$$

Denoting the fraction of the incident light transmitted by the film by

$$D \equiv e^{-kL} \quad (7)$$

we obtain upon substituting eqs. (2) and (3) into eq. (4) and integrating

$$\begin{aligned} w_z(B, D) &= \bar{M}_{n0} \cdot w_M(R_0, \phi_d, \bar{M}_{n0}, k, L) \\ &= ze^{-z} + (\ln D)^{-1} ze^{-z} \left[ \sum_{n=1}^{\infty} (-1)^n \frac{(BDz)^n}{n \cdot n!} - \sum_{n=1}^{\infty} (-1)^n \frac{(Bz)^n}{n \cdot n!} \right] \\ &\quad + 2e^{-z} (\ln D)^{-1} (e^{-Bz} - e^{-BDz}) \\ &\quad + \frac{e^{-z}}{z} (\ln D)^{-1} [(Bz + 1)e^{-Bz} - (BDz + 1)e^{-BDz}] \quad (8) \end{aligned}$$

or, utilizing the definition of the exponential integral,<sup>4</sup>  $Ei(-x)$ , to restate the infinite series,

$$w_z(B, D) = ze^{-z}(\ln D)^{-1}[Ei(-BDz) - Ei(-Bz)] \\ + 2e^{-z}(\ln D)^{-1}[e^{-Bz} - e^{-BDz}] \\ + \frac{e^{-z}}{z}(\ln D)^{-1}[(Bz + 1)e^{-Bz} - (BDz + 1)e^{-BDz}] \quad (8a)$$

Equations (8) present the weight fraction of molecules having molecular weight  $z$  times the initial number-average molecular weight of the polymer as a function of  $z$ , of the fraction of the incident light transmitted by the film,  $D$ , and of the number of scissions in the incident surface per original molecule in the surface,  $B$ .

The number- and weight-average molecular weights of the degraded films are given by eqs. (9) and (10) [cf. eqs. (6) and (9a) of reference 1 with  $\phi_c = 0$ . Equation (9b) of reference 1 is incorrect; the ratio of logarithms therein should be inverted].

$$\bar{M}_n(B, D) = \bar{M}_{n0}/[1 + (\ln D)^{-1}B(D - 1)] \quad (9)$$

$$\bar{M}_w(B, D) = 2\bar{M}_{n0}\{1 + (\ln D)^{-1} \ln [(1 + B)/(1 + BD)]\} \quad (10)$$

At times it is more informative to express the weight distribution in terms of a reduced molecular weight relative to the number-average molecular weight of the degraded film, i.e.,

$$y = [\bar{M}_{n0}/\bar{M}_n(B, D)]z = M/\bar{M}_n(B, D) \quad (11)$$

$$w_y(B, D) = [\bar{M}_n(B, D)/\bar{M}_{n0}]w_z(B, D) \quad (12)$$

By using photodegradable polymers which conform to the requirements specified in the above derivation it is possible to obtain molecular weight distributions of chosen  $\bar{M}_w/\bar{M}_n \geq 2$  by varying  $B$  and/or  $D$ . Figure 1 shows  $\bar{M}_w/\bar{M}_n$  plotted against  $B$  for chosen values of  $D$  ranging from 0.05 to 0.0001.  $\bar{M}_w/\bar{M}_n = 10$  distributions can, according to Figure 1, be obtained by photodegradation by using  $B, D$  combinations: 200.0, 0.005; 88.5, 0.001; 78.5, 0.0001. Figure 2 represents these molecular weight distributions and the initial MPD.

Figure 3 presents plots of the weight distribution functions  $w_y$  versus  $y$  for polymer films of five different optical densities (O.D. =  $-\log D$ ) when the number of chain scissions in their incident surfaces per original surface molecule is 50.

In order to visualize more clearly the molecular weight distribution changes occurring during the photodegradation of an optically thick film Figure 4 is shown. This depicts the weight distribution function  $w_z$  plotted against  $z$  on log coordinates for a polymer film of optical density 3.00 at the photolyzing wavelength when subjected to 0, 1, 5, 10, 20, 40, and 100 chain scissions per original molecule in the incident surface.

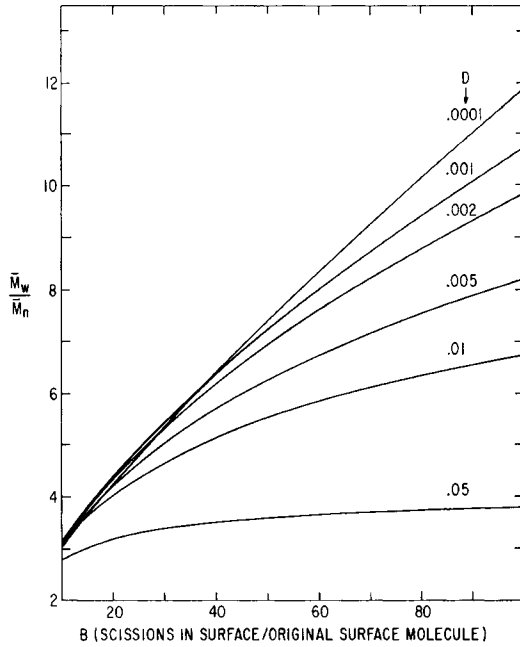


Fig. 1. The ratio of weight-average molecular weight to number-average molecular weight [cf. eqs. (9) and (10)] plotted vs. the number of scissions in the incident surface per original molecule (number-average) in the incident surface. Optical densities of the six films depicted are  $O.D. = -\log D$ .

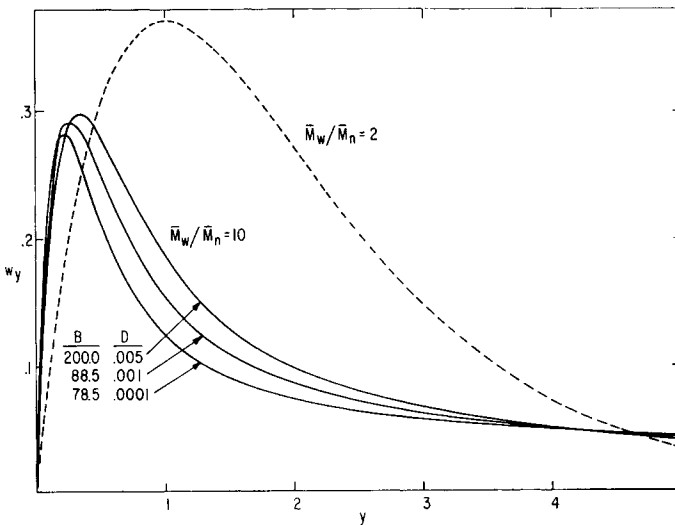


Fig. 2. Weight fractions of  $y$ -mer vs.  $y = M/\bar{M}_n$  are illustrated for three photodegraded films in which the indicated combinations of  $B$  and  $D$  yield  $\bar{M}_w/\bar{M}_n = 10$ . The distribution curve for the original MPD polymer is shown as a broken line. The area under each curve is unity ( $y$  range 0 to  $\infty$ ).

One method of observing and characterizing the molecular weight distributions of photodegraded films is gel permeation chromatography. Figure 5 illustrates the form of gel permeation chromatograms predicted for the original MPD polymer,  $\bar{M}_w/\bar{M}_n = 2$ , and for the polymers obtained by photodegrading films of optical density 3.00 ( $D=0.001$ ) to  $\bar{M}_w/\bar{M}_n$  ratios of 4 ( $B = 16.5$ ) and 10 ( $B = 88.5$ ). These theoretical curves were computed by means of eq. (8) and the empirical treatment of gel permeation chromato-

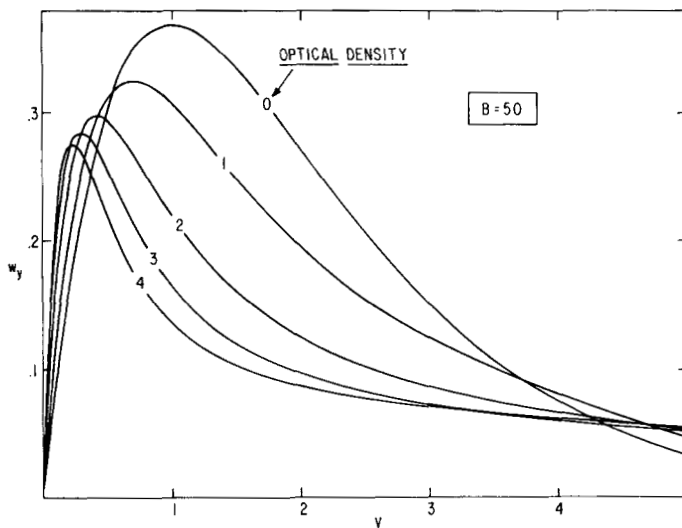


Fig. 3. Weight distribution curves for films of differing optical densities (O.D. =  $-\log D$ ) after subjecting to photodegradation producing 50 chain scissions in their incident surfaces per original surface molecule.

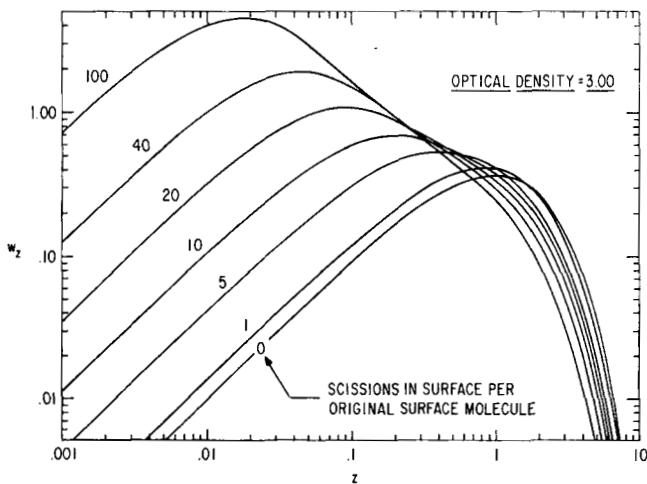


Fig. 4. A representation of  $w_z$  vs.  $z$  on log scale coordinates for films of optical density 3.00 subjected to chosen extents of photodegradation ( $0 \leq B \leq 100$ ).

grams described in a previous publication.<sup>5</sup> The abscissa,  $z$  (log scale), in Figure 5 are found approximately to be related linearly to the flow volume (linear scale) between sample injection and appearance in the effluent solution at the differential refractometer of a gel permeation column. The ordinate,  $zw_z$ , is proportional to the difference in refractive index,  $\Delta n$ , between the effluent solution and the solvent. Figure 6 plots  $yw_y = zw_z$  against  $y = M/\bar{M}_n$  (log scale) rather than against  $z$

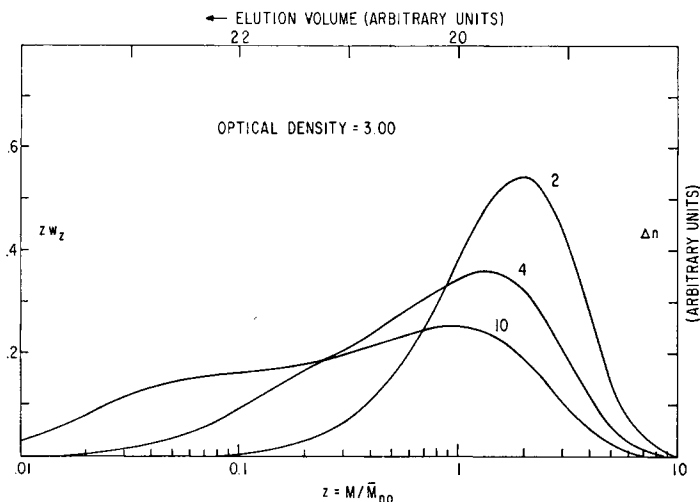


Fig. 5.  $zw_z$  vs.  $\log z$  representation of a MPD polymer ( $\bar{M}_w/\bar{M}_n = 2$ ) and two photodegraded films ( $\bar{M}_w/\bar{M}_n = 4$  and  $10$ ) of optical density 3.00. These should correlate empirically with gel permeation chromatograms plotted as effluent refractive index difference vs. elution volume (reversed linear scale).

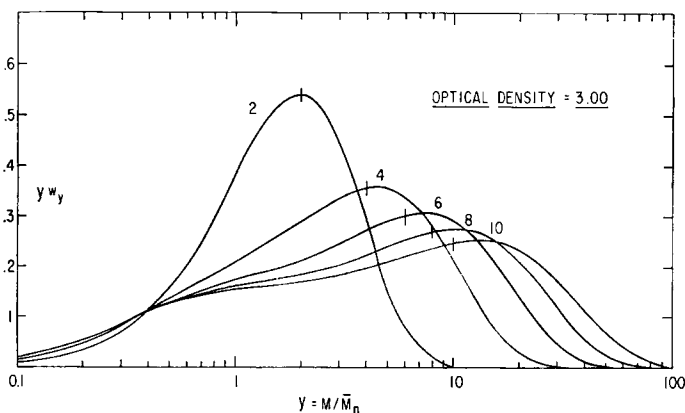


Fig. 6.  $yw_y$  vs.  $y = M/\bar{M}_n$  are shown for the original polymer ( $\bar{M}_w/\bar{M}_n = 2$ ) and four photodegraded films, optical densities 3.00 ( $\bar{M}_w/\bar{M}_n = 4, 6, 8,$  and  $10$ ). The value of  $y$  equal to  $\bar{M}_w/\bar{M}_n$  for each curve is indicated by a vertical line through the curve. Note that the curve maxima lie to the right of these lines for the photodegraded films.

=  $M/\bar{M}_{n0}$  (log scale). This representation makes obvious the interesting fact that the maxima in the gel permeation chromatograms for these photodegraded films are predicted to lie at molecular weights slightly greater than  $\bar{M}_w$ ; i.e.,  $y$  (of maximum)  $> \bar{M}_w/\bar{M}_n$ . The gel permeation chromatogram maxima for the three distribution functions previously examined<sup>5</sup> lay at molecular weights equal to or less than  $\bar{M}_w$ .

All computations in the present study were made on a GE-235 digital computer using Fortran source programs.

Photodegradation of films is a method of achieving special molecular weight distributions of some polymers. Conversely, a mathematical formulation of the molecular weight distributions within photodegraded polymer films permits more satisfactory characterization of their resultant physical properties and of the quantum yields involved in their photodegradation.

### References

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### Résumé

Une expression explicite a été dérivée pour la fonction de distribution en poids de molécules de polymères dans un film photodégradé. Une distribution en poids la plus probable des molécules linéaires est supposée être présente initialement. La radiation provoquant la photolyse est une lumière normale incidente monochromatique obéissant à la relation d'absorption simple de Beer-Lambert. La dépendance de la distribution en poids suivant l'épaisseur optique du film et le flux de lumière incidente intégré est illustrée par des courbes se rapportant aux diverses fonctions dérivées. Les chromatogrammes de perméation sur gel prévus sont indiqués.

### Zusammenfassung

Ein expliziter Ausdruck wird für die Gewichtsverteilungsfunktion der Polymermoleküle in einem Film bei Abbau durch Licht abgeleitet. Eine wahrscheinlichste Gewichtsverteilung der linearen Moleküle wird als anfänglich vorhanden angenommen; normal einfallendes, monochromatisches Licht, das einer einfachen Beer-Lambert-Absorptionsbeziehung gehorcht, bildet die photolysierende Strahlung. Die Abhängigkeit der Gewichtsverteilung von der optischen Dicke des Films und dem integrierten einfallenden Lichtfluss wird an Kurven gezeigt, die entsprechend den abgeleiteten Funktionen berechnet wurden. Berechnete Gelpermeationschromatogramme werden angegeben.

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