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A Method for Following Changes in Molecular Weight Distributions of Polymers on Degradation: Development and Comparison with Ultrasonic Degradation Experiments

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ABSTRACT

When polymers are degraded by submitting them to shearing action, neither the probability of scission of a macromolecule, as a function of molecular weight (MW), nor the probability distribution of the lengths of the resulting fragments is known a priori. Information about these probabilities can be obtained by comparing observed changes in the molecular weight distributions (MWD) of degrading polymer with changes calculated from models. These models are based on assumed functions relating the probabilities mentioned to the MW of the polymer and that of the fragments. In order to make this comparison, equations are derived for various moments of the MWDs in terms of arbitrary initial MWDs and probability functions. Some simplified forms of these equations arising from chosen simple functions for the probabilities are also given. Data are presented to show that the precision of the weight-average MW calculated from gel-permeation chromatography (GPC) is about twice that

of the number-average and z-average MW. On the basis of this observation, a particular index is recommended to indicate the shape of MWDs derived from GPC. This index, calculated from the experimental MWDs of degrading polystyrene as a function of degree of degradation, is compared with index curves computed from models with specified forms for the two probability functions. These comparisons suggest that this polymer has a minimum degradable MW of about 40,000. Finally experimental MWDs are shown to agree well with those calculated.

INTRODUCTION

When a polymer is subjected to mechanical shear the macromolecules may break to form fragments which carry chemically active end groups. In the presence of sufficiently active chemical compounds the fragments can be deactivated so that reactions between them is prevented. Scission of macromolecules thus results in changes of the molecular weight distribution (MWD) of the polymer. The course of these changes is determined by the mechanism of the scission process. The MWDs of a series of samples taken during degradation contain information about this mechanism. In order to extract this information, models for theoretical mechanisms are assumed. From these, MWDs are calculated with which to confront the experimentally obtained MWDs.

Methods have been given in the literature for calculating the changes in the various averages of molecular weight (MW) on degradation and/or crosslinking by radiation or chemical means [1-7]. It follows from the nature of these processes, that the probability P of a particular macromolecule being affected is proportional to its length and, further, that the probability distribution Q of scission or crosslinking to occur at a particular location of the polymer molecule is uniform along its length. In the papers referred to above, it is indeed assumed, explicitly or implicitly, that these probabilities have the properties mentioned.

When degradation by mechanical means is considered, it is not at all obvious that P is proportional to the length of the molecule. The theory of Bueche [8] on the mechanical breakdown of rubber, for example, predicts that P varies with $\exp \{MW\}$. Further, experimental data have prompted several authors to assume a molecular length such that shorter macromolecules do not rupture [9-12]. This assumption is not compatible with the one that P is proportional

to chain length. With regard to the site of breakage, it has been deduced from the nature of the shear degradation process that the probability of scission is maximum at the centre and decreases toward the chain ends [8]. This nonuniform shape of the probability distribution Q has been confirmed experimentally [13-19]. Therefore, in evaluating data on the changes in MWDs resulting from shear degradation, considerations must be given to theoretical models based on probabilities P and Q other than P is proportional to chain size and Q is uniform along the chain length.

In this paper equations are derived from which certain moments of the MWDs of degraded polymer can be calculated from the initial MWD and a model which specifies the probability of scission as a function of molecular weight and the probable lengths of the resulting fragments.

MATHEMATICAL DEVELOPMENT

The length of polymer molecules is restricted to multiples of the length of the repeat unit. Therefore, the molecular weight distributions are histograms. For ease of mathematical operations we have preferred to consider molecular length as a continuous variable and can, therefore, represent the MWDs by continuous curves. The difference between histograms and curves is insignificant for high MW polymers. Notation is summarized in Table 1.

Let us consider $N(t)$ molecules of a polymer with a normalized number fraction distribution $f(t,x)$, where x is the degree of polymerization (DP) and t is the number of breaks that have occurred. After t scissions the number of molecules is $N(0) + t$. To indicate the extent of degradation the degradation index, DI , is defined as $u = t/N(0)$.

Let $g(u,y)N(0)dy$ be the number of molecules whose DP lies between y and $y + dy$ when $DI = u$. Assume now that the probability of scission of one of these molecules on the $(t + 1)$ th break is a function $P(y)$ of its length y , and is proportional to their number, then the probability of having broken a molecule whose DP lies between y and $y + dy$ when DI changes from u to $u + 1/N(0)$ is $P(y) g(u,y) / \int_0^\infty P(y) g(u,y) dy$. Since only one molecule breaks at any scission, this expression is also the number, per molecule present, of these molecules which break on the $(t + 1)$ th break.

Let, further, $Q(x,y)dx$ be the probability that, on scission of a molecule with DP between y and $y + dy$, the break will occur within x and $x + dx$ units from either end of such a molecule. The equation for the

TABLE 1. List of Symbols

$a_{r,j}$	Coefficients in the power series expansion of $H_r^*(v)$ in terms of v .
$f(t,x)$	Normalized number fraction MWD after t breaks
$g(u,x)$	Number of molecules with DP = x at DI = u per original molecule
m,n	Positive integers
p	Momental skewness of distribution
q	Index characterizing shape of MWD defined by Eq. (32)
r	Standard deviation relative to molecular length of Q_1
t	Number of breaks
u	Degradation index DI, $u = t/N(0)$
v	Auxiliary variable related to u by Eq. (7)
x	Degree of polymerization DP
$\bar{x}_n, \bar{x}_w, \bar{x}_z$	Number, weight, and z-average DP
y	Degree of polymerization of a molecule undergoing scission
z	Auxiliary variable: $z = x/y$
DI	Degradation index
DP	Degree of polymerization
DP_m	Minimum degradable degree of polymerization
G_r, G_r'	Generalized moments of $g(0,x)$ defined in text
$H_r, H_r^*, H_r^{*'} $	Generalized moments of $g(u,x)$ defined in text
$\bar{M}_n, \bar{M}_w, \bar{M}_z$	Number, weight, and z-average MW
MW	Molecular weight
MWD	Molecular weight distribution
$N(t)$	Number of polymer molecules after t breaks
$P(x)$	Weighting factor proportional to the probability of scission of a molecule with DP = x
$Q(x,y)$	Probability that on scission of a molecule with DP = y a fragment with DP = x is formed

TABLE 1. (cont.)

$Q_r^*, Q_r^{*'} $	Generalized moments of $Q(x,y)$ defined in text
$Q_1^{(t,n)}(x,y,r)$	Gaussian distribution of sites of scission (not truncated and normalized)
$Q_2(x,y,\beta)$	Symmetrical Beta function of sites of scission
$Q_3^{(t,n)}(x,y,\gamma,r)$	Exponential power distribution of sites of scission (not truncated and normalized)
$R_{a,b}$	Ratio \bar{M}_a to \bar{M}_b
$\alpha_{r,i}, \alpha_{r,i}'$	Coefficients in the power series expansion of H_r^* or $H_r^{*'}$
$\alpha_{r,i}^*, \alpha_{r,i}^{*'}$	Coefficients in the power series expansion of Q_r^* ; Eq. (4)
β	Exponent in the symmetrical Beta function
γ	Parameter in the exponential power distribution
δ	Kronecker delta function
μ_n	n-th moment of MWD about the origin
Γ	Gamma function

net number of molecules, with DP between x and $x + dx$, resulting when the change in DI is $\Delta u = 1/N(0)$ may then be written as:

$$\begin{aligned}
 [g(u + \Delta u, x) - g(u, x)]N(0) &\simeq \partial g(u, x)/\partial u \\
 &= \frac{2 \int_0^\infty g(u, y) P(y) Q(x, y) dy - g(u, x) P(x)}{\int_0^\infty g(u, x) P(x) dx} \quad (1)
 \end{aligned}$$

On introduction of

$$G_r = \int_0^\infty P^r(x) g(0, x) dx$$

and

$$H_r(u) = \int_0^\infty P^r(x) g(u, x) dx / G_r$$

the integro-differential equation can be transformed into a differential-difference equation for generalized moments of the distribution:

$$H_1(u)G_1G_r \frac{dH_r(u)}{du} = 2 \int_0^\infty P^r(x) \int_0^\infty P(y) Q(x,y) g(u,y) dy dx - \int_0^\infty P^{r+1}(x) g(u,x) dx \quad (2)$$

Upon interchanging the order of integration and noting that $Q(x,y) = 0$ for $x > y$ we obtain:

$$H_1(u)G_1G_r \frac{dH_r(u)}{du} = 2 \int_0^\infty P(y) Q_r^*(y) g(u,y) dy - G_{r+1} H_{r+1} \quad (3)$$

where

$$Q_r^*(y) = \int_0^y P^r(x) Q(x,y) dx$$

In the following it is assumed that $Q_r^*(y)$ may be written as a polynomial in $P(y)$ of no higher degree than r , i.e.:

$$Q_r^*(y) = \sum_{i=0}^r \alpha_{r,i} P^i(y) \quad (4)$$

We then have:

$$H_1 \frac{dH_r}{du} = - \sum_{j=1}^{r+1} \alpha_{r,j} H_j \quad H_j(0) = 1 \quad (5)$$

where

$$\alpha_{r,j} = (C - 2\alpha_{r,j-1}^*) G_j / G_1 G_r \quad (6)$$

with $C = 1$ for $j = r + 1$ and $C = 0$ when $j \neq r + 1$. Note here that $H_0 = 1 + u$.

In order to calculate H_r , the variable v is introduced related to the independent variable u by:

$$dv = du/H_1 \tag{7}$$

H_r is now rewritten as:

$$H_r^*(v) = H_r[u(v)] \tag{8}$$

Thus,

$$u(v) = \int_0^v H_1^*(v)dv \tag{9}$$

and

$$dH_r^*(v)/dv = - \sum_{j=1}^{r+1} \alpha_{r,j} H_j^*(v) \tag{10}$$

Application of the Laplace transform, $\mathcal{L}_v[H_r^*(v)] = H_r^*(s)$, to the above equation yields:

$$H_r^*(s) = - \frac{1}{s} - \frac{1}{s} \sum_{j=1}^{r+1} \alpha_{r,j} H_j^*(s) \tag{11}$$

This recurrence relation can be developed into a series expression for $H_r^*(s)$, viz:

$$H_r^*(s) = - \frac{1}{s} - \frac{1}{s^2} \sum_{j=1}^{r+1} \alpha_{r,j} + \frac{1}{s^3} \sum_{j=1}^{r+1} \sum_{k=1}^{r+1} \alpha_{r,j} \alpha_{j,k} - \frac{1}{s^4} \sum_{j=1}^{r+1} \sum_{k=1}^{j+1} \sum_{\ell=1}^{k+1} \alpha_{r,j} \alpha_{j,k} \alpha_{k,\ell} + \dots \tag{12}$$

It follows that

$$H_r^*(v) = \sum_{j=0}^{\infty} (-1)^j a_{r,j} v^j/j! \tag{13}$$

where

$$a_{r,0} = 1 \tag{13}$$

and

$$a_{r,j} = \sum_{i_1=1}^{r+1} \sum_{i_2=1}^{i_1+1} \sum_{i_3=1}^{i_2+1} \dots \sum_{i_j=1}^{i_{j-1}+1} \alpha_{r,i_1} \alpha_{i_1,i_2} \alpha_{i_2,i_3} \dots \alpha_{i_{j-1},i_j} \text{ for } j \neq 0 \tag{14}$$

$H_r(u)$ can thus be calculated from $H_r^*(v)$ with the aid of Eqs. (8) and (9) and can then be compared with H_r values computed from $P(x)$ of the model assumed and $g(u,x) = (1 + u) f(t,x)$ obtained from GPC results.

To illustrate the procedure outlined above, it is worthwhile to consider the case $P(x) = x^{n/m}$ (n and m are integers) and leaving, for the moment, the distribution $Q(x,y)$ unspecified except for the condition that Q is symmetrical about $x = y/2$. To simplify notation it is, in this case, advantageous to modify the definitions of G_r , H_r , and $Q_r^*(y)$ thus:

$$G_r' = \int_0^\infty x^{r/m} g(0,x) dx, H_r'(u) = \int_0^\infty x^{r/m} g(u,x) dx / G_r' \tag{15}$$

and

$$Q_r^*(y) = \int_0^\infty x^{r/m} Q(x,y) dx = \sum_{i=0}^r \alpha_{r,i} y^{i/m} \tag{16}$$

Eq. (2) now becomes:

$$H_n' G_n' G_r' dH_r' / du = 2 \int_0^\infty x^{r/m} \int_0^\infty y^{n/m} Q(x,y) g(u,y) dy dx - \int_0^\infty x^{(r+n)/m} g(u,x) dx \tag{17}$$

and the derivative of $H_r(u)$ now is:

$$dH_r'/du = - \sum_{j=1}^{r+1} \alpha_{r,j}' H_{j+n-1}'/H_n'$$

with

$$\alpha_{r,j}' = (C - 2\alpha_{r,j-1}^{*'})G_{n+j-1}'/G_n'G_r' \tag{18}$$

with C = 1 for j = r + 1 and C = 0 when j ≠ r + 1.

Equation (17) is identical to Eq. (2) but for the subscripts of H; therefore, H_r^{*}' must be calculated with another set of coefficients

a_{r,j}' viz.: a_{r,0}' = 1

and

$$a_{r,j}' = \sum_{i_1=1}^{r+1} \sum_{i_2=1}^{i_1+n} \sum_{i_3=1}^{i_2+n} \sum_{i_j=1}^{i_{j-1}+n} \alpha_{r,i_1}' \alpha_{i_1+n-1,i_2}' \alpha_{i_2+n-1,i_3}' \dots \alpha_{i_{j-1}+n-1,i_j}' \tag{19}$$

The commonly used chain length averages now are simple ratios of H_r^{*}' viz.:

$$\begin{aligned} \bar{x}_n &= H_m^{*'}/H_0^{*'} \\ &= H_m^{*'}/(1 + u) \end{aligned}$$

$$u = \int_0^v H_n^{*'}(v) dv \tag{20}$$

$$\bar{x}_w = H_{2m}^{*'}/H_m^{*'} \tag{21}$$

$$\bar{x}_z = H_{3m}^{*'}/H_{2m}^{*'} \tag{22}$$

On a mill, in an extruder, and in other mechanical or otherwise degrading processes a polymer is often mixed while being exposed to

a steady-state shear field in which shear rates occur ranging from insufficient to more than sufficient to cause chain scission. During these operations the probability of breakage of a macromolecule may be assumed to be proportional to its length: $P(x) = x$ or $n = m$. In this case the expression for $H_r^{*'}$ can be further simplified. From

Eq. (4) we obtain

$$Q_r^{*'}(y) = \sum_{i=0}^r \alpha_{r,i}^{*'} y^i$$

Since $Q_r(x,y)$ is symmetrical, this expression with $r = 1$ yields:

$$Q_1^{*'}(x,y) = \alpha_{1,0}^{*'} + \alpha_{1,1}^{*'} y = y/2$$

and, therefore,

$$\alpha_{1,0}^{*'} = 0$$

and

$$\alpha_{1,1}^{*'} = 1/2.$$

With these values and $r = 1$ we obtain from Eq. (18): $dH_1'/du = 0$.

Therefore $H_1'(u) = H_1'(0) = 1$ and from this, with Eqs. (8) and (9), and $m = 1$, $H_r^{*'} = H_r'$, and $v = u$. Equation (13) now reads:

$$H_r^{*'}(u) = \sum_{j=0}^{\infty} (-u)^j a_{r,j}'/j! \quad (23)$$

where the coefficients $a_{r,i}$ are the same as before, namely Eq. (19)

with $n = 1$. The chain length averages, in this case, are as above with $m = 1$, viz.:

$$\bar{x}_n = H_1^{*'} / (1 + u)$$

$$\bar{x}_w = H_2^{*'} / H_1^{*}'$$

$$\bar{x}_z = H_3^{*'} / H_2^{*}'$$

For the distribution of the sites of breaks the Gaussian distribution

$$Q_1^{(t,n)}(x, y, r) = \exp \left\{ - \left[\left(\frac{x}{y} \right) - \frac{1}{2} \right]^2 / 2r^2 \right\} / ry\sqrt{2\pi} \quad (24)$$

was assumed in model calculations reported previously [19, 20]. $Q_1(x,y,r)$ is necessarily truncated at $x = 0$ and $x = y$ and then normalized [these operations are indicated by the superscript (t,n)]. In those reports the "best" value of the adjustable parameter r was 0.35. For this value truncation of Q_1 occurs at about 1/3 of its maximum. This is undesirable. Therefore, two other distributions have been applied viz.: the symmetrical Beta function

$$Q_2(\beta) = [\Gamma(2\beta)/y \Gamma^2(\beta)] \{ (x/y) [1 - (x/y)] \}^{\beta-1} \quad (25)$$

with one parameter (β) and the exponential power distribution with two parameters, γ and r :

$$Q_3^{(t,n)}(\gamma,r) = f(\gamma) \exp \left\{ - \left[\left(\frac{x}{y} - \frac{1}{2} \right) 2r \right]^{2/(1+\gamma)} \right\} / ry \quad (26)$$

The assumption underlying Eq. (4) holds for Q_2 as well as for the truncated functions Q_1 and Q_3 . With the "best" values of the parameters β , and γ and r , respectively, the residual sum of squares for models with Q_2 and Q_3 are about 3/4 of that with Q_1 . It follows that, at least in the case reported, the detailed shape of Q has only little effect on the goodness of fit. Because of the simple form of Q_2 and since this function does not need to be truncated, we have developed the solution for the case $Q = Q_2$ and $P(x) = x^n$. Now

$$\begin{aligned} Q_r^*(y) &= \int_0^y P^r(x) Q_2(x,y) dx \\ &= \frac{\Gamma(2\beta)}{y\Gamma^2(\beta)} \int_0^y x^{rn} \left[\frac{x}{y} \left(1 - \frac{x}{y} \right) \right]^{\beta-1} dx \end{aligned} \quad (27)$$

On introducing $z = x/y$ we can write:

$$\begin{aligned} Q_r^*(y) &= [\Gamma(2\beta)/\Gamma^2(\beta)] y^{rn} \int_0^1 z^{rn+\beta-1} (1-z)^{\beta-1} dz \\ &= [\Gamma(2\beta)\Gamma(rn + \beta)/\Gamma(\beta)\Gamma(rn + 2\beta)] y^{rn} \end{aligned} \quad (28)$$

Hence

$$\alpha_{r,r}^* = \Gamma(2\beta)\Gamma(rn + \beta)/\Gamma(\beta)\Gamma(rn + 2\beta) \quad (29)$$

and

$$\alpha_{r,i}^* = 0 \text{ for } i \neq r$$

From this we obtain

$$\alpha_{r,r+1} = [1 - 2\Gamma(2\beta)\Gamma(rn + \beta)/\Gamma(\beta)\Gamma(rn + 2\beta)] G_{r+1}/G_1 G_r \quad (30)$$

$$\alpha_{r,i} = 0 \text{ for } i \neq r + 1 \text{ and } a_{r,0} = 1,$$

$$a_{r,i} = \prod_{j=1}^{i-1} \left[1 - 2 \cdot \frac{\Gamma(2\beta)\Gamma(\{r + j - 1\}n + \beta)}{\Gamma(\beta)\Gamma(\{r + j - 1\}n + 2\beta)} \cdot \frac{G_{r+j}}{G_1 G_{r+j-1}} \right] \quad (31)$$

Inserting this expression for the coefficients $a_{r,i}$ into Eq. (13) yields an expression for H_r^* of a form suitable for computer calculations.

MOLECULAR WEIGHT DISTRIBUTIONS FROM GEL-PERMEATION CHROMATOGRAPHY

In comparing a theoretical with an experimental MWD it would at first seem best to consider the entire distributions and to calculate, as a measure of conformity, the sum of the squares of the differences between them at regular MW intervals. In doing so it is, however, tacitly assumed that the precision of the fractions is independent of MW. This is, however, not the case when MWDs are calculated from data collected by gel-permeation chromatography (GPC). In this technique a graph is obtained of the increment in refractive index of an eluting polymer solution over that of the solvent versus elution volume. This volume is then related to the size of the polymer molecules via a calibration curve. To obtain the increment,

the index of the solvent is subtracted from the one measured over the entire range of elution volume. The index of the solvent is recorded as a base line at elution volumes smaller than, and larger than the volumes at which polymer solution elutes. For elution volumes at which polymer leaves the columns, the base line must be added to the graph to obtain the increment by connecting the base line portions recorded for times before and after elution of polymer solution. Polymer molecular weight distributions nearly always have a tail; i.e., the weight or number fraction slowly approaches zero as the MW increases. Subtraction of a base line obtained by interpolation, therefore, results in low precision (repeatability) of the polymer fraction at the high MW end. For the same reason the precision of the low MW front of the distribution is affected, though to a lesser degree, because the front often rises more sharply than the tail falls. However, polymer species diffuse axially during their travel through the chromatographic columns over increasingly longer distances the lower their MW. Therefore, the correction for this diffusion, applied in calculating MWD from chromatograms, becomes increasingly larger as the MW decreases. Thus, the precision is low at both ends of the MWDs. Since the number-average molecular weight \bar{M}_n and the z-average molecular weight \bar{M}_z are sensitive to the front and the tail end portions of the MWD, respectively, the precision of \bar{M}_n and \bar{M}_z is less than that of the weight-average molecular weight \bar{M}_w . The averages of orders higher than z (\bar{M}_{z+n}) become increasingly uncertain with increasing n.

The ratio of the standard deviations to the mean values of various MW averages, obtained by two operators each with his own set of columns, are given in Table 2. Experimental and computational details are given elsewhere [20]. The data refer to polymer A, a

TABLE 2. Ratio of Standard Deviations to Mean Values of Molecular Weight Averages

	No. of expt.	Standard deviation (%)			
		\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_{z+1}
Operator A	14	6.9	2.9	5.9	11.4
Operator B	8	7.8	3.0	6.4	15.0
Overall	22	7.2	2.9	6.1	12.7

"monodisperse" polystyrene, $\bar{M}_w = 862,000$ g/mole, $\bar{M}_w/\bar{M}_n = 1.08$ (Pressure Chemical Co.). It is to be noted that the standard deviations of \bar{M}_n and \bar{M}_z are about equal and double the value for \bar{M}_w .

CHARACTERIZATION OF MOLECULAR WEIGHT DISTRIBUTIONS

A continuous distribution is equivalently described by the infinite series of its moments. It is common practice to characterize the MWD of a polymer roughly by the polydispersity or heterogeneity index

$$R_{w,n} = \bar{M}_w/\bar{M}_n = \mu_2/\mu_1^2$$

where μ_n is the n-th moment of the distribution about the origin.

This index is not sensitive to the shape of the tail end of the distribution, whereas the index $R_{z,w} = \bar{M}_z/\bar{M}_w = \mu_3/\mu_2^2$ is insensitive to the front of the distribution. The figures listed in Table 2 show that both these indices, when calculated from GPC data, are obtained with about equal precision. Because of the uncertainties in the higher moments of the distribution little further information is gained from higher order indices.

Another indicator of the shape of a distribution is its degree of asymmetry which is expressed by the momental skewness, defined by $p = \mu_3/\mu_2^{3/2}$. This indicator can be written in terms of the indices R: $p = [R_{w,n}^2 R_{z,w} + 2 - 3 R_{w,n}]/(R_{w,n} - 1)^{3/2}$. The difference in the exponents of the ratios R in the first and last term of the numerator and the subtractions in numerator and denominator cause considerable uncertainty in the value of p. The skewness is, therefore, not well suited as an indicator of the shape of polymer MWDs obtained from GPC data. Instead the ratio $R_{z,w}/R_{w,n} = R_{z,n} = \bar{M}_n \bar{M}_z/\bar{M}_w^2$ will be used. In order to compare the course of changes in MWDs of one polymer with that of another, it is desirable to divide $R_{z,n}$ by its value $R_{z,n}(0)$, for the undegraded polymer. The index q is now introduced, defined by:

$$q = 1 - R_{z,n}(u)/R_{z,n}(0) \quad (32)$$

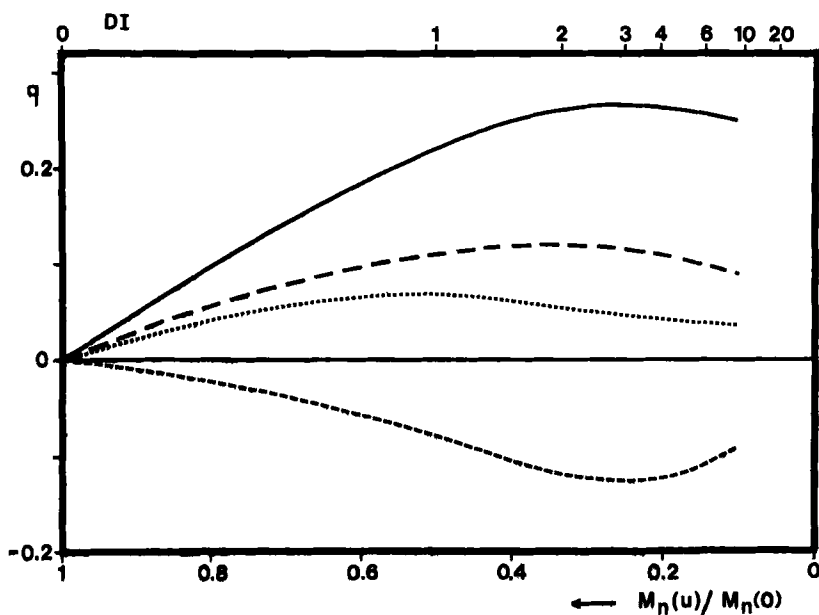


FIG. 1. MWD shape index q as a function of number-average MW $\bar{M}_n(u)$, relative to initial number-average MW $\bar{M}_n(0)$; degradation index $DI = u$: (—) initial polymer molecularly homogeneous, random breakage; (··) initial polymer molecularly homogeneous, center breakage; (---) initial polymer MWD uniform, random breakage; (-·-) initial polymer MWD uniform, center breakage.

where $R_{z,n}(u)$ is the value of $R_{z,n}$ at a $DI\ u = t/N(0)$. In Fig. 1, q is plotted as a function of relative \bar{M}_n , i.e., $\bar{M}_n(u)/\bar{M}_n(0) = 1/(1 + u)$. Four curves are shown for $P(x) = x$ and combinations of initially, molecularly homogeneous polymer ($R_{w,n} = 1$) or uniform initial MWD ($R_{w,n} = 4/3$) and random scission ($Q = 1/y$) or center breakage [$Q = \delta(x - y/2)$]. For a given initial MWD the course of q on scission depends on both P and Q which can be calculated for any function P and for any Q from the function $H(u)$ or $H^*(u)$ with Eqs. (8), (9), (13) or (23) and (14), or (19), or (31). The curves in Fig. 1 were computed from Eqs. (23) and (31) with $n = 1$ and $\beta = 1$ (random scission) or $\beta = \infty$ (center scission).

COMPARISON OF CALCULATED WITH
EXPERIMENTAL VALUES OF INDEX q

In a previous paper [20], experimental results were discussed on the course of changes in MWDs during ultrasonic degradation in solution of polystyrenes with narrow MWDs. The model used was:

$P(x) = x^s$, $Q = Q_1^{(t,n)}(x,y,r)$. For comparison between experimental and calculated MWD, six "feature" points were chosen along the distribution. The "best" set of values of the parameters, $r = 0.35$ and $s = 5/4$, was determined by minimizing the sum of the squares of the differences between observed and calculated values at the feature points. The choice of these points, however characteristic for the general shape of the MWDs considered, remains arbitrary. The ultrasonic degradation data are now evaluated with the aid of the index q . In Fig. 2 the filled circles are the q values calculated

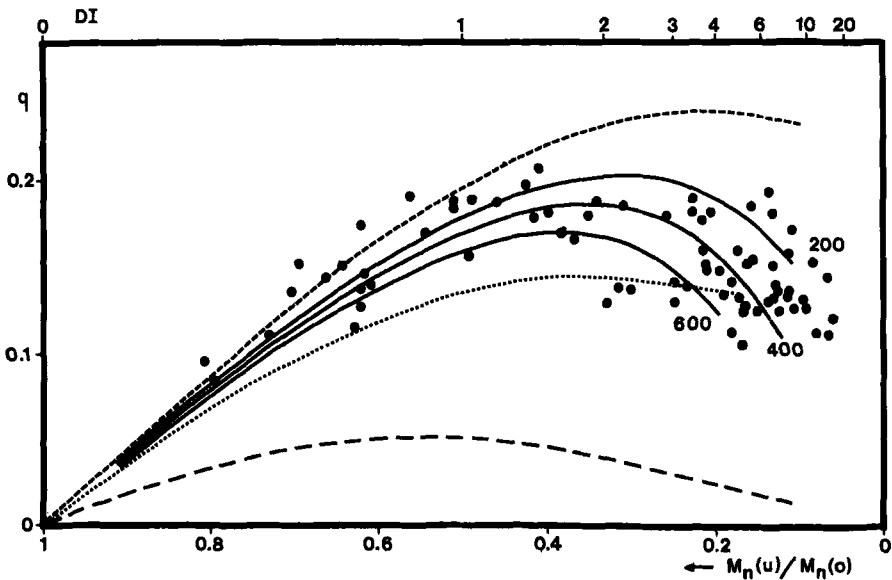


FIG. 2. MWD shape index q as a function of number-average MW $\bar{M}_n(u)$, relative to initial number average MW $\bar{M}_n(0)$ for polymer A [20]; degradation index $DI = u$: (--) $P(x) = x$, random breakage; (- -) $P(x) = x$, center breakage; (—) $P(x) = x$, random breakage, minimum degradable length, parameter DP_m ; (···) $P(x) = x^{5/4}$, $Q = Q_1(x,y,0.35)$.

from the experimental data and the dotted line is computed from the above model. The shape of the line only roughly conforms to that suggested by the experimental data points. Up to about one break per molecule ($DI = 1$) the data are scattered around the upper dashed line representing the model: $P = x$, $Q = Q_2(x, y, 1) = 1/y$ (random breakage). At higher values of DI q decreases markedly, i.e. the distribution narrows. For comparison the lower dashed line for the model $P = x$, $Q = Q_2(x, y, \infty) = \delta(x - y/2)$ (center breakage) is shown. It was found by trial that no combination of positive values for n and m of $P = x^{n/m}$, and for β of Q_2 yields a line which fits the data at DI values both less than, and greater than unity. Substituting Q_1 or Q_3 for Q_2 leads to similar conclusions. It appears necessary to change the model more drastically to obtain a satisfactory fit. It can be seen from Fig. 2 that the q values deviate from random breakage toward a more centered distribution of scission sites as the average molecular weight decreases. This suggests that the tail ends of the macromolecules are less likely to break than the rest of the polymer chains. To incorporate this feature into the model, it is simplest to assume that small molecules do not break, i.e., there is a minimum degradable chain length, DP_m . This assumption has often been made in the literature on degradation of polymers [9-12]. The integrals in Eq. (1) now have the limits DP_m and ∞ . The nonzero lower limit renders the solution to the integro-differential equation more complex since the assumption expressed in Eq. (4) is no longer valid. This solution is the topic of a future paper. The q values referred to in the following paragraphs have been calculated by the Monte Carlo technique, computational aspects of which have been given before [19]. This method has the advantage that it yields the MWDs themselves after any number of breaks.

Because the experimental q values show considerable scatter, it was deemed advisable to consider models with only one adjustable parameter. Since introduction of a minimum degradable chain length leads to sharpening of MWDs, on degradation, $q(DP_m)$ values will be smaller than $q(0)$. Therefore, we consider the model $P = x$, $Q = 1/y$ (random scission) with DP_m as parameter. The full lines in Fig. 2 show the course of the index q on degradation for three values of DP_m . The shape of these lines corresponds rather well to that of the data. It can be seen that DP_m has a value of about 400. This number agrees as well as can be expected with the value 300 found by an independent method viz. analysis of the rate of scission [21]

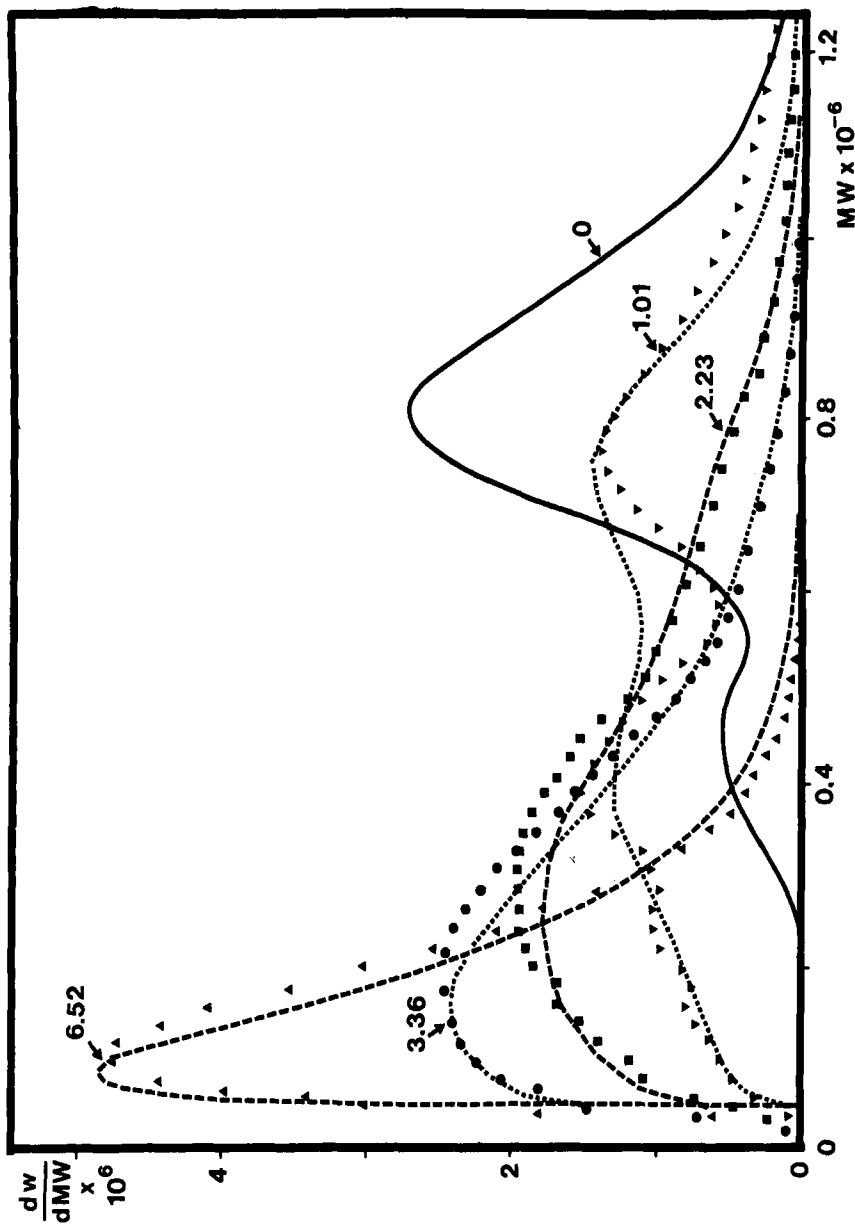


FIG. 3. Molecular weight distributions of polymer A [20], before and after degradation, where lines are calculated, symbols are experimental results: (—) DI = 0; (▼, ...) DI = 1.01; (■, --) DI = 2.23; (●, ...) DI = 3.36; (▲, - -) DI = 6.52.

in the same experiments. It is to be noted that these values of DP_m are roughly the same as DP_c , the critical DP where the exponent in the power law, relating viscosity and DP, changes from 1 to 3.4. Values of 300 to 370 have been given in the literature for DP_c [22].

In Fig. 3 the model-generated and observed MWDs are compared for four values of DI. The observed distributions, depicted by symbols, are averages of N experimental MWDs at nearly equal DI values; N is 8, 3, 4, 4, and 5 for average DI of 0, 1.01, 2.23, 3.36, and 6.52, respectively. Bearing in mind that experimental values of DI are calculated from $DI = \overline{M}_n(0)/\overline{M}_n(t) - 1$ and that the \overline{M}_n is known with limited precision, the agreement between calculated and observed MWDs may be considered good.

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