A General Model for Prediction of Molecular Weight Distributions of Degraded Polymers. Development and Comparison with Ultrasonic Degradation Experiments

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ABSTRACT

A general model has been developed for the process of
polymer chain breakage. The molecular weight distributions
(MWDs) of the degraded polymer, after a specified number
of chain ruptures, can be calculated from the model, given
the MWD of the initial material. The calculations can
easily be handled numerically on a digital computer. The
model is applicable to any process in which polymer chains
break, e.g., ultrasonation and high shear mechanical action.
The course of degradation is described in terms of the
probability that a molecule of a given length will break
and the probability that a molecule of a particular length
will result from this rupture. Any form of both these
probability distributions and the initial MWD can be used
in the model.

The degradation of polystyrene in solution by ultrasonic irradiation has been studied. Calculated MWDs are compared with experimental MWDs which were obtained by gel permeation chromotography after exposure of narrow distribution polystyrene dissolved in tetrahydrofuran to ultrasonation for various time periods. It was found that the experimental results are in disagreement with calculated MWDs based on a model which allows breakage at the midpoint of the polymer chains only. Two other probability distributions for the location of rupture sites along the chain have been considered, namely, random along the chain, and a Gaussian curve centered around the midpoint of the polymer molecule. Calculated MWDs based on this last model closely follow the experimentally obtained MWDs.

INTRODUCTION

Polymer molecules are ruptured under the influence of ultrasonic irradiation and high shear mechanical action. Several models for the mechanisms of these degradation processes, based on kinetic and molecular considerations, have been reported [1-6]. Heymach and Jost [3] have pointed out that a rigorous treatment of polymer degradation requires the simultaneous solution of a very large number of differential rate equations; viz., one for each molecular weight species present in the sample. It also requires knowledge of the values of the rate constants entering into these equations. The same authors have proposed a method of computer simulation for some ultrasonic degradation models. The present work takes a new approach to polymer degradation modeling, which is applicable to ultrasonic and mechanical degradation processes.

The information available from a degradation experiment is the continuous change in the molecular weight distribution (MWD) during the course of the degradation process. The validity of a theoretical model for the mechanism of degradation can be assessed by comparing the MWD changes calculated from the assumed breaking mechanism and the actual changes found experimentally. The information gained from an experiment can be divided into two parts; first, data on the time-dependent rate of bond breakage and, second, the MWD obtained after various numbers of chain ruptures. These numbers can be calculated from the number-average molecular weights of the degraded polymers.

This paper deals with a computer simulation model from which the MWD after a specified number of breaks can be calculated from the initial distribution. It describes the degradation process in terms of two probability distributions, namely, the probability that a molecule of a given length will break and, further, the probability that on rupture of this molecule a fragment of a particular length will be formed. The treatment is general and applicable, with any form of both probability distributions, to any initial MWD.

The method is applied to data obtained from an ultrasonic degradation experiment. It is demonstrated that the method allows the discrimination between three assumed forms for the probability distribution of the location of rupture along the polymer chain.

DEVELOPMENT OF THE MODEL

The following nomenclature is used in the model equations.

$f_n(t,x)$ number fraction of molecules of degree of polymerization (DP) x after t breaks.

$p(x)$ weighting factor describing the relationship between probability of break and the DP of the polymer molecules.

$A(t)p(x)f_n(t,x)$ the probability of choosing a molecule of DP x to rupture, after break t. For convenience this will be represented by $P(t,x)$. $A(t)$ is the normalization factor which arises from the fact that $P(t,x)$ is a probability and, therefore,

$$\sum_{x=1}^{\infty} P(t,x) = 1 \tag{1}$$

$Q(y,x)$ probability that a molecule of DP y, on breaking, produces a fragment of DP x.

$$\sum_{x=1}^{\infty} Q(y,x) = 1$$

since $Q(y,x)$ is a probability.

N   initial number of molecules. The total number of molecules
       after t breaks is then N + t.

The derivation of the model equations is as follows: The average
increment in the number of molecules of DP x, resulting from break
t + 1, can be evaluated in two ways. First, it is the difference
between the products of the total number of molecules and the num-
ber fraction for DP x after break t and after break t + 1. Second,
it is the sum of the products of the probability of choosing the
molecule to be broken and the probability that it produces a mole-
cule of DP x, minus the probability of choosing a molecule of DP x
to be broken. Equating these two expressions for the average
increment yields

$$(N + t + 1)f_n(t + 1,x) - (N + t) f_n(t,x) = 2\left\{ \sum_{u=x+1}^{\infty} P(t,u)Q(u,x) \right\} - P(t,x) \qquad (2)$$

The upper limit ∞ is placed on the summation to indicate that there
is a term for each DP up to the highest present. For DPs higher
than those of any of the molecules present, $P(t,u)$ vanishes and there
is, therefore, no corresponding term in the summation. For the
sake of simplicity the model equation has been written out for a
linear homopolymer and a Q distribution symmetrical with respect
to the midpoint of the molecular chains. This symmetry gives rise
to the factor 2 in the right-hand side of Eq. (2) because fragments
of length x are produced with equal probability on rupture at x units
from either end of the linear polymer molecule. If this symmetry
is not present, the model can be easily modified to accommodate
its absence. In general, equations can be developed using this
model for polymers with different chemical composition or
architecture.

With Eq. (2), $f_n(t + 1,x)$ can be calculated from $f_n(t,x)$ for all
possible values of x. Thus the number distribution $f_n(t,x)$ can be
built up, for any value of t, from the initial MWD, $f_n(0,x)$, by
repeated application of the above calculation scheme for each
integral value from 0 to t. It should be borne in mind that between
consecutive calculation steps the value of A(t) must be determined
so that Eq. (1) is satisfied.

The model allows for the inclusion of the concept that molecules
below a certain molecular weight will not break. This assumption

of a minimum degradable length has been made repeatedly in the literature (see, for example, Ref. 3). It can be incorporated by imposing the condition that $P(t,x) = 0$ for all x smaller than the minimum degradable degree of polymerization (dp). The normalizing factor $A(t)$ is now calculated from $\sum_{x=dp}^{\infty} P(t,x) = 1$.

Because of the generality of this model, any combination can be considered of the probability of choosing a molecule for rupture $(P(t,x))$ and the probability distribution of the site of the breakage along the chain $(Q(y,x))$. The following probability distributions for $P(t,x)$ and $Q(y,x)$ are mentioned. Some of their combinations are considered in a comparison with experimental data (see below).

P distributions:

For $1 \le x < dp$: $P(t,x) = 0$
For $x \ge dp$:

(1) $P(t,x) = A(t)f_n(t,x)$ The probability of choosing a molecule for rupture is proportional to its number fraction.

(2) $P(t,x) = A(t)M_o x f_n(t,x)$ The probability of choosing a molecule is proportional to its weight fraction, i.e., random in space. M_o is the molecular weight of the repeat unit.

(3) $P(t,x) = A(t)(M_o x)^s f_n(t,x)$ The probability of choosing a molecule is proportional to its molecular weight to the power s. If $s = 0$ it reduces to Case (1); if $s = 1$ it reduces to Case (2).

Q distributions:

(a) $Q(y,x) = 1/(y-1)$ Random distribution of rupture sites, i.e., equal probability of rupture along the polymer chain. This will be termed random breakage.

(b) $Q(y,x) = 1$ for $x = y/2$ and   Breakage of the molecules only at their
     $Q(y,x) = 0$ for all other values of x   midpoint. This will be termed center breakage.

(c) $Q(y,x) = \dfrac{1}{\sigma\sqrt{2\pi}}\exp(-(x - y/2)^2/2\sigma^2)$ The probability of rupture sites is a Gaussian distribution about the midpoint with standard deviation σ, a constant fraction of the total length of the molecule: $\sigma = ry$. If σ is very large ($r > 10$), this case approaches Case (a). If σ is small ($r < 0.005$), it approaches Case (b). This will be termed Gaussian breakage.

COMPUTATIONAL ASPECTS

A FORTRAN language program has been written to calculate $f_n(t,x)$ numerically on an IBM 360/75 computer for the combination of Case (3) of the P distributions and Case (c) of the Q distributions. Restrictions imposed by computer memory capacity and execution time do not permit calculations for all possible rupture sites along the chain. The DP of chain segments between consecutive rupture sites allowed will be termed DP_r. We have used values for DP_r in the range 10-200. The input data consist of the values of s, r, DP_r, and the initial polymer MWD, $f_n(0,x)$, as discrete values at DP_r intervals. The effect of varying DP_r for a particular initial distribution was tested. It was found that decreasing DP_r had a negligible effect on the calculated weight distributions provided that 90% of the area under these curves fall within a range of 10 DP_r. The initial number of molecules considered in the calculations need not be large. It was found experimentally that for one particular distribution an increase from 25 to 100 initial molecules did not affect the calculated distributions significantly.

For random or center breakage, Eq. (2) can be simplified considerably. These simplified forms, which are given in the Appendix, lead to marked savings in computer costs.

COMPARISON OF THE MODEL WITH
EXPERIMENTAL RESULTS

A narrow molecular weight distribution polystyrene sample dissolved in tetrahydrofuran was degraded ultrasonically. The concentration was 0.1% by weight. The material was obtained from the Pressure Chemical Co., had a nominal MW of 860,000, and M_w/M_n = 1.15. The sample was subjected to ultrasonation at a frequency of 22 kHz, an input power of 35 W/cm^2, and a temperature of 35°C. The original weight distribution, and the weight distributions of the sample after 1, 3, and 15 min irradiation time, are shown in Fig. 1. The MWDs were determined by gel permeation chromatography using a Waters Model 200 GPC. The chromatograms were corrected for instrumental spreading using the method of Chang and Huang [7].

For convenience the term Degradation Index (DI), defined as the ratio of the number of bonds broken to the original number of
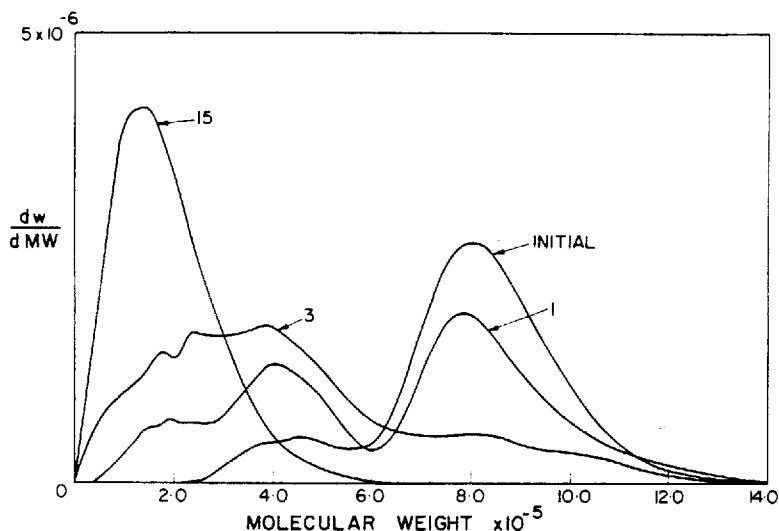

FIG. 1. Molecular weight distributions of ultrasonically degraded polystyrene. The parameter is irradiation time in minutes. The Degradation Index, DI, for each curve is: 1 min, 0.4; 3 min, 1.6; 15 min, 4.5.

molecules, has been chosen to describe the extent of degradation. It can be calculated from the number-average molecular weights (M_n) of the original polymer and of the degraded sample by means of

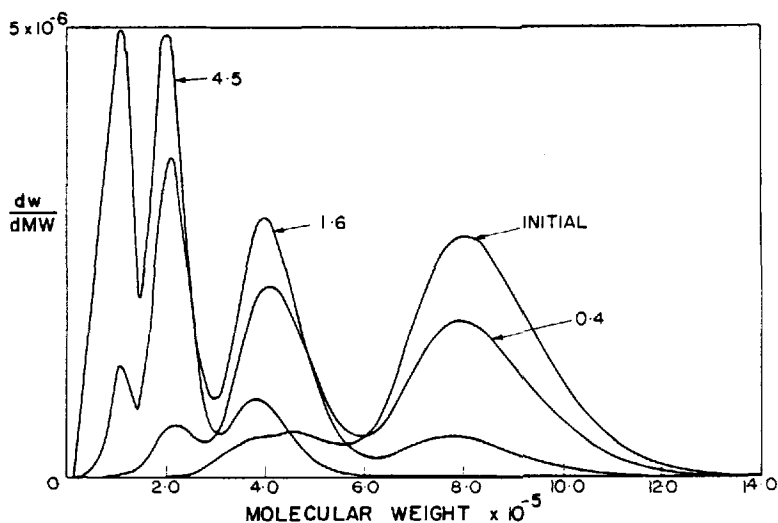$$DI = \frac{M_n \text{ (original)}}{M_n \text{ (after degradation)}} - 1$$

FIG. 2. Molecular weight distributions calculated by the center breakage model. The parameter is DI.

Figures 2, 3, and 4 (solid lines) show the molecular weight distributions for three values of DI, calculated for the cases of center, random, and Gaussian breakage, respectively, with $r = 0.15$ determined empirically. The original experimental MWD shown in Fig. 1 was used as the initial distribution in all cases. The value of s was taken to be unity.
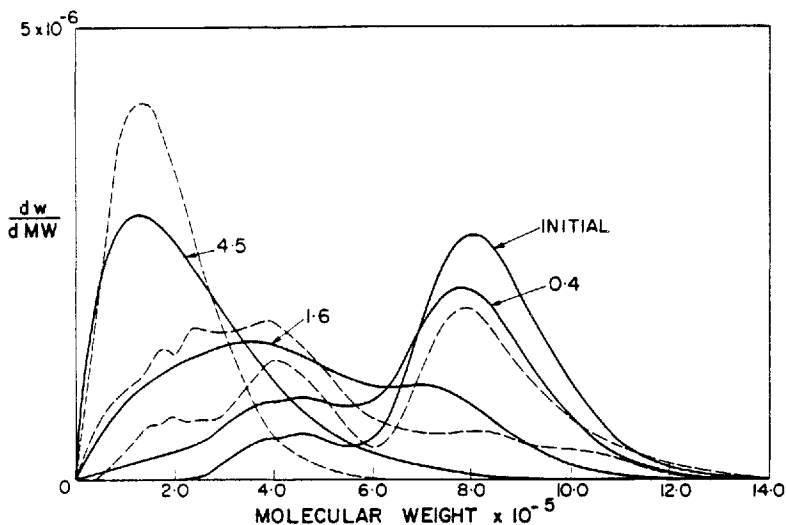
FIG. 3. Molecular weight distributions calculated by the random breakage model (solid lines). The broken lines are the experimental distributions from Fig. 1. The parameter is DI.

It can clearly be seen that distributions calculated by the center breakage model differ considerably from the experimental distributions. In contrast, the calculated distributions for random and Gaussian breakage are seen to resemble the experimental distributions (Figs. 3 and 4, broken lines). Comparison of calculated and experimental distributions can be made by considering the following features; the height of the original peak, the production of a pronounced peak at 400,000 MW, and the height of the curves in the region of 125,000 MW. It is concluded from this analysis that the Gaussian breakage model predicts the MWD of the experimentally degraded polymer more closely than does the random breakage model.

In future publications a more detailed study on the comparison of this model to a large number of experimental results from ultrasonic degradation studies will be presented.
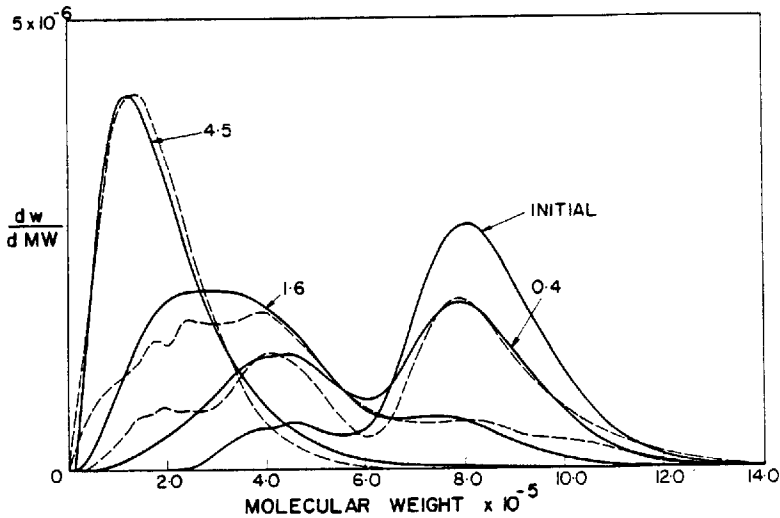
FIG. 4. Molecular weight distributions calculated from the Gaussian breakage model (r = 0.15) (solid lines). The broken lines are the experimental distributions from Fig. 1. The parameter is DI.

ACKNOWLEDGMENTS

APPENDIX

a. Random Breakage

Equation (2), when applied to the case of random breakage of polymer molecules $[Q(y,x) = 1/(y - 1)]$, can be simplified in the following manner:

For $1 \leq x \leq n$, the right-hand side of Eq. (2) becomes

$x = 1$ $2[P(t,2)(1/1) + P(t,3)(1/2) + P(t,4)(1/3) + ... + P(t,n)(1/n - 1)] - P(t,1)$
$x = 2$ $2[P(t,3)(1/2) + P(t,4)(1/3) + ... + P(t,n)(1/n - 1)] - P(t,2)$
$x = 3$ $2[P(t,4)(1/3) + ... + P(t,n)(1/n - 1)] - P(t,3)$
.
.
.
$x = n - 1$ $2[P(t,n)(2/n - 1)] - P(t,n - 1)$
$x = n$ $- P(t,n)$

Combination of the simplified form with the left-hand side of Eq. (2), for the applicable x, yields n equations, each of which can be solved for $f_n(t + 1,x)$. This array of equations is particularly suited for computer calculations.

b.   Center Breakage

Because breakage is allowed only at DP_r intervals, it is necessary to define what is meant by center breakage when DP/DP_r is odd. In this case center breakage will be taken to mean that a molecule with DP of $(2u + 1)DP_r$ breaks into fragments of length uDP_r and $(u + 1)DP_r$. Therefore, the number of molecules of length uDP_r, for any u, is increased by one from the breakage of molecules of length $(2u + 1)DP_r$ and $(2u - 1)DP_r$, and is increased by two molecules from the breakage of the molecules of length $2uDP_r$. It then follows that $Q(y,u) = 1/2$ when $y = 2u - 1$ or $y = 2u + 1$; $Q(y,u) = 1$ for $y = 2u$; and $Q(y,u) = 0$ for all other values of y.

For $1 \le x \le n$, the right-hand side of Eq. (2) becomes

$x = 1$ $2[P(t,2)(1) + P(t,3)(1/2)]$ $- P(t,1)$
$x = 2$ $2[P(t,3)(1/2) + P(t,4)(1) + P(t,5)(1/2)] - P(t,2)$
$x = 3$ $2[P(t,5)(1/2) + P(t,6)(1) + P(t,7)(1/2)] - P(t,3)$
.
.
.

$$\begin{bmatrix} x = n/2 \quad\quad 2[P(t,n - 1)(1/2) + P(t,n)(1)] \quad\quad\quad\quad - P(t,n/2) \\ \text{(for n is even)} \end{bmatrix}$$

$$\begin{bmatrix} x = \dfrac{n + 1}{2} \quad\quad 2[P(t,n)(1/2)] \quad\quad\quad\quad\quad\quad - P(t,\dfrac{n + 1}{2}) \\ \text{(for n is odd)} \end{bmatrix}$$

$$x = \frac{n + 1}{2} \qquad\qquad\qquad - P(t, n/2 + 1)$$

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$x = n - 1$ $- P(t, n - 1)$

$x = n$ $- P(t, n)$

The number distribution $f_n(t + 1, x)$ is then calculated in the same manner as outlined above for random breakage.

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