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Degradation of Polystyrene in Solution by Ultrasonation—A Molecular Weight Distribution Study

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ABSTRACT

Ultrasonically induced degradation of polystyrene in tetrahydrofuran solutions has been studied. Four narrow molecular weight distribution (MWD) samples, a material with a wide MWD, and a bimodal MWD sample were degraded at various concentrations, temperatures, and ultrasonic intensities. The MWDs after a number of ultrasonation time periods were obtained from gel permeation chromatograms corrected for instrumental spreading. Degradation index DI, defined as the number of bonds broken per original number of molecules, has been used to describe the extent of degradation. The results of the experiments were used to determine the values of two parameters occurring in the degradation model developed previously. It was found that the course of the changes in MWDs predicted by the model are in good agreement with those observed experimentally when the following values of the model parameters are used. The probability of scission of a molecule with molecular weight M is proportional to the product of its number fraction and the 1.25 power of M.

The probability density function of the location of scission along the chain is described by a Gaussian curve centered at the midpoint of the chain with a standard deviation of 35% of the chain lengths and truncated at the chain ends. The agreement between observed and calculated MWDs was good for degrees of degradation as high as DI = 15. The course of the changes in MWDs was independent of the initial MWD and of the experimental conditions of concentration, temperature, and sonation intensity and, therefore, independent of the rate of degradation which varied greatly.

INTRODUCTION

The study reported in this paper is concerned with the breaking of bonds of polymer molecules in solution by the action of ultrasound. This phenomenon has been known since 1933. Since that time more than 100 papers have appeared on this subject. In the experiments on which these reports are based, ultrasonic degradation was usually detected and measured by viscosity measurements from which, in most cases, average molecular weights were calculated. It has been shown by chemical means [1] that free radicals are formed during the degradation of polymer. Therefore, the consumption of a free-radical scavenger is a direct measure of bond breakage. A few authors have applied this method using the stable free radical 2,2-diphyenyl-1-picrylhydrazyl (DPPH) to follow the degradation process [1-4]. This technique provides better information than the measurement of the decrease in the viscosity-average molecular weight because it yields the number of bonds broken or, equivalently, the number of molecules present. Viscosity averages of molecular weight depend not only on the number of molecules, but also on the shape of the molecular weight distribution (MWD) which changes as the degradation proceeds.

It is obviously most informative to follow directly the changes in MWD throughout the degradation. Some authors reported these changes by methods which only coarsely describe them. Not until the recent development of gel permeation chromatography (GPC) was a convenient and reliable method for measuring MWD available. Over the last few years the results of studies in which this analytical technique was used have been published [5-8].

In the study reported here, GPC was used to measure MWD as a function of ultrasonation time under a variety of experimental conditions to gain insight into the mechanism of the chain rupture process. Since a quantitative measure of the degree of degradation is calculated from the number-average molecular weight M_n, obtained from the MWD, it is necessary that the distributions be as accurate as possible. The GPC curves were therefore corrected for instrumental spreading. Polystyrene was chosen as the polymer for this study since it is available as well-characterized narrow MWD samples. These materials were used for both the degradation experiments and for the calibration of the gel permeation chromatograph. Tetrahydrofuran was the solvent. The degradation was studied of four narrow MWD polystyrene samples, a material with a wide MWD, and a sample with a bimodal MWD over a range of concentrations, temperatures, and ultrasonic intensities. The resulting MWDs are compared with MWDs calculated from a degradation model. This model, developed in a previous paper [9], contains two adjustable parameters which are evaluated for one of the polystyrene samples with narrow MWD. It is then shown that the course of the changes in MWD can be described by a single set of values for the parameters which are independent of the MWD of the starting material and of the experimental conditions during degradation, at least within the range of the conditions investigated. The effect of these experimental conditions on the rate of degradation will be the subject of a separate paper.

EXPERIMENTAL

Apparatus for the Ultrasonation of Polymer Solutions

The experimental arrangement for the ultrasonation of polymer solutions consisted of four main parts: an ultrasonic transducer, an ultrasonic generator to drive the transducer, circuitry for the measurement of the input power, and a jacketed cell containing the solution.

Ultrasonic Transducer

The piezoelectric probe-type transducer operated at a nominal frequency of 22 kHz. The transducer was designed by Mr. A. J. Last of the Ultrasonics Section of the Ontario Research Foundation. The unit had a narrow frequency bandwidth at its resonant frequency. The main part of the probe body was fabricated from a titanium alloy (90 T, 6 Al, 4 V). The probe tip of the same material was screwed into the main body and could easily be replaced when its surface became eroded by cavitation. The tip area was 1.0 cm^2. The probe was calibrated by a calorimetric method. The sonic output was found to be 85% of the electrical input power at the resonant frequency.

Ultrasonic Generator

The generator was a high power, variable frequency instrument supplied by Macrosonics Corporation (model MC 500-1). It can provide an input power level of up to 500 W at frequencies from 10 kHz to 1 MHz. The output impedance of the generator was matched to that of the ultrasonic transducer.

Input Power Measurement Circuitry

The power applied to the solutions was determined accurately from the measured input power to the transducer and the transducer efficiency. The voltage and current waveforms of the transducer circuitry were compared on a dual-beam oscilloscope. The current waveform was produced by measuring the voltage across a fixed noninductive resistor. The generator was tuned by varying the frequency so that the two waveforms were in phase. It was, therefore, not necessary to measure the phase angle.

Sample Cell

Ultrasonation of the polymer solutions was carried out in a conical jacketed glass cell of about 80 ml. This cell has three external glass circulation arms from the vessel bottom to about 3/4 of its height. These arms ensure complete mixing of the solution during ultrasonation and aid in heat transfer to the cooling water circulating in the jacket. Flow through the arms is provided by the ponderomotive action of the sound field on the solution.

The cell is held in place by a framework to which a screw mechanism is attached for the raising and lowering of the transducer. The mechanism is provided with a scale which enables the operator to ensure that the tip of the transducer is immersed in the solution to the same depth in each experiment.

The jacket of the cell is connected to a constant temperature bath. The temperature of the solution is measured by a small (0.043 in. o.d.) stainless steel encapsulated copper constantan thermocouple.

Procedure for the Ultrasonation of Polymer Solutions

A solution of the required concentration of polystyrene in tetrahydrofuran (THF) was made up. The volume of the solution was sufficient to provide for a predetermined number of 50 ml samples, namely one for each solution to be irradiated for different time periods, plus one 50 ml sample, which was not irradiated, as a control.

For each irradiation time the following procedure was followed. Fifty milliliters of solution were introduced into the sample cell and brought to a temperature about 10° C above that at which the experiment was to be performed. For most experiments about 1 mg of DPPH was added to the sample in the cell to repress recombination of polymer radicals formed on scission. It was found that this amount was sufficient to ensure that the characteristic purple color of the radical persisted throughout the ultrasonation period. Although in two series of experiments no systematic differences could be detected in the MWDs after various irradiation time periods between samples sonated in the presence and in the absence of DPPH, this compound was added routinely as a precautionary measure since it had not been established that no recombination occurs under all experimental conditions.

After the addition of DPPH the transducer tip was lowered to a depth of 3 cm below the surface of the solution in the cell. The cell jacket was connected to a constant temperature bath. The temperature of this bath was preset at a level which would maintain the sample solution at the required experimental temperature while the ultrasonic transducer was in operation. This temperature was found empirically; it is about 6°C lower than the reaction temperature. When the temperature in the cell reached a value slightly higher than the experimental temperature, the transducer was activated. The generator was immediately tuned so that the voltage and current waveforms were in phase. The solution temperature stabilized to the desired experimental temperature in less than 30 sec.

At periodic intervals during the experiment the current and voltage waveforms were checked on the oscilloscope to ensure that they were in phase. The generator was retuned if required.

After irradiation the samples (including the unirradiated control sample) were evaporated to dryness. The polymer was redissolved in 10 ml of THF and precipitated by pouring into 1 liter of methanol. It was recovered by vacuum filtration using a Millipore filter having a pore size of 0.2 μ. The samples were then dried at 50°C for 48 hr under a pressure of about 1/3 atm. This procedure was tested by identical treatments of low MW, narrow MWD polystyrenes. The recovery of polymers with MWs of 10,300, 4,800, and 2,000 was 95, 87, and 49%, respectively. It can, therefore, be concluded that practically all the polymer species having MWs greater than about 3000 are recovered in this procedure.

Determination of Average Molecular Weights and Molecular Weight Distributions

Experimental Technique

The MWs and MWD of the recovered polymer samples were determined by GPC, using a Waters Model 200. The following conditions apply to calibration and sample analysis: eluting solvent, tetrahydrofuran; flow rate, 1.00 ± 0.03 ml/min; oven temperature, 25.0 ± 0.5°C; sample concentration, 1.0 g/liter; sample volume, 1.00 ml; and column specifications, 4 columns with nominal pore sizes of 1×10^{7}, $(1.5 \text{ to } 7) \times 10^{5}$, $(1.5 \text{ to } 5) \times 10^{4}$, and $(0.7 \text{ to } 2) \times 10^{3}$ Å.

Calibration was performed using eleven narrow MWD polystyrene standards having peak molecular weights of 900, 2,030, 4,800, 10,000, 19,750, 50,000, 97,200, 171,000, 402,000, 830,000, and 1,987,000. These values are those of the supplier (Waters Associates). The calibration curve was determined following the procedure proposed by Boni et al. [10]. The instrumental spreading parameter was calculated by the method of Tung and Runyan [11]. The chromatogram heights were recorded on a digital printer at 0.5 ml intervals of elution volume, i.e., every 0.1 of an elution count (5.0 ml).

Evaluation of the Chromatograms

In order to follow the degradation process accurately, absolute MWds must be calculated from the GPC chromatograms. The procedure for calculating the MWD from a chromatogram is comprised of two parts: correction of the chromatogram for instrumental spreading and conversion of the corrected chromatogram to the MWD.

The experimental chromatogram was corrected for instrumental spreading to yield the corrected chromatogram by means of an iterative technique developed by Chang and Huang [12]. In this method it is assumed that each molecular weight species is spread according to a symmetric distribution on the elution volume axis. The chromatogram is then considered to be an envelope of the sums of the contributions of the individual components. The chromatogram which results when the effect of instrumental spreading is applied to the corrected chromatogram will be termed the back-calculated envelope. The corrected chromatogram is considered true when the back-calculated envelope and the experimental chromatogram coincide.

It was found for samples with large changes in slope of their MWDs that, if the experimental chromatogram is used as the initial estimate for the corrected chromatogram in the iterative calculations, then the procedure did not result in convergence to a corrected chromatogram. Artificial oscillations in the regions with high values of the second derivative of the MWD were produced which could not be eliminated by continuing the iterative computations. For samples with narrow peaked MWD, the experimental chromatogram differed considerably more from the corrected chromatogram than is usually the case. However, by using a different initial estimate, the chromatograms for narrow MWDs could be successfully corrected by the method of Chang and Huang. For this estimate a Gaussian distribution was taken which is much narrower than the experimental chromatogram and centered at its peak. With this initial estimate the results converged to corrected chromatograms even for samples with large changes in slope of their MWDs. The iterations were stopped when the back-calculated envelope and the experimental chromatogram agreed to within 1% of the peak height. Only for very few points in a few chromatograms was a larger difference (up to 2.5%) accepted for reasons of computer costs. Artificial oscillations were not completely eliminated by using this procedure, but they were very considerably reduced.

The corrected chromatograms were then converted to normalized molecular weight distributions. The nonlinearity of the calibration curve was taken into account. All calculations were programmed in Fortran language and executed on an IBM 360/75 digital computer.

As a check on the validity of the correction procedure described above, two polymers were tested. The MWDs of these materials were such that they would provide a severe test of the correction method. The test consisted of reverting the MWDs obtained to their respective chromatograms by back-calculation using the GPC calibration curve. The appropriate spreading correction was then applied to calculate the uncorrected chromatograms. These back-calculated "original" chromatograms were used as input for the correction procedure. The corrected chromatograms which resulted were converted to their respective MWDs. For a mixture of equal parts of narrow MWD polymers with nominal MWs of 860,000 and 160,000 the original MWD and the back-calculated MWD were virtually indistinguishable. Their M_n values differed by 0.8%. For a slightly degraded wide MWD polymer with a shoulder at about half the MW of the main peak, the two distributions were slightly different; their M_n values differed by 4%. It may, therefore, be concluded that the method of Chang and Huang for spreading correction, when used with an appropriate initial estimate for the corrected chromatogram, yields adequately reliable MWDs.

Materials

Polymer Samples

Molecular weight data of the polystyrene samples used are listed in Table 1.

Solvent

Pure benzene was initially used as solvent. However, a dark brown floc was formed on ultrasonic irradiation of high intensity in this solvent. All data reported here were obtained from solutions in tetrahydrofuran, which showed no change after long and intense ultrasonation.

MODEL FOR THE DEGRADATION OF POLYMERS

In a previous paper [9] a general computer simulation model was developed 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 the probability that on rupture of this molecule a fragment of a particular length will be formed. The treatment is general and applicable to any initial MWD for any form of both probability distributions.

TABLE 1. Molecular Weights of Samples

	Values from supplier[a]			Values obtained in this study[b]		
Nominal MW $\times 10^{-3}$	$M_w \times 10^{-3}$ from light scattering	$M_n \times 10^{-3}$ from osmometry	M_w/M_n	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
860 (Batch no. 6a)	862	735	$\simeq$ 1.15	794	736	1.08
498 (Batch no. 5a)	507	404	$\simeq$ 1.20	494	444	1.11
160 (Batch no. 1a)	160[c]	-	-	163	153	1.07
97 (Batch no. 4a)	96.2	97.6	-	94.7	85.0	1.11
Wide MWD[d]	258 288[e]	136	2.1	270	125	2.16

[a] Pressure Chemical Co., Pittsburgh, Pa.

[b] These values depend on the calibration curve of the chromatograph (see text) and on the correction technique used. Agreement between these values and those of the supplier indicates little more than the validity of the correction procedure.

[c] Viscosity average MW.

[d] Standard Sample 706 supplied by National Bureau of Standards, Washington, D.C.

[e] From sedimentation equilibrium.

It was shown that the number fraction distribution $f_n(t,x)$ after t scissions of polymer molecules can be calculated from the following relation:

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

where x is the degree of polymerization (DP), t is the number of breaks of polymer chains, and p(x) is a weighting factor describing the relationship between probability of break and the DP of the polymer molecules. $A(t)p(x)f_n(t,x)$ is the probability of choosing a molecule of DP x to rupture after break t. For convenience this product of three terms will be represented by P(t,x). A(t) is a normalization factor which arises from the fact that P(t,x) is a probability and, therefore,

$$\sum_{x=1}^{\infty} P(t,x) = 1 \qquad (2)$$

Q(y,x) is the 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 is the initial number of molecules. The total number of molecules after t breaks is then N + t.

With Eq. (1), $f_n(t + 1,x)$ 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. (2) is satisfied.

For comparison with the experimental data of this investigation, the weighting factor p(x) was assumed to be x^s. Thus the probability P(t,x) of choosing a polymer molecule for rupture is proportional to the s-th power of its MW. It is known from the literature [4, 7, 8, 13-16] that the chains preferentially break near their center. It has also been shown [9] that scission of molecules exclusively at their center leads to MWDs incompatible with observed distributions. Therefore, the probability distribution Q(y,x) of the site of breakage along the chain was taken to be a Gaussian distribution about the midpoint with the fraction r of the chain length as standard deviation and truncated at the ends of the molecules.

Thus

$$P(t,x) = A(t)x^{s}f_{n}(t,x)$$

and

$$Q(y,x) = \{ry(2\pi)^{\frac{1}{2}}\}^{-1}\exp\{-(x - y/2)^{2}/2(ry)^{2}\}$$

The model thus contains two adjustable parameters: r and s.

For convenience the term degradation index (DI), defined as the ratio of the number of bonds broken to the original number of molecules, is introduced to describe the extent of degradation. It can be calculated from the number-average molecular weight of the original polymer $M_n(0)$ and that of the degraded sample $M_n(t)$ after t breaks by means of

$$DI = \frac{M_n(0)}{M_n(t)} - 1$$

RESULTS AND DISCUSSION

Precision and Reproducibility of Data

In order to estimate the precision of the GPC analysis, 14 independently determined MWDs of the 860,000 MW standard were compared. The coefficient of variation of the M_n values was found to be 7%. Braks [17], using the same GPC and column set, has reported a coefficient of variation for M_n of 4% for a sample with $M_n = 140{,}000$ and $M_w/M_n = 1.98$. These coefficients are in agreement with those of Hudson [18] who reported that "typical 2-sigma units" for moderately skewed distributions are ~15% for M_n and ~6 to 8% for M_w.

The reproducibility of the data reported here can be judged from Fig. 1 which shows the MWDs obtained in duplicate experiments on the 160,000 MW standard polymer. The lines and the symbols depict different experiments. A comparison of molecular weight averages is presented in Table 2. The figure and table show that both the experimental procedure and the method of analysis reproduce well. The differences are about the same as the accuracy that can be achieved in gel permeation chromatography.

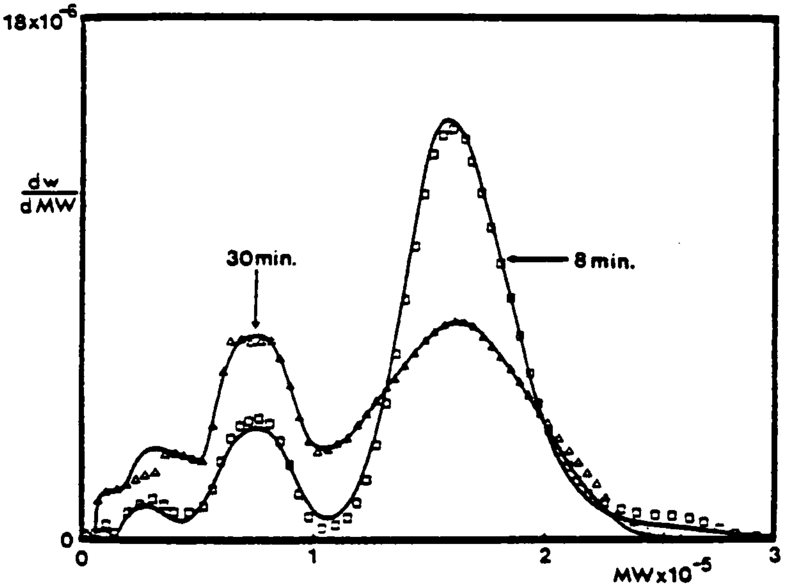

FIG. 1. MWD after 8 and 30 min ultrasonation. Polymer nominal MW 160,000. Lines and symbols are duplicate experiments. Concn 0.088%, temp 35°C, and power 29.5 W/cm^2.

General Results

For a typical experiment the changes in M_n, M_w, and M_z as a function of ultrasonation time are shown in Fig. 2. The trends in this figure are similar to those found in the literature [19-21], i.e., an initial rapid decrease in MW followed by a period of decreasing rate of degradation. The experimental MWDs as a function of time for this experiment are depicted in Fig. 3. The original distribution is the average of eight measurements of the undegraded polymer. This figure illustrates the effect of ultrasonation on the MWD. The following features can be distinguished:

1. The decrease in the peak of the original MWD, which remains at about the same MW.
2. The development of a maximum at a MW of about 400,000, which on further sonation decreases and then vanishes.
3. The development of a low MW maximum at about 200,000 MW, which shifts to lower MWs as the ultrasonation time increases.

TABLE 2. Comparison of Molecular Weight Averages for Two Sets of Duplicate Experiments

Experiment No.	Sonation time (min)	$M_n \times 10^{-3}$	Difference (%)	$M_w \times 10^{-3}$	Difference (%)
C1[a]	8	123		150	
C2[a]	8	121		152	
			-1.6		+1.3
C1	30	80.3		123	
C2	30	83.3		127	
			+3.6		+3.2
A5[b]	8	167		306	
A7[b]	8	168		290	
			+0.6		-5.2
A5	15	141		219	
A7	15	128		207	
			-9.2		-5.5
A5	30	100		154	
A7	30	93.6		151	
			-6.4		-1.9

[a] Starting material 160,000 MW standard, concentration 0.088%, temperature 35°C, power C_1 29, C_2 30 W/cm^2.

[b] Starting material 860,000 MW standard, concentration 0.18%, temperature 35°C, power 28 W/cm^2.

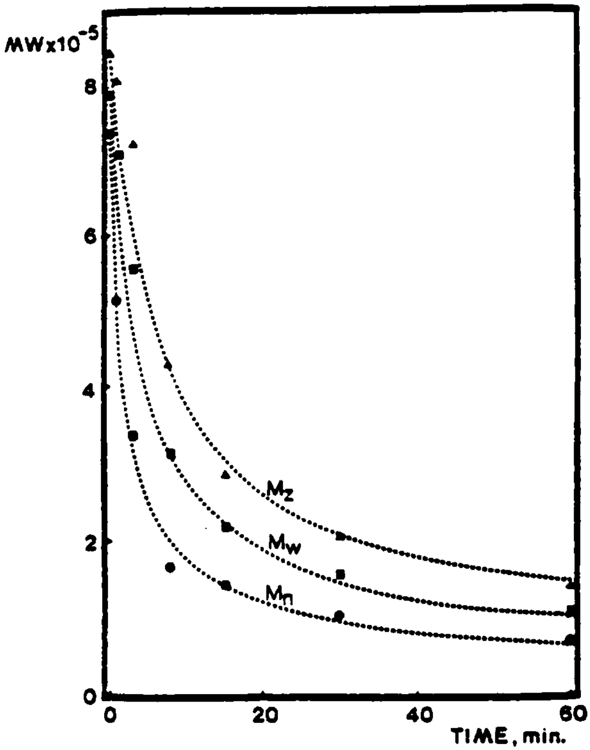

FIG. 2. MW averages as a function of ultrasonation time. Polymer nominal MW 860,000. Concn 0.18%, temp 35°C, and power 28 W/cm^2. Lines calculated from model.

Determination of Model Parameters

In order to compare experimental results with MWDs calculated from the degradation model, the values of the parameters r and s must be known. Their "best" values were determined from the experimental runs in which the 860,000 MW polymer was used as the starting material because more data were available for this polymer than for the others.

The ideal method of comparing model and experimental MWDs would be the application of a curve-fitting technique to the experimental MWD over its complete range of MW. This, however, is a cumbersome procedure because of the discrete nature of both the model calculations and the form in which the experimental MWDs are obtained

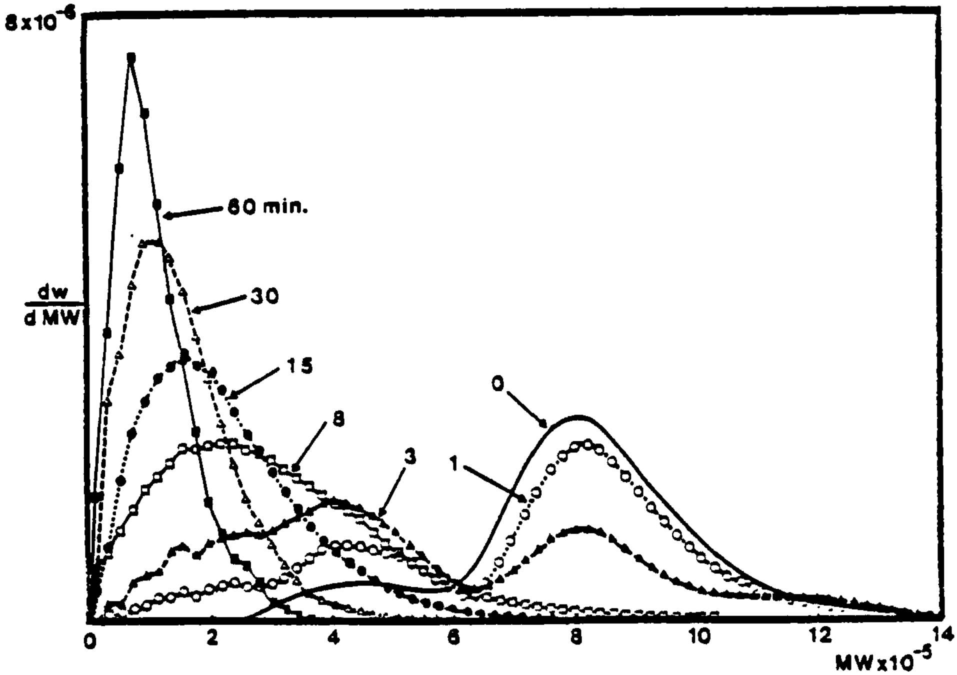

FIG. 3. MWDs after various ultrasonation times. Polymer nominal MW 860,000. Experimental conditions as in Fig. 2. Lines connect symbols.

from the correction procedure of the GPC data. It is, furthermore, difficult to establish a properly weighted criterion for fit or lack of fit because the accuracy of the MWD curves varies with MW and with the height of the curve. For these reasons another procedure was employed. In this method the heights of the experimental and model MWDs are compared at six particular points along the curve. These weight fractions and their corresponding DPs are considered to be characteristic features of the distribution. The features chosen are:

1. The weight fractions at the DP of the original peak and about at 1/2, 1/4, and 1/8 of this value: DP = 7700, 3900, 2000, and 1000.
2. The weight fraction of the maximum with the lowest DP.
3. The DP of this maximum, i.e., its location along the abscissa.

The model MWDs were compared with the experimental MWDs over a range of DIs for various sets of values of r and s using all available data for the 860,000 MW polymer irrespective of the experimental conditions prevailing during the degradation. The data used for the determination of r and s consisted of weight fraction data from 49 MWDs for each of the first four features (listed above under 1), and 32 points for the last two features (listed under 2 and 3). Fewer data were available for these last two because the lowest DP maximum cannot be clearly distinguished until DI reaches a value of about 2.5.

The data from the model used for comparison with these weight fractions were generated in the following manner. An average original MWD was calculated for the 860,000 MW polystyrene sample from eight replicate experiments. This average MWD is indicated by time = 0 or by DI = 0 in the figures. It was used as the input for the model. From the model, MWDs were computed at equal DI intervals for the range studied. The weight fractions at experimental DIs for each of the features were obtained by interpolation of the model data for each set of values of r and s considered. Plots were made of experimental weight fractions vs DI for the first five features and of DP vs DI for the sixth feature. The difference between the experimental weight fraction and the weight fraction at the same DI calculated from the model was computed. The differences were weighted by multiplying them with the

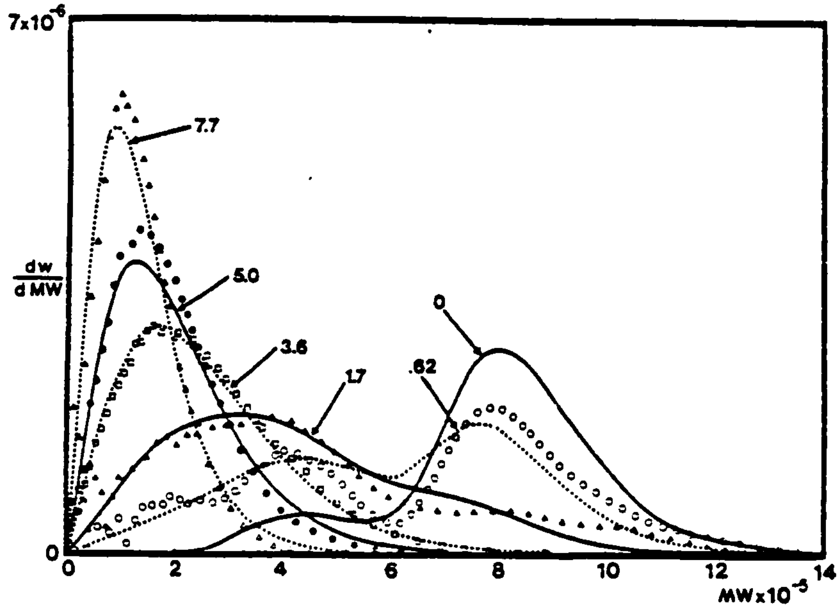

FIG. 4. Comparison of experimental MWDs (symbols) with MWDs calculated from model (lines) after degradation to various degrees. Parameter is degradation index. Polymer nominal MW 860,000. Concn 0.088%, temp 35° C, and power 28 W/cm^2.

DI values because of the cumulative nature of the degradation, i.e., the differences become more sensitive to the values of r and s as the number of breaks increases. The sum of squares of these weighted differences was obtained for each feature and each set of r and s values tested. These sum of squares values are taken to be a measure of the fit of the model MWD to the experimental distribution. Variations of r in steps of 0.05 and of s in steps of 0.25 were examined. It was found that the sum value was least for the combination $r = 0.35$; $s = 1.25$. This set of model parameters was used for all the calculated lines shown in the figures.

Comparison of Experimental MWDs with Model Distributions

In Figs. 4 and 5 the experimental MWDs (symbols) and the calculated MWDs (lines) are plotted for the 860,000 MW polymer after degradations. to 10 different values of DI. The original MWD (DI = 0) is also shown. In the model calculations the molecules were allowed to break at DP intervals of 100, i.e., $DP_r = 100$, see Ref. 9.

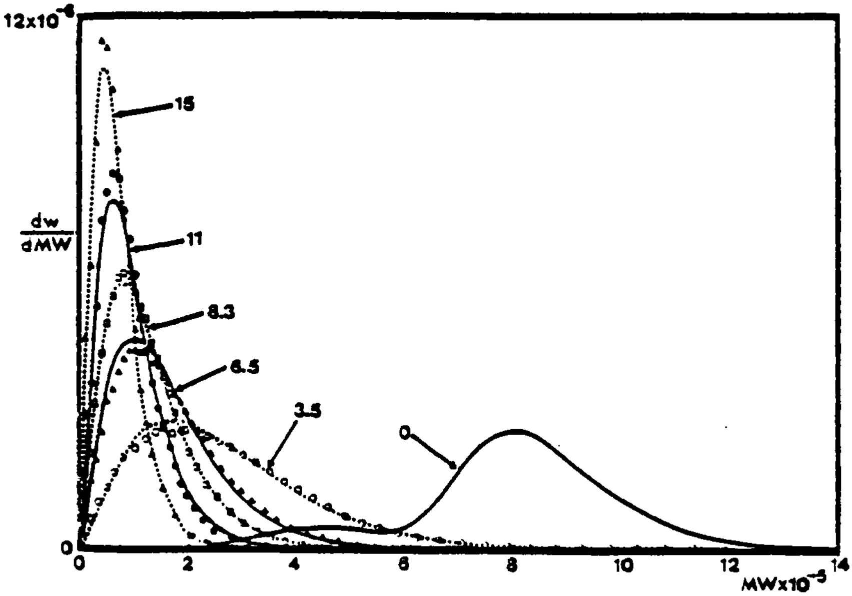

FIG. 5. Comparison of experimental MWDs (symbols) with MWDs calculated from model (lines) after degradation to various degrees. Parameter is degradation index. Polymer nominal MW 860,000. Concn 0.18%, temp 35°C, and power 111 W/cm^2.

The model MWDs are seen to follow the experimental MWDs quite closely even after, on the average, 15 scissions per original molecule have taken place. This agreement demonstrates the applicability of the model and confirms the selected "best" values of r and s. Differences between experimental and calculated distributions can be attributed to three sources listed in their probable order of importance:

1. Errors in DI resulting from inaccuracy of the experimental M_n value. The precision of M_n varies with MW; it is at best ±5%. In the majority of the runs the precision is lower.
2. Errors arising from the correction of the GPC chromatogram and its conversion to a MWD. (See Experimental Section.)
3. Differences associated with the simplicity of the model, particularly because the power dependence of the probability of scission on molecular weight is a form of dependence chosen for convenience rather than one based on insight in the mechanism of the scission process.

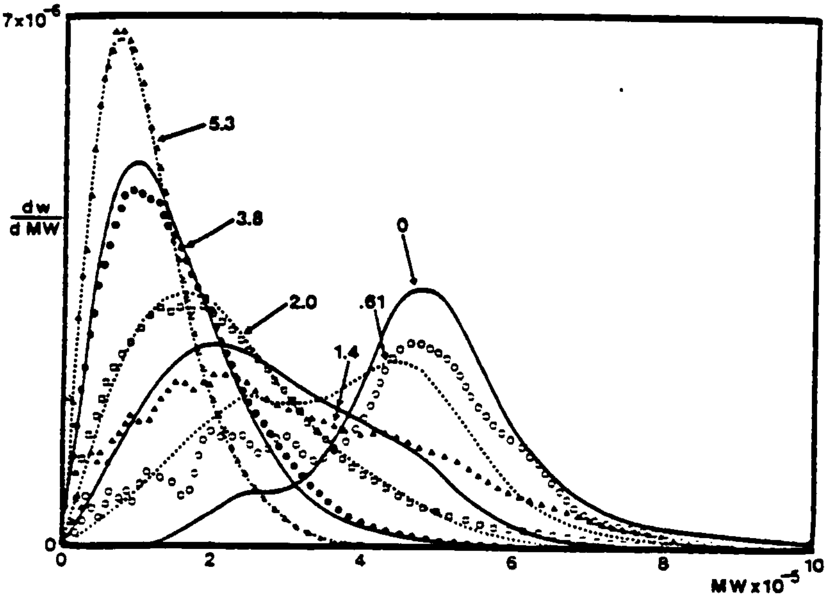

FIG. 6. Comparison of experimental MWDs (symbols) with MWDs calculated from model (lines) after degradation to various degrees. Parameter is degradation index. Polymer nominal MW 498,000. Concn 0.27%, temp 35°C, and power 26 W/cm².

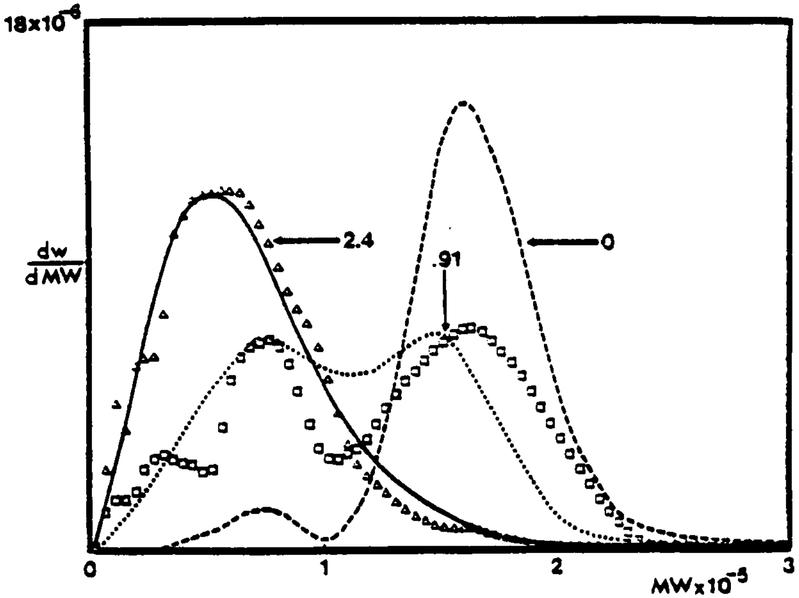

FIG. 7. Comparison of experimental MWDs (symbols) with MWDs calculated from model (lines) after degradation to various degrees. Parameter is degradation index. Polymer nominal MW 160,000. Concn 0.088%, temp 35°C, and power 29 W/cm^2.

The error in the measurement of DI is the most important cause of the differences between experimental and model MWD. If the DI is incorrect, the experimental MWD is being compared with a calculated distribution for a polymer degraded too much or too little. This point is indicated by the particularly good agreement between the MWDs at DI 3.5, 3.6, and 8.3 while those at DIs of 5.0, 6.5, and 7.7 show small discrepancies. The differences between model and experiment for DIs of 0.62 and 1.7 at the high MW tail of the distributions (MW > ~10^6) likely arise from errors in calculating the corrected chromatogram, which at the tails is very sensitive to baseline error. In the region of about 600,000 MW the model predicts a more pronounced minimum at low DI values than is observed. This is probably due to a combination of all three error sources listed above.

Figure 6 illustrates the fit of model (DP_r = 50) and experiment for a polymer with an initial MW of 498,000. The original MWD is the average of two experiments. The good fit for the curves with experimental DIs of 2.0 and 5.3 shows that the model is applicable to a different original MWD than that used for the determination of the

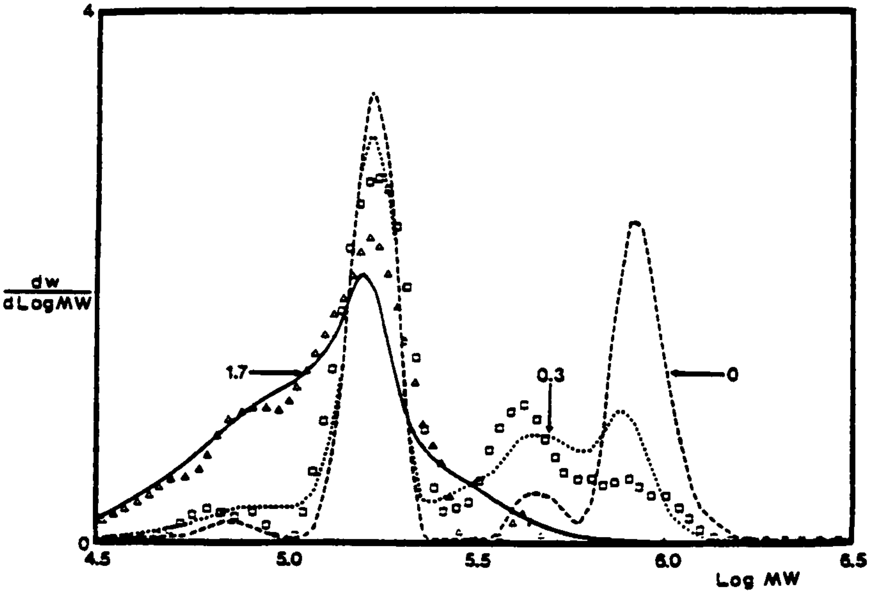

FIG. 8. Comparison of experimental MWDs (symbols) with MWDs calculated from model (lines) after degradation to various degrees. Parameter is degradation index. Polymer: equal weights of materials with nominal MWs 860,000 and 160,000. Concn 0.18%, temp 35°C, and power 28 W/cm^2. Note logarithmic MW scale.

optimum values of r and s. It is at least insensitive to the MWD of the sample.

The MWD results of the degradation of a polymer with a MW of 160,000 are shown in Fig. 7 ($DP_r = 20$). The original MWD is the average of three measurements. For the sake of clarity, only representative MWDs for two DIs have been plotted. The excellent agreement between model and experiment for the curves with DI = 2.4 lends substantial support to the model and the values of r and s. The differences between the model and experimental MWDs for DI = 0.91 may be attributed to the factors described previously; in particular the value of DI appears to be somewhat high.

The model MWDs and experimental MWDs for a sample made up of equal weights of the 860,000 and 160,000 MW materials is shown in Fig. 8 (note logarithmic abscissa scale). The peaks in the MWD are clearly separated. While the fit of model to experiment is not particularly good at MWs between the original peaks, generally

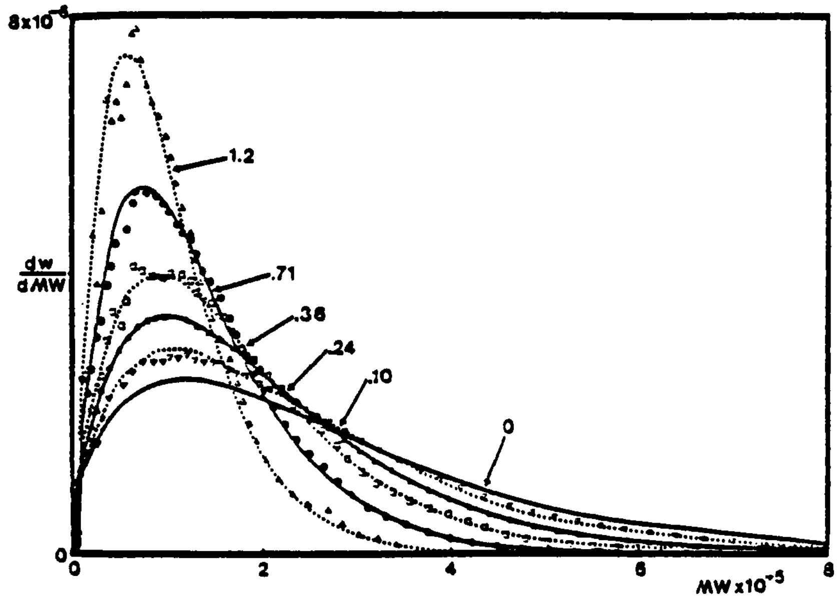

FIG. 9. Comparison of experimental MWDs (symbols) with MWDs calculated from model (lines) after degradation to various degrees. Parameter is degradation index. Polymer: Standard Sample 706 National Bureau of Standards. Concn 0.44%, temp 35° C, and power 28 W/cm^2.

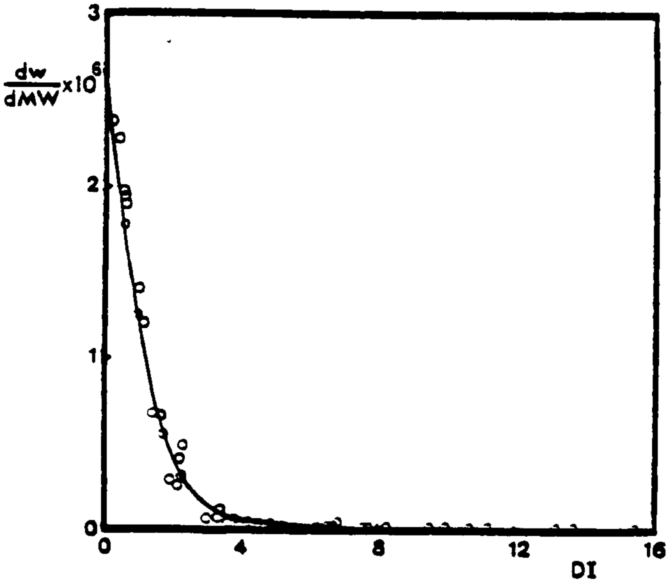

FIG. 10. Weight fraction at 7700 DP as a function of degradation index. Symbols: experimental results. Line calculated from degradation model. Polymer nominal MW 360,000.

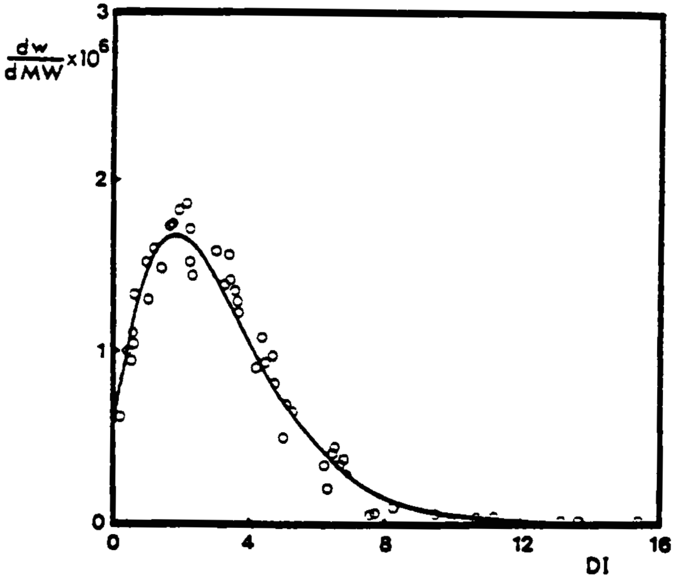

FIG. 11. Weight fraction at 3900 DP as a function of degradation index. Symbols: experimental results. Line calculated from degradation model. Polymer nominal MW 860,000.

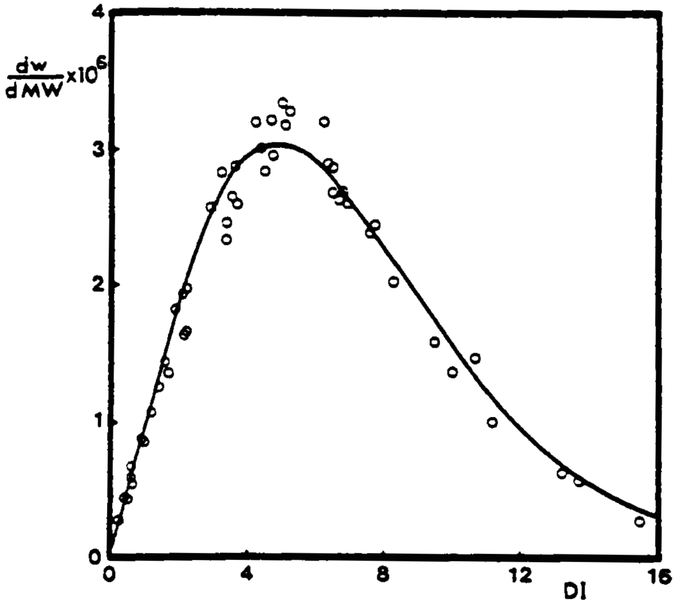

FIG. 12. Weight fraction at 2000 DP as a function of degradation index. Symbols: experimental results. Line calculated from degradation model. Polymer nominal MW 860,000.

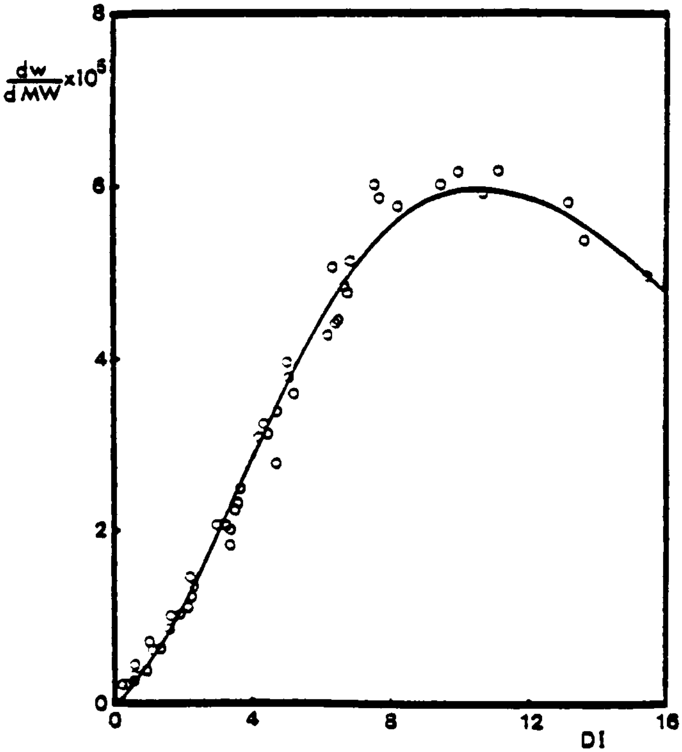

FIG. 13. Weight fraction at 1000 DP as a function of degradation index. Symbols: experimental results. Line calculated from degradation model. Polymer nominal MW 860,000.

speaking the model predicts the experimental MWDs reasonably well. The discrepancies can be attributed to the factors mentioned.

Figure 9 illustrates the agreement between the model (DP_r = 50) and experimental data for a sample with a wide MWD. The fit at every DI is very good.

For the experiments shown in Figs. 8 and 9, the original MWDs were calculated from single chromatograms and are, therefore, less reliable. Furthermore, the sharp changes in slope of the corrected chromatogram of the bimodal distribution cause difficulties in calculating experimental MWDs. The application of the model to the bimodal sample is a rigorous test. In order to predict the experimental MWDs with any degree of accuracy, the model must incorporate a correct relationship between the relative preference of breakage of different MW species and the distribution of the resulting fragments.

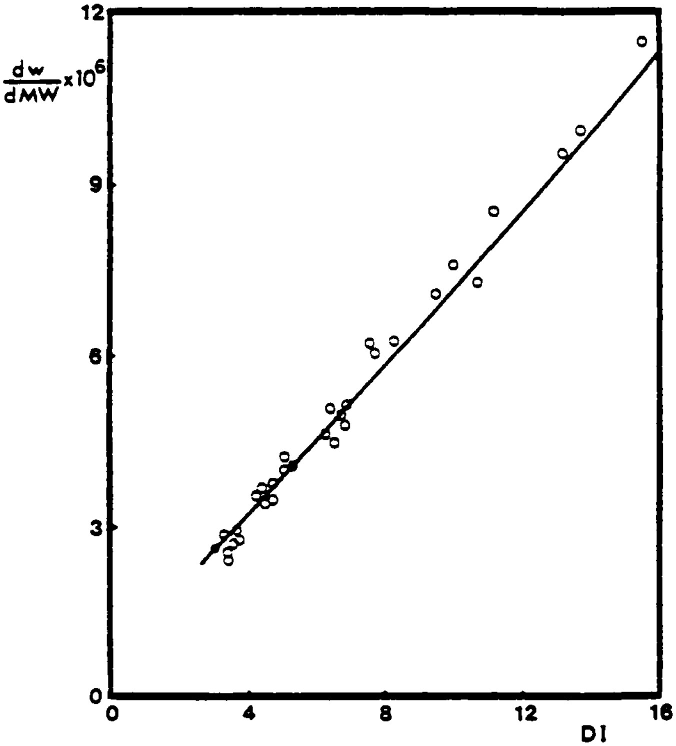

FIG. 14. Weight fraction at lowest MW maximum as a function of degradation index. Symbols: experimental results. Line calculated from degradation model. Polymer nominal MW 860,000.

The bimodal sample shows that the model has this capability. In view of these comments the agreement between the sets of MWDs in Fig. 8 is considered reasonably good.

In Figs. 10 to 15 the experimental data for all experiments with the 860,000 MW polymer (symbols) and the MWD changes calculated from the model (lines) with $r = 0.35$ and $s = 1.25$ are compared for the six features chosen. The experimental weight fractions were obtained over a range of DI from 0.10 to 15.5 under a variety of experimental conditions, namely: solutions with concentrations ranging from 0.05 to 1.0%, temperatures from 11 to 55° C, and power intensities between 30 and 110 W/cm^2. It is important to note that these plots demonstrate that the experimental conditions over the range studied had no effect on the course of the changes in MWD even though the rate of degradation varied greatly.

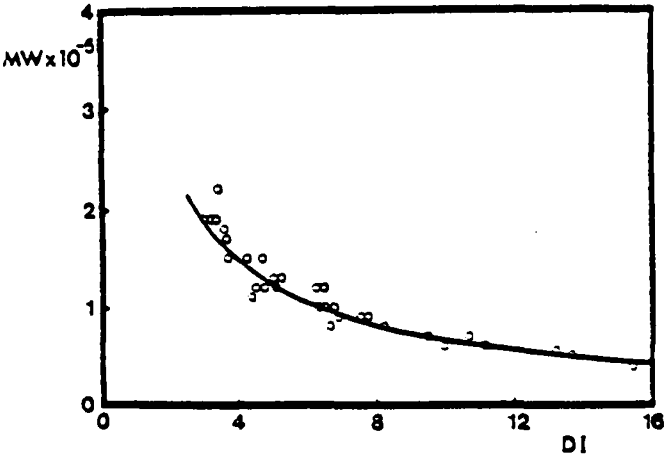

FIG. 15. Molecular weight of the lowest MW maximum as a function of degradation index. Symbols: experimental results. Line calculated from degradation model. Polymer nominal MW 860,000.

The lines in Figs. 10 to 15 are seen to predict successfully the change in weight fraction or DP with degradation. It should be emphasized that the model predicts the trends in the experimental values simultaneously for all six features. The scatter of the experimental values about the model curve is about the same for each feature. The model closely follows the production and subsequent degradation of material with DP 3900, 2000, and 1000. The height and location of the low DP maximum is seen to be equally well predicted.

In summary, the MWDs calculated from the model presented agree well with experimental distributions, even to high degrees of degradation, for polymers with a variety of initial MWDs regardless of the experimental conditions and, therefore, the rate of degradation.

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