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B. M. E. Van Der Hoff<sup>a</sup>; P. A. R. Glynn<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

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## The Rate of Degradation by Ultrasonation of Polystyrene in Solution

B. M. E. VAN DER HOFF and P. A. R. GLYNN

Department of Chemical Engineering  
University of Waterloo  
Waterloo, Ontario,  
Canada

### ABSTRACT

The rate of degradation by ultrasonation of polystyrene in tetrahydrofuran solutions has been measured at various concentrations, temperatures, and irradiation intensities. As reported earlier, the course of the changes in molecular weight distributions is independent of the molecular weight (MW) of the initial polymer and of the degradation conditions. Therefore, the time dependence of the extent of the degradation can be meaningfully compared for various reaction conditions and for polymers with different original MWs. The extent of the scission process was expressed in terms of the degradation index (DI), the ratio of the number of chain bonds broken to those initially present. The problem of the existence of a minimum MW required for sonic scission is considered and arguments are advanced in favor of the assumption of a minimum degradable chain length for the purpose of evaluation of degradation data. This minimum MW was found to be about 30,000. DI values were corrected for the "unbreakable" chain ends.

It was observed that curves representing the time dependence of DI were linear on double logarithmic plots for all experiments, DI being proportional to  $t^{0.85}$ . By shifting these lines along the time axis a master curve was obtained representing all data for all experimental conditions over almost three decades of DI. Thus the time-dependent rate of scission of any run relative to that under reference conditions can be expressed by a single value of the time transposition factor, a measure of the shift. This transposition factor provides a simple method for assessing the effects of experimental conditions. Some data are reported expressing the effect of MW of the initial polymer, concentration, temperature, and irradiation intensity on degradation rate.

## INTRODUCTION

In the extensive literature on degradation by ultrasonation of polymers in solution, the rate of degradation is often discussed and many numerical data are given for the rate of decrease of an average molecular weight or for a rate constant of degradation defined in various ways. These measures of rate are reported to be dependent on, among other variables, molecular weight (MW) [1-8], concentration [9, 10], temperature [9], pressure [11], and weakly dependent or independent of frequency of sonation [12, 13].

In general no cross-comparison is possible between the reports of different authors because of the various definitions of rate, its dependence on many experimental conditions, and also because the intensity of the irradiation absorbed by the solution is usually not given. Many authors [4, 14-16] quote nominal generator output power or approximate power level but fail to report transducer efficiency or irradiation power absorbed by the solution.

The most instructive definition of the extent of degradation is the number of chain bonds broken relative to the number of molecules initially present. The corresponding rate of scission is the time derivative of this extent of degradation. In a previous paper [17] we reported that the course of the changes in molecular weight distributions (MWD) was determined only by the extent of degradation as defined above and was independent of the initial MWD and of the experimental conditions of concentration, temperature, and sonation intensity and, therefore, independent of the rate of scission which varied greatly. It follows that this rate can now be analyzed separately from the sonation-time dependent MW for all samples and experimental conditions. This analysis is the subject of this report. Although scission rate decreases with irradiation time, analysis shows that it is possible to express rate of degradation, relative to that observed

for a reference experiment, by a single number. This factor, which is not unlike the well-known time-temperature shift factor,  $a_T$ , of linear viscoelasticity theory, is independent of the MW and MWD of the initial polymer and thus provides a simple measure for expressing the effect of experimental conditions on rate.

In the course of the development of this rate factor we will refer to a minimum MW required for scission. The existence of such a quantity has been assumed, demonstrated, and denied in the literature. Therefore, this concept needs discussion, which is presented in the following section.

### Theoretical Considerations

When a liquid is exposed to ultrasonic irradiation, a variety of phenomena occur. In a discussion of the question of whether a minimum degradable chain length exists, the topic of this section, it suffices to consider only two of these, viz., streaming and cavitation.

High intensity sound in liquids is accompanied by acoustic radiation pressure which results in steady-state flow known as acoustic streaming. This flow occurs near the walls of the containing vessel or near obstacles in the liquid. It has a vortex character. Flow also occurs in the bulk of a liquid exposed to a nonuniform sound field in which the size scale of the inhomogeneities is much larger than the sound wavelength. This flow phenomenon is called macrostreaming. The maximum velocities observed to date are of the order of several meters per second. Normally, however, relatively small velocities occur, less than centimeters per second. The theoretical and experimental work on macrostreaming to date has been surveyed by Nyborg [18].

Considerable flow activity on a microscopic scale has also been observed [19] in the neighborhood of air bubbles in irradiated liquids. These bubbles may resonate with the sound frequency. This phenomenon gives rise to small-scale eddies [20]. Local flow of this type is sometimes called microstreaming. Its scale is much smaller than the acoustic wavelength and the streaming velocities are of the order of meters per second [21, 22].

The effect of ultrasound irradiating into a liquid is to alternately increase and decrease local pressures. During the negative half of a pressure cycle the liquid may be subjected to a tensile stress, which, if sufficiently large, causes the formation of cavities. During the positive half of the pressure cycles, such cavities collapse. Degradative sonation of polymer solution is normally carried out under conditions where cavitation occurs. The continuous changes of volume on formation and collapse of cavities must be accompanied by local flow at greatly varying rates. Since cavities may be formed spontaneously in the liquid or around inhomogeneities (dust, polymer

molecules [23]), there is a considerable size distribution of cavities which further increases the range of local flow rates.

It is now generally accepted [4, 5, 15, 16, 23, 24-26] that degradation of polymer molecules by ultrasound is induced by the shear gradients occurring in the liquid adjacent to forming and collapsing cavities and by the shear actions which give rise to macro- and microstreaming. Such shear gradients cause friction between macromolecule and solvent. The friction forces accumulate along the chain, building up until they can overcome the backbone bond strength provided the chain is long enough.

The distribution of the shear gradients rapidly changes in time and space. Because of the macroscopic flow of the solution each polymer chain is, in time, subjected to a wide spectrum of shear gradients. Since a large number of factors affect the magnitude of these gradients, and because the spacial distribution of sonic energy constantly changes, it may be assumed that the time distribution of local shear energy densities has a Gaussian character. For a given chain length a minimum energy density is necessary for bond breakage. The minimum degradable length corresponding to each shear energy density is inversely related to this density, i.e., the longer the chain the smaller is the energy density which will cause scission because frictional forces build up along the chain. These considerations are illustrated in Fig. 1. The heavy solid line has the shape of an integral Gaussian distribution and indicates the relative frequency of occurrence, in a small volume element, of shear energy densities (SED) equal to or greater than the abscissa values of SED (increasing from right to left).

The probability of scission of a polymer chain is proportional to two factors. The first is the probability that the macromolecule is situated in a particular volume element. This probability is proportional to the MW of the chain. The second factor is the frequency of occurrence, in that same volume element, of a SED large enough to break the chain. This factor is proportional to  $F$ , the ordinate in Fig. 1. For Polymer I, with very high average MW and narrow MWD, the rate of bond breakage is closely proportional to the MW of the individual chains because  $F$  is about constant. However, for Polymer II, with low average MW, the rate of scission diminishes rapidly with MW of the individual molecular species. The MWD of Polymer II narrows on degradation while the width of the MWD of Polymer I initially remains about the same.

Recalling that the two quantities measured on the abscissa, SED and MW, are related, it is to be expected, on the basis of the distribution of SEDs, that the rate of chain scission should decrease rapidly as the MW becomes comparable to that corresponding to the inflection point of the  $F$  distribution. It is in principle possible to evaluate quantitatively the influence of a Gaussian distribution of

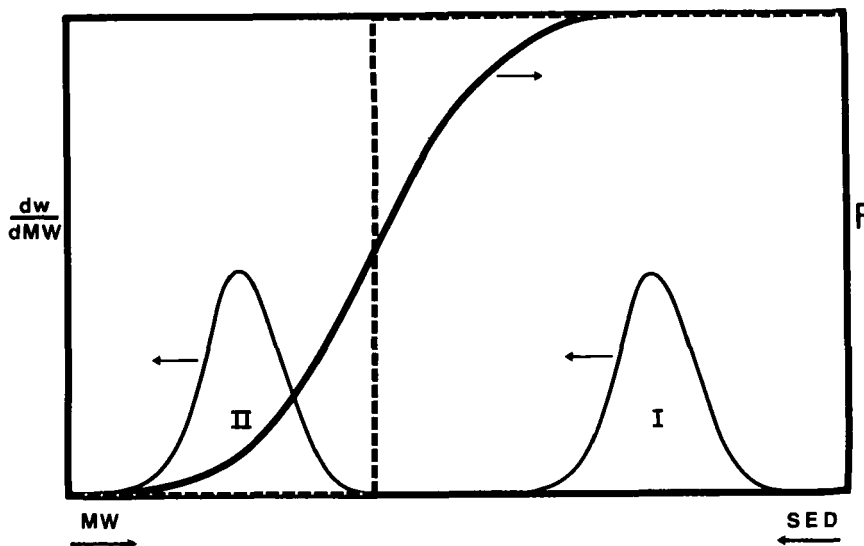


FIG. 1. Frequency of occurrence  $F$  of shear energy densities  $SED$  greater than  $SED$ s indicated along abscissa axis (increasing from left to right) and examples of molecular weight distributions. Dashed line: see text. Schematic.

$SED$ s on degradation rate. However, in order to do this at least three new parameters need to be introduced. Two parameters are necessary to describe the  $F$  distribution, viz., the mean and standard deviation. Further, a functional form needs to be assumed relating chain length and minimum  $SED$  necessary for breakage of a macromolecule of this length. Such a relation requires at least one parameter. In order to obtain meaningful values for these three or more adjustable parameters, a large number of accurate experimental data on  $MWD$ s of degraded, low  $MW$  polymers would be required. Such data are not available. Therefore, the  $F$  distribution is approximated by a step function (dashed line in Fig. 1). This is equivalent to assuming that there is a minimum degradable length, which is now the only adjustable parameter and its value can be determined from a reasonable number of data. It must be understood, however, that this length represents a quasi-minimum degradable  $MW$  which is introduced here as a matter of expediency in order to keep the number of adjustable parameters to a minimum.

## EXPERIMENTAL

Apparatus and Procedure

The apparatus and procedure have been fully described earlier [17]. It may suffice here to state that the frequency of the sonation was 22 kHz and that the power values quoted are those of the sonic power absorbed. The MWDs and average MWs were determined by gel permeation chromatography. The experimental chromatograms were corrected for instrumental spreading by the method described in the previous paper [17]. This method was checked for internal consistency.

Materials

Polystyrene samples with narrow MWDs from Pressure Chemical Co., Pittsburgh, Pennsylvania, were used. Their weight-average MWs ( $M_w$ ) and number-average MWs ( $M_n$ ) are listed in Table I of Ref. 17.

For the purpose of identification the polymers are indicated here by the letters A to F. Samples A, B, C, and D have nominal values of  $M_w \times 10^{-3}$  of 860, 498, 160, and 97, respectively. Polymer E consists of a mixture of equal weights of Polymers A and C. In addition, one experimental run was conducted with Polymer F: the Standard Sample 706 of the National Bureau of Standards, Washington, D.C. Its MWD is relatively wide:  $M_w/M_n = 2.1$ .

The solvent used was tetrahydrofuran.

## RESULTS AND DISCUSSION

Degradation Rate

The polymers used and the experimental conditions are listed in Table 1. The results after various sonation times are recorded in terms of the degradation index (DI) defined as the number of chain bonds broken relative to the initial number of molecules. The other results listed in Table 1 will be referred to below.

The analysis of the time rate of bond breakage was pursued in an empirical manner. The experimental data were first assessed with the purpose of finding the relation between DI and time. It was found that the lines representing experimental runs in double logarithmic plots of these two variables had the same shape for all experiments.

In the region  $DI = 0$  to 4, the slope for all runs is constant and approximately the same. For  $DI > 4$  the lines curve toward the time axis. If the lines are shifted parallel to this axis a master curve results, which is shown in Fig. 2. The transposition was carried out visually. The line through the data for the experiments on Polymer D, the sample with the lowest initial MW, was used as the reference curve onto which the other experimental lines were transposed, i.e., for Polymer D actual irradiation time and transposed time are the same by choice. The transposition factor,  $\tau$ , is listed in Table 1.

Allowing for experimental scatter, it is seen from Fig. 2 that all data have the same trend. Therefore, the functional relation between  $DI$  and time is not affected by the experimental conditions although the absolute rate of bond breakage does depend on these conditions. The points for all experiments up to  $DI = 4$  lie on a straight line irrespective of the MW of the initial or the degraded polymer. The straight line in the figure is the linear least squares fit for this portion of the data. The slope of the line is 0.83, i.e., the rate of breakage decreases somewhat with time. If in the breakage process only very small sections of the polymer chains partake,  $DI$  should be proportional to time as is indeed the case for scission by high energy  $\gamma$ -irradiation. Thus it seems indicated that fairly large sections of chains are involved in the breakage process and that the fraction of polymer molecules longer than these sections decreases with time.

For  $DI > 4$  the points fall below the line. Detailed inspection of the data shows that the lower the MW of the original polymer, the lower is the  $DI$  at which departure occurs. (The data for Polymer D with the lowest initial MW are indicated by circles.) Since at  $DI < 4$  the same functional relationship between  $DI$  and time holds for samples differing in initial MWs by a factor of 10, the same relationship is expected to hold for experiments on polymers with the highest initial MW degraded to  $DI$  values of more than 10. This is not the case.

The observations of a slope less than unity at  $DI < 4$  and the departures from the straight line in Fig. 2 for  $DI > 4$  prompted consideration of the assumption that a (quasi) minimum chain length is required for degradation in the sense and for the purpose expressed in the theoretical section above.

If such a minimum degradable length is assumed, then the end portions of polymer molecules cannot be sheared off. These unbreakable end portions should be ignored when counting the number of bonds present for a quantitative measure of degradation. The ratio of bonds broken to breakable bonds present is then calculated as follows.

The number of bonds broken  $N_b(t) = WN_A [1/M_n(t) - 1/M_n(0)]$ , where  $W$  is the weight of the sample,  $N_A$  is Avogadro's number, and  $M_n(t)$  is the number-average MW at time  $t$ . The number of breakable bonds where  $M_{\min}$  is the MW of the smallest breakable molecule,



TABLE 1. Experimental Conditions and Results of Ultrasonation of Polystyrene in Tetrahydrofuran Solution

Polymer	Experimental conditions		Transposition factor		Sonation time (min)	DI	DI*
	Conc (wt%)	Temp (°C)	Power (W/cm <sup>2</sup> )	$\frac{\tau}{\tau^*}$			
A	0.044	35	29	120	60	0.96	1.1
						2.2	2.5
						4.7	6.2
						6.2	9.0
						7.6	11.9
A	0.044 <sup>a</sup>	35	31	120	60	1.0	1.1
						2.2	2.6
						4.0	5.1
						5.6	7.7
						7.6	11.9
A	0.088	35	28	80	40	0.62	0.66
						1.7	1.9
						3.6	4.5
						5.0	6.8
						7.7	12.3
A	0.088 <sup>a</sup>	35	29	80	40	0.64	0.69
						1.9	2.2
						3.7	4.6
						5.0	6.7
						8.0	12.9

A	0.18	35	28	65	32	1	0.44	0.47
						3	1.2	1.3
						8	3.4	4.2
						15	4.2	5.4
						30	6.4	9.2
						60	10.0	15.8
A	0.18 <sup>a</sup>	35	30	65	32	1	0.52	0.56
						3	1.4	1.6
						8	3.4	4.2
						15	4.6	6.1
						30	6.7	10.0
A	0.18	35	28	65	32	8	3.4	4.2
						15	4.8	6.3
						30	6.9	10.3
A	0.44	35	28	30	17	1	0.24	0.25
						3	0.61	0.66
						8	1.6	1.8
						15	3.0	3.6
						30	5.1	6.9
A	0.44 <sup>a</sup>	35	29	30	17	1	0.17	0.18
						3	0.77	0.84
						8	1.8	2.1
						15	3.0	3.6
						30	4.8	6.4
A	0.88	35	27	24	14	3	0.55	0.59
						8	1.0	1.1
						15	2.2	2.6
						30	3.7	4.6
						60	6.5	9.6

(continued)

Table 1 (continued)

Polymer	Experimental conditions			Transposition factor		Sonation time (min)	DI	DI*
	Conc (wt%)	Temp (°C)	Power (W/cm <sup>2</sup> )	$\tau$	$\tau^*$			
A	0.18	11	27	130	70	3	2.3	2.7
						8	4.5	5.9
						15	6.7	9.9
						30	11.9	17.0
						60	13.0	24.9
A	0.18	55	27	25	14	3	0.59	0.63
						8	1.4	1.6
						15	1.9	2.2
						30	3.3	4.0
						60	5.2	7.1
A	0.18	35	54	120	60	3	2.3	2.6
						8	4.4	5.7
						15	6.8	10.1
						30	5.9	14.6
						60	13.0	24.3
A	0.18	35	111	210	100	3	3.5	4.4
						8	6.5	9.5
						15	8.3	12.2
						30	11.2	18.6
						60	15.1	32.5
B	0.27	35	26	25	15.5	3	0.61	0.69
						8	1.4	1.6
						15	2.0	2.6
						30	3.8	5.6
						60	5.3	8.2

B	0.55	35	28	18	10.5	3	0.42	0.47
						8	1.0	1.2
						15	1.5	1.8
						30	2.9	4.0
						60	4.4	7.2
						8	0.24	0.33
C	0.088	35	29	3.0	2.8	15	0.40	0.55
						30	0.91	1.3
						60	1.3	2.1
						120	2.0	3.6
						180	2.4	4.7
						8	0.26	0.36
C	0.088	35	30	3.0	2.8	30	0.84	1.2
						8	0.20	0.27
	0.18	35	29	2.6	2.1	15	0.29	0.39
C						30	0.63	0.93
	0.088	35	103	5.2	4.8	8	0.33	0.45
						15	0.62	0.89
						30	1.1	1.7
						60	2.0	3.7
						120	2.7	5.9
D	0.053	35	28	1 <sup>b</sup>	1 <sup>b</sup>	15	0.14	0.22
						30	0.23	0.37
						60	0.46	0.73
						120	0.78	1.43
						240	1.3	2.7

(continued)

Table 1 (continued)

Polymer	Experimental conditions			Transposition factor		Sonation time (min)	DI	DI*
	Conc (wt%)	Temp (°C)	Power (W/cm <sup>2</sup> )	$\tau$	$\tau^*$			
D	0.11	35	26	1 <sup>b</sup>	1 <sup>b</sup>	8	0.10	0.16
						15	0.16	0.26
						30	0.23	0.38
						60	0.42	0.73
						120	0.79	1.46
						720	2.2	8.1
E <sup>c</sup>	0.18	35	28	12	8.5	1	0.13	0.16
						3	0.30	0.37
						8	0.76	0.97
						15	1.2	1.7
						30	1.7	2.7
						1440	3.1	13.3
F <sup>d</sup>	0.44	35	28	3.2	2.5	3	0.10	0.13
						8	0.24	0.33
						15	0.36	0.53
						30	0.71	1.0
						60	1.2	1.9

<sup>a</sup>No DPPH was added to the solution.

<sup>b</sup>The degradation rate of Polymer D was the lowest observed. The DI-time plot for these experiments was chosen as the basis for the transposition, i.e., the transposition factor is unity.

<sup>c</sup>Polymer E consisted of a mixture of equal weights of Polymers A and C.

<sup>d</sup>Polymer F is the Standard Sample 706 of the National Bureau of Standards, Washington, D.C.

Its MWD is relatively wide:  $M_w/M_n = 2.1$ .

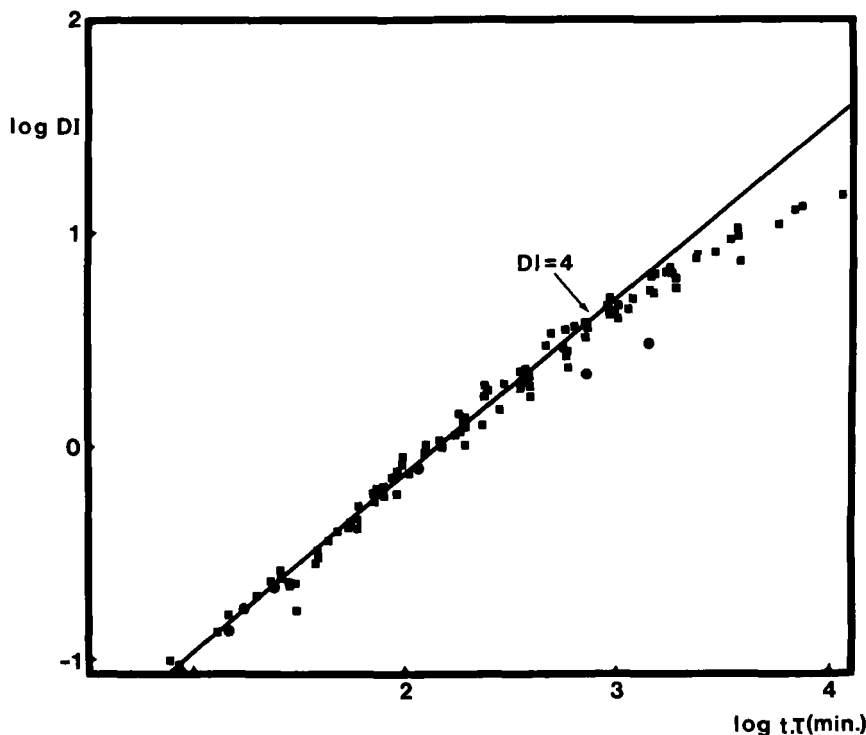


FIG. 2. Degradation index DI as a function of the product of time  $t$  and transposition factor  $\tau$ .

$$N_{bb}(t) = 2g_w(t)WN_A [M_{nb}(t) - M_{min}] / M_{nb}(t)M_1 \tag{1}$$

$g_w(t)$  is the weight fraction of molecules which have a MW greater than  $M_{min}$ , and  $M_{nb}(t)$  is the number-average MW of this weight fraction.

For most experiments  $g_w$  is close to unity throughout the runs and, therefore,  $M_{nb}$  is about equal to  $M_n$ . It can be derived from the above expressions that in these cases the number of bonds broken per breakable bond is

$$\frac{N_b(t)}{N_{bb}(t)} = \left[ \frac{M_n(0) - M_{min}}{M_n(t) - M_{min}} - 1 \right] / \frac{2 M_n(0)}{M_1} \tag{2}$$

It should be noted that the denominator is the total number of bonds per original molecule. Therefore the numerator resembles the degradation index defined earlier as the number of bonds broken per original molecule:  $DI \equiv [M_n(0)/M_n(t)] - 1$ . We now define the degradation index corrected for unbreakable bonds as the numerator in the above expression:

$$DI^* \equiv \frac{M_n(0) - M_{\min}}{M_n(t) - M_{\min}} - 1 \quad (3)$$

$DI^*$  is conceptually comparable to  $DI$  to which it reduces when  $M_{\min} = 0$ .

For some experiments the approximations  $g_w = 1$  and  $M_{nb} = M_n$  do not hold. Without these approximations the expression for the ratio  $N_b(t)/N_{bb}(t)$  is more complex than the one given above. Based on the fraction  $g_w$  of the total number of bonds per original molecule, the corresponding corrected degradation index is now given by

$$DI^* \equiv \frac{M_n(0) - M_{\min} M_n(t)/M_{nb}(t)}{M_n(t) - M_{\min} M_n(t)/M_{nb}(t)} - 1 \quad (4)$$

Double logarithmic plots of  $DI^*$  vs time were made and the data were transposed with the factor  $\tau^*$  for assumed values of  $M_{\min}$  from 20,000 to 35,000 at 5,000 MW increments. The plot for  $M_{\min} = 30,000$  yielded the best straight line for all the data. This plot is shown in Fig. 3. As in Fig. 2, experiments with Polymer D were used as the reference line for transposition of time by the factor  $\tau^*$ , the values of which are listed in Table 1 together with  $DI^*$  values. It is observed that the data fit a straight line rather well over almost three decades of  $DI^*$ . The least squares line is given by

$$DI^* = 0.0255(t\tau^*)^{0.85} \quad (5)$$

where  $t$  is the irradiation time in minutes. The standard deviation of log  $DI$  is 0.048. The exponent in Eq. (5) is about the same as that for the corresponding relation for the uncorrected  $DI$ , which is 0.83. It follows that the decrease in scission rate with time is not primarily due

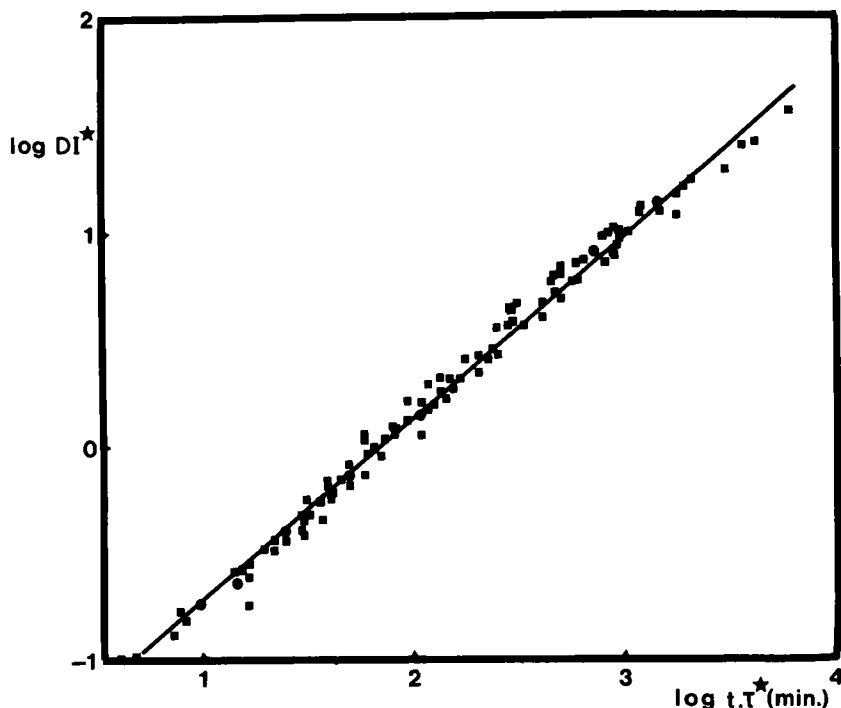


FIG. 3. Degradation index corrected for "unbreakable" chain ends  $DI^*$  as a function of the product of time  $t$  and transposition factor  $\tau^*$ .

to the increasing concentration of "unbreakable" chain ends. As discussed in the theoretical section, this decrease is the result of the distribution in time and space of local shear energy densities acting on polymer with decreasing average MW. This explanation is supported by a result obtained from analysis of the course of changes in MWDs on degradation [17], which course is independent of degradation rate. This analysis shows that the probability of breakage of a polymer chain is about proportional to its MW raised to the power 1.25.

Three MW averages for a typical experiment are shown in Fig. 4 as a function of sonation time. The dotted lines have been calculated from the initial MWD, the model reported earlier, and Eq. (5). It is seen that there is close agreement between the experimental data and the calculated curves.

That a master plot can be obtained by transposition along the time axis, in a manner not unlike the time-temperature shift for viscoelastic



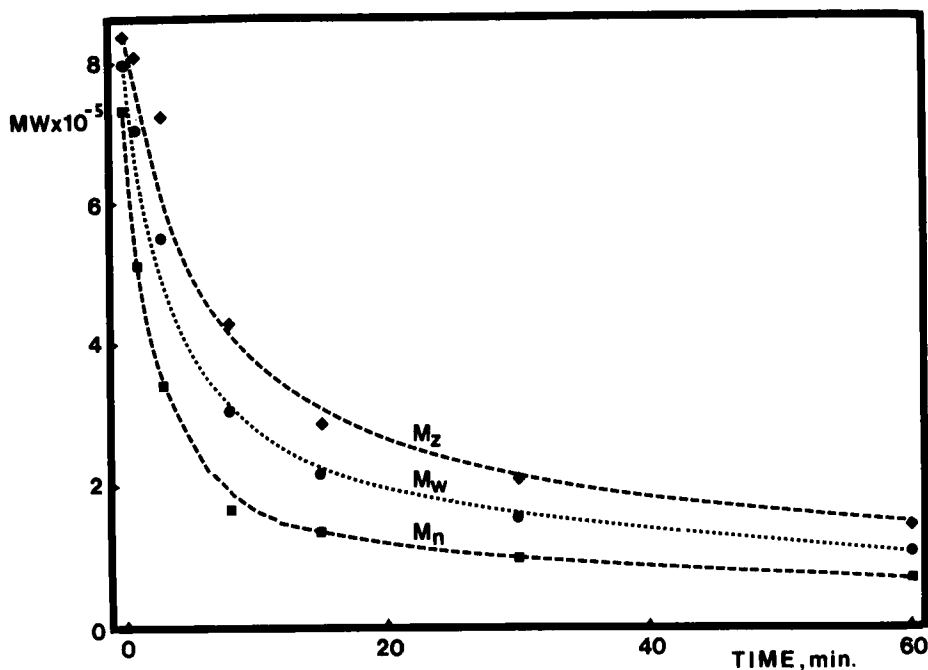


FIG. 4. Molecular weight averages as a function of sonation time. Polymer A, conc 0.18%, temp 35°C, and power 28 W/cm<sup>2</sup>.

properties, provides a convenient method for studying the effects of experimental conditions on the degradation process, because these effects can now be expressed in terms of  $\tau^*$ , a single quantitative measure of degradation rate independent of sonation time.

#### Effect of Concentration

The effect of concentration on degradation of Polymer A is shown in Fig. 5. Bearing in mind that the values of  $\tau^*$ , via  $DI^*$ , derive from number-average MWs, the scatter of the data around the least squares straight line is considered acceptable. Values of  $\tau^*$  were also obtained for Polymers B, C, and D at two concentrations from which the constants  $a$  and  $b$  of the relations  $\tau^* = aC^b$  were calculated. These constants are listed in Table 2.

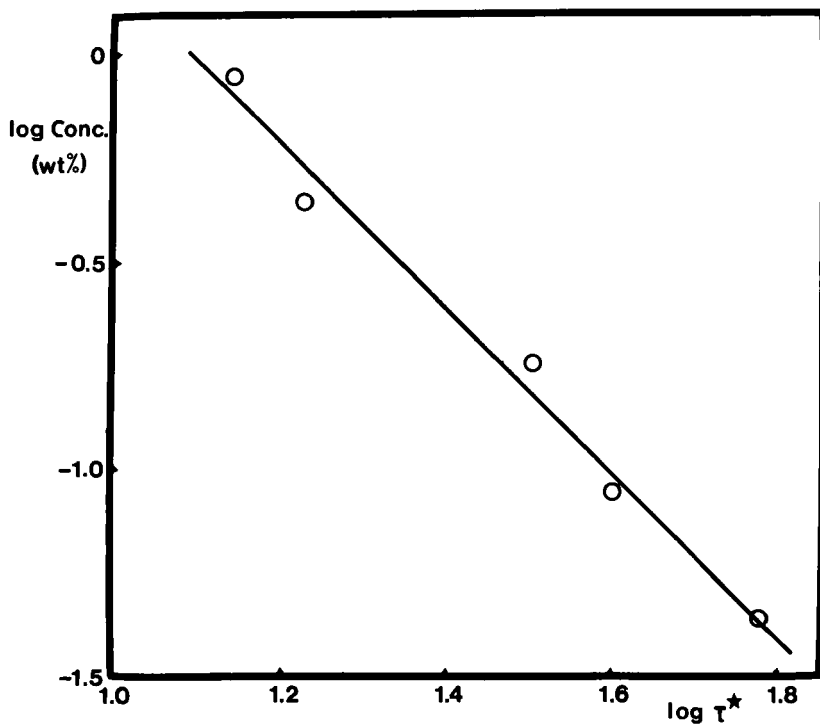


FIG. 5. Transposition factor  $\tau^*$  as a function of polymer solution concentration. Polymer A, temp 35°C, and power 29 W/cm<sup>2</sup>.

TABLE 2. Values of the Constants a and b in the Relation  $\tau^* = aC^b$

Polymer	A <sup>b</sup>	B	C	D
Nominal MW × 10 <sup>-3</sup>	860	498	160	97
a	12.6	7.6	1.05	1
b	- 0.50	- 0.55	- 0.40	0

<sup>a</sup>C is concentration in weight percent.

<sup>b</sup>The standard deviation of log  $\tau^*$  is 0.075.

A physical basis for quantitative assessment of the above experimental relations given in the above paragraph is at present not obvious. For the lowest MW Polymer D,  $\tau^*$  and  $\tau$  are independent of concentration. Since the number of bonds broken  $N_b(t)$  is proportional to  $N_{bb}(t)(\tau^*)^{0.85}$  the rate of bond breakage at any time is proportional to the number of breakable bonds  $N_{bb}$ , i.e., proportional to concentration as might be expected. However, for the high MW Polymer A,  $\tau^*$  decreases inversely with the root of the concentration. Therefore, the absolute scission rate at a given time decreases with about the same power of the concentration. This is possibly due to increasing dissipation with increasing viscosity of sonic energy via processes in which polymer chains partake but which are nondegradative, keeping in mind that the rate of viscosity increase with concentration is much less pronounced for the low MW material than for the high MW polymer. The value of  $\eta_{\text{spec}}/c$  is 0.4 g/dl for Polymer D and varies between 2.2 and 3.3 g/dl for Polymer A in the concentration range used.

#### Effect of Initial Molecular Weight

From the relations between  $\tau^*$  and  $C$  given above, the values of  $\tau^*$  were calculated for Polymers A, B, C, and D at 0.2 wt% concentrations. The results are plotted in Fig. 6 as a function of  $M_n$ . The least squares line is given by  $\tau^* = 6.9 \times 10^{-9} M_n^{1.65}$  with a standard deviation of the exponent of 0.09.

For solutions containing the same amount of polymer  $N_b(t)$  is about proportional to  $(\tau^*)^{0.85}/M_n$ . Therefore, the absolute scission rate increases approximately with  $M_n$  raised to the power 0.40. This value of the exponent is much lower than 0.72, that of the Mark-Houwink relation for polystyrene in THF. The latter value is directly related to the MW dependence of the polymer coil dimensions. It seems therefore that, on the average, less than whole polymer coils are involved in the breaking process, while above it was concluded that the sections partaking in scissions are not very small.

The low value of 0.40 for the exponent of  $M_n$  further indicates that chain entanglements do not play a significant role in the scission processes at the concentrations employed here.

In accordance with the discussion in the theoretical section it seems more likely that the higher frequency of occurrence of low sheer energy densities sufficient to break long molecules compared to the frequency of high SEDs necessary to degrade small chains is the reason for the MW dependence of scission rate. This explanation is supported by considering the quantity  $\tau^*/\eta_{\text{spec}}$ , which is the ratio of a measure for

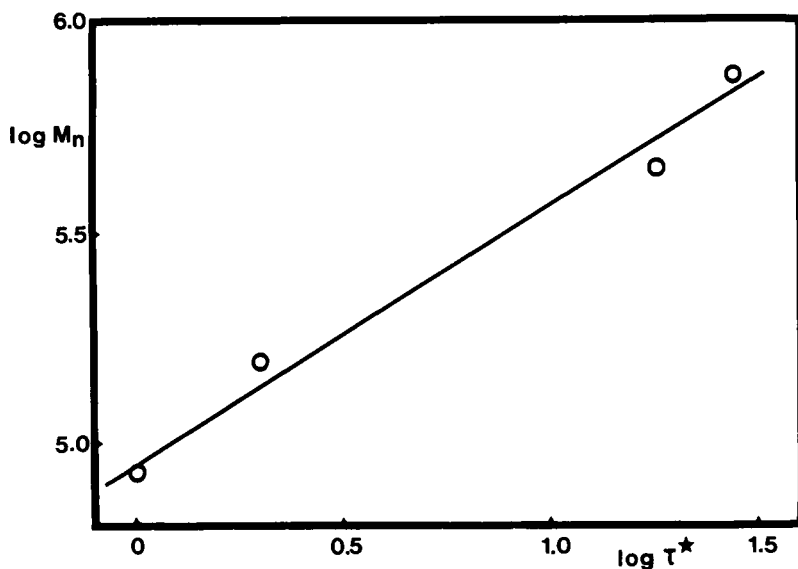


FIG. 6. Transposition factor  $\tau^*$  as a function of number-average molecular weight  $M_n$ . Conc 0.2%, temp 35°C, and power 27 to 29 W/cm<sup>2</sup>.

energy absorbed at the very high shear rates involved in bond breakage to a measure for viscous energy dissipation at very low shear rates. At a concentration of 0.2 wt% the values for this ratio are 74, 74, 17 and 13 for polymers A, B, C, and D, respectively. It appears that sonic energy is relatively more effective in degrading high MW polymer than low MW macromolecules.

#### Effect of Sonation Intensity

Polymer A was irradiated at three different intensities: 29, 54, and 111 W/cm<sup>2</sup>. The relative rates of degradation as measured by  $\tau^*$  for these experiments were 32, 60, and 100, respectively, i.e., the rates were about proportional to intensity. This is in agreement with the theoretical considerations for a high MW polymer (I in Fig. 1). The frequency  $F$ , at low shear rates and at the relatively low power levels applied here, may be expected to vary proportionally to intensity [27].

Two experiments have been conducted with the lower MW Polymer C at power levels of 30 and 103 W/cm<sup>2</sup>. The corresponding  $\tau^*$  values were 2.8 and 4.8. In this case the rates are less than proportional to

the intensities. This is not necessarily inconsistent with the considerations illustrated in Fig. 1. With increasing intensity the value of frequency  $F$  increases but it remains well possible that the shape and the position along the abscissa axis of the  $F$  curve also change with intensity. This makes the scission rate of low MW Polymer II at present unpredictable.

### Effect of Temperature

Two experimental runs with Polymer A were conducted at temperatures different from the standard 35°C. The transposition factors were found to be 70, 32, and 14 for temperatures of 11, 35, and 55°C, respectively. The rate of scission diminishes strongly with increasing temperature in agreement with observations reported by other authors [28].

An increase in temperature changes a number of factors which affect the scission process. The viscosity of the solvent decreases from 0.51 cP at 11°C to 0.36 cP at 55°C, therefore the rate of sonic energy dissipation decreases. The flexibility of the polymer molecules increases somewhat, and their probability of breakage diminishes accordingly because of the chains' increased ability to accommodate to shearing flows. Further the vapor pressure of the solvent increases with increasing temperature, thus diminishing the rate of collapse of cavities, the intensity of the ensuing shockwave, and the shear rate of the accompanying local flow. The complexities of the phenomena mentioned in this paragraph preclude interpretation of the few results obtained.

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