Contribution to the ultrasonic degradation of polystyrene solutions

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Narrow fractions of polystyrene and more heterogeneous samples were subjected to ultrasonic irradiation in tetrahydrofuran and toluene. Degraded products were investigated by gel permeation chromatography. Compared with Ovenall's results, the kinetic analysis of the degradation process shows an additional effect of molecular weight on rate. Experimental chromatograms obtained with classical styragel columns do not reveal clearly the non-random character of the degradation. However, bimodal distribution curves characteristic of a chain scission near the centre of the molecule are observed for degraded products of very narrow fractions analysed by high resolution microstyragel packings. It appears that the breakage does not occur exclusively near the centre but the probability of chain rupture decreases very rapidly out of the central part of the chain.

INTRODUCTION

Ultrasonic degradation of polymer solutions has been extensively investigated[1]. Experimental evidence has been given in many papers[2–8] for the non-random character of the degradation: multimodal molecular weight distributions were observed in the course of the reaction indicating that the probability of chain scission is higher far from the ends of the polymer chain. Nevertheless, such distributions were not clearly obtained by all investigators[9–12] even when monodisperse samples were irradiated.

As a contribution in this field, solutions of monodisperse and polydisperse polystyrenes were degraded by ultrasonic irradiation and the reaction products were analysed by gel permation chromatographs equipped with styragel and high resolution microstyragel columns. Experimental results are discussed in relation to distribution curves obtained through a computer simulation program.

EXPERIMENTAL

Solutions of monodisperse and polydisperse polystyrenes in toluene and tetrahydrofuran (50 ml) were subjected to ultrasonic irradiation using a Macrosonic Corporation instrument model MC 100-I operated by a 860 kHz cell (maximum) intensity 100 W).

The following polymer samples were irradiated at a concentration of 0.5 g/dl: Pressure Chemical polystyrene standards, nominal molecular weights 2.0×10^4, 3.7×10^4, 2.0×10^5, 4.11×10^5 ($\bar{M}_w/\bar{M}_n < 1.1$ for all samples) 8.6×10^5 ($\bar{M}_w/\bar{M}_n \approx 1.2$) and BDH heterogeneous polystyrene (number-average molecular weight, 1.55×10^5, $\bar{M}_w/\bar{M}_n = 2.56$).

The temperature of the solutions was maintained below 20°C during the irradiation. Some of the experiments were followed in the presence of DPPH (a stable free radical, 2,2-diphenyl-1-picrylhydrazyl) in order to prevent a possible recombination of the macroradicals formed in the degradation process.

The molecular weight distributions of the degraded products were determined using a g.p.c. Waters model 200 equipped with styragel columns (10^7, 3×10^5, 3×10^4, 3×10^3 Å – 2800 plates/m) and also with a high speed g.p.c. Waters model 501 operated with high resolution microstyragel columns (10^6, 10^5, 10^4, 10^3 Å – 10 000 plates/m).

Simulations of ultrasonic degradations were carried out on an IBM 370/158 computer.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the number-average molecular weight against ultrasonication time for different polymer fractions. Experimental conditions (for example, THF – low ultrasonic intensity – microstyragel) refer to degradation occurring at low ultrasonic intensity in tetrahydrofuran and leading to degraded products analysed by microstyragel columns.

As reported in the literature, all the polystyrene samples subjected to ultrasonic irradiation show a decrease in their molecular weight average except polystyrene, 2.0×10^4. The degrading effect was particularly marked for the high molecular weight fractions, 8.6×10^5 and 4.11×10^5. It was noted that the presence of DPPH had no influence on the evolution of molecular weights which indicates there is no recombination between macroradicals formed during irradiation.

In order to elucidate the mode of chain scission, it is essential, at first, to determine the degradation rate. Various rate expressions have been proposed[13–17], most of them based on the number of bonds broken in the polymer molecule against ultrasonication time. The direct estimation of the macroradical concentration by DPPH titration[17] or the evolution of the number-average molecular weight[13–16] are then a measure of the degradation rate. Empirical adjustable functions have also been determined directly from the distribution curves and used as rate expressions in connection with various modes of chain scission[7–9]. All the relations assume a dependence of rate on molecular weight.

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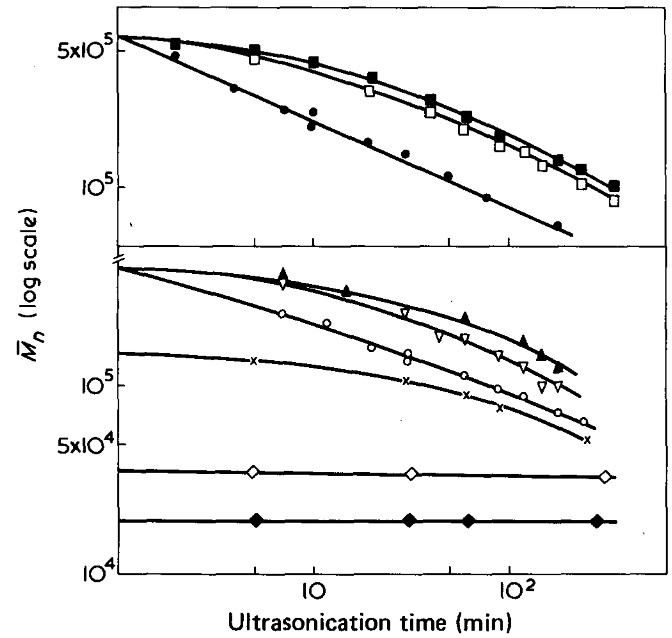

Figure 1 Plots of $\bar{M}_n$ against ultrasonication time t for polystyrenes ●, 8.6 × 10^5; ○, 4.11 × 10^5; ×, 1.55 × 10^5; ◇, 3.7 × 10^4 and ◆, 2.0 × 10^4 (tetrahydrofuran – high ultrasonic intensity – styragel); for polystyrenes ■, 8.6 × 10^5 and ▲, 4.11 × 10^5 (tetrahydrofuran – low ultrasonic intensity – microstyragel); for polystyrenes □, 8.6 × 10^5 and ▽, 4.11 × 10^5 (toluene – low ultrasonic intensity – styragel)

We found it very convenient to express the rate of chain breakage by the well-known basic equation (1):

$$\frac{\mathrm{d}\Sigma n_i}{\mathrm{d}t} = k\Sigma n_i(M_i - M_e) \qquad (1)$$

where n_i is the number of polymer molecules having a molecular weight M_i and M_e is a limiting molecular weight below which the chain will not degrade. According to the definition of the number-average molecular weight, $\bar{M}_n$, equation (1) gives:

$$-\frac{\mathrm{d}\bar{M}_n}{\mathrm{d}t} = k\bar{M}_n(\bar{M}_n - M_e) \qquad (2)$$

In order to investigate the possibility of an additional effect of molecular weight on rate constant, k, we have also considered the following equation:

$$k = k'\bar{M}_n^x \quad \text{with } x \geqslant 0 \qquad (3)$$

Equations (2) and (3) allow for the concept of a limiting molecular weight and for the effect of molecular weight on rate.

The limiting molecular weight was determined by a long ultrasonication time for a polystyrene sample of molecular weight 4.11 x 10^5. A number-average molecular weight of 3.0 x 10^4 was obtained after 90 h of constant irradiation. Furthermore, as shown in *Figure 1*, the low molecular weight fraction 3.7 x 10^4 was very slightly affected by the radiation and polystyrene 2.0 x 10^4 appeared unchanged. Consequently, the limiting molecular weight was chosen near 3.0 x 10^4, in agreement with a recent value reported in the literature[7].

Assuming that there are no molecules with molecular weights less than M_e in the original polymer, equation (2) is easily integrated for different values of x in the expression for k (equation 3). Integration with x = 0 leads to a modified form of the well-known Ovenall expression[16] (equation 4); the original Schmid relation is obtained with x = 1[13] (equation 5):

$$\ln\left(\frac{1}{M_e} - \frac{1}{\bar{M}_n}\right) = \ln\left(\frac{1}{M_e} - \frac{1}{\bar{M}_{n0}}\right) - kM_e t \qquad (4)$$

$$\ln\left(\frac{1}{M_e} - \frac{1}{\bar{M}_n}\right) + \frac{M_e}{\bar{M}_n} = \ln\left(\frac{1}{M_e} - \frac{1}{\bar{M}_{n0}}\right) + \frac{M_e}{\bar{M}_{n0}} - k'M_e^2 t \qquad (5)$$

In equations (4) and (5), $\bar{M}_{n0}$ is the number-average molecular weight of the original polymer.

Table 1 shows typical values of k' obtained with different values of x for narrow distribution polystyrenes of molecular weights 8.6 x 10^5 and 4.11 x 10^5 and heterogeneous polystyrene of molecular weight 1.55 x 10^5 irradiated at high ultrasonic intensity in tetrahydrofuran. The number-average molecular weights were obtained with styragel columns.

Lower molecular weight fractions of narrow distribution were not examined here; the fractions of molecules having molecular weights below M_e in these polymers are not negligible so that a simple integration of equation (2) is then a very imprecise and unsuitable rate expression.

Table 1 indicates clearly that only the integration for x = 1 (equation 5) gives constant k' values against time and also against molecular weight. According to these results, equation (5) was applied to other experimental conditions. *Figure 2* shows that equation (5) fits in well with experimental data obtained in toluene and tetrahydrofuran. From this good agreement, we can deduce that there is an additional dependence of degradation rate on molecular weight. This effect was also observed by other authors[8,18] and could reveal the influence of the hydrodynamic characteristics of the polymer (hydrodynamic volume, polymer–solvent interactions) as already pointed out for ultrasonic or high speed stirring mechanical degradations[19,20].

The mode of chain scission can be clarified by comparing experimental results with theoretical data obtained by a computer simulation program using various rate expressions

Table 1 Rate constants k' from equations (2) and (3) integrated with different x values for polystyrenes 8.6 × 10^5, 4.11 × 10^5 and 1.55 × 10^5 in tetrahydrofuran – high ultrasonic intensity – styragel system

		k' (min)			
M × 10^{-5}	t(min)	x = 0 10^7	x = 0.5 10^{10}	x = 1.0 10^{12}	x = 1.5 10^{15}
8.6	1	6.7	20.0	1.1	1.5
	2	4.0	11.0	0.9	1.0
	4	4.5	6.0	1.1	1.5
	7	4.0	6.0	1.1	1.8
	12	3.8	7.9	1.2	2.3
4.11	2	2.7	4.3	1.1	1.2
	7	2.8	5.2	1.0	1.8
	12	2.2	4.2	0.8	1.6
	20	2.3	6.4	1.1	2.4
	30	2.0	6.4	1.0	2.5
1.55	30	1.2	3.3	0.9	2.6
	60	1.1	3.1	0.9	2.8
	90	1.0	3.1	1.0	3.1

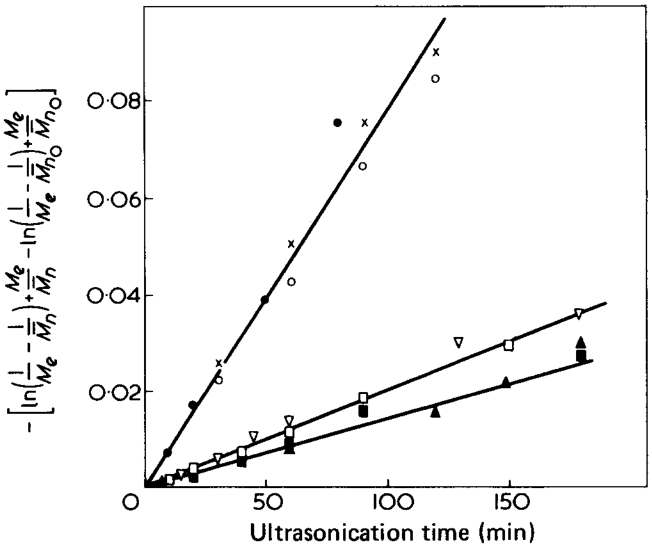

Figure 2 Schmid's rate expression for polystyrenes ■, 8.6 X 10^5 and ▲, 4.11 X 10^5 (tetrahydrofuran – low ultrasonic intensity – microstyragel); for polystyrenes □, 8.6 X 10^5 and ▽, 4.11 X 10^5 (toluene – low ultrasonic intensity – styragel); for polystyrenes ●, 8.6 X 10^5; ○ 4.11 X 10^5 and X, 1.55 X 10^5 (tetrahydrofuran – high ultrasonic intensity – styragel)

and assuming random, central or other ruptures in the polymer chain. Such computer programs have been described in the literature[6,7,18,21] and were easily adapted to our experimental conditions. Details concerning our computer program are given elsewhere[22].

Figure 3 shows typical examples of simulated distribution curves dW/dV_e against elution volume V_e, assuming pure random (for $M_i > M_e$) and pure central ruptures in polystyrene 4.11 x 10^5. These curves were calculated using the rate expression (equation 1) and equation (3) with $x = 1$; they correspond to simulated degraded products with number-average molecular weights 3.5 x 10^5 and 2.0 x 10^5, respectively. As expected, central rupture leads to bi- or multimodal distributions.

Styragel and microstyragel columns were used to determine the experimental distribution curves; the chromatograms obtained from classical styragel columns did not clearly reveal the non-random character of the ultrasonic degradation: for both monodisperse and polydisperse samples, the maximum of the molecular weight distribution changes continuously towards the high elution volumes; no bimodal or polymodal distributions were observed.

However, multimodal distributions can be masked by a large diffusion process occurring inside the chromatographic columns. Therefore, the diffusion correction methods of Chang and Huang[23] were applied in order to find the real distribution curve. Unfortunately, the results were ambiguous, particularly for narrow distribution curves.

The high resolution power of microstyragel columns (10^4 plates/m), should minimize peak broadening, which must lead to more correct chromatograms: as shown in *Figure 3,* bimodal distribution curves were in fact found with a monodisperse sample 4.11 x 10^5. In this case, the uncorrected chromatogram shows a second peak at an elution volume corresponding to a molecular weight near $M_0/2, M_0$ being the maximum in the original polymer; this distribution is quite characteristic of a non-random process with a high probability of scission at the centre of the chain.

Such behaviour was also observed for a narrow polystyrene, 2.0 x 10^5 ($\bar{M}_w/\bar{M}_n < 1.1$), but did not appear with more polydisperse polystyrene, 1.55 x 10^5 ($\bar{M}_w/\bar{M}_n \approx 2.5$), and even polystyrene 8.6 x 10^5 ($\bar{M}_w/\bar{M}_n \approx 1.2$).

From these results, we can conclude that both very narrow samples and very high resolution columns are required to observe polymodal structures in the experimental chromatograms of degraded products. We can also postulate that the apparent contradictory behaviour reported in the literature results both from the use of samples with different heterogeneities and from the use of chromatographic columns with different resolution powers.

The determination of the exact location of the point of breakage evidently requires a rigorous correction of the experimental curves for peak broadening, even when high resolution packings such as microstyragel are used.
As already noted, this correction is particularly hazardous for monodisperse fractions where oscillations can lead to artificial peaks in the distribution curves. Therefore, we have found that the comparison of simulated and experimental polydispersity index $\bar{M}_w/\bar{M}_n$ is more critical than the comparison of the corresponding molecular weight distributions. Indeed, experimental polydispersities are more easily corrected for peak broadening with best results[24,25].

Figure 4 exhibits typical plots of polydispersity index $\bar{M}_w/\bar{M}_n$ against $\bar{M}_n$ for degraded products issued from polystyrene 4.11 x 10^5 under various experimental conditions.

We note immediately that experimental conditions seem to have no marked influence on the evolution of polydisper-

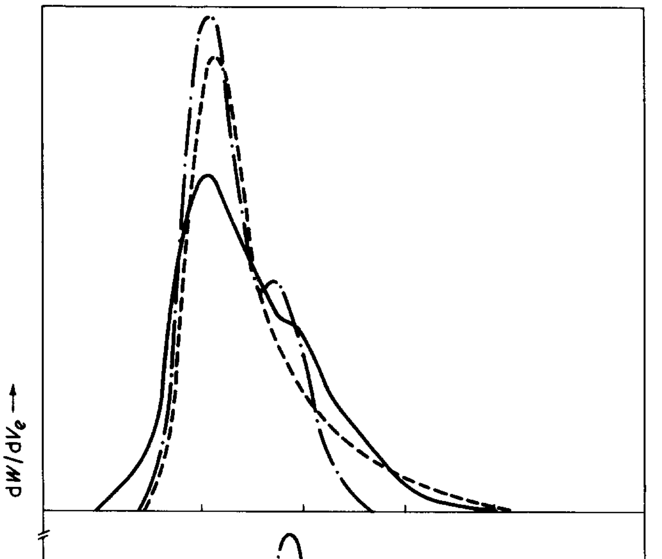

Figure 3 Uncorrected chromatograms (———) of degraded products and simulated curves assuming central (— · —) and random (— — — —) rupture for polystyrene 4.11 X 10^5 (tetrahydrofuran – low ultrasonic intensity – microstyragel)

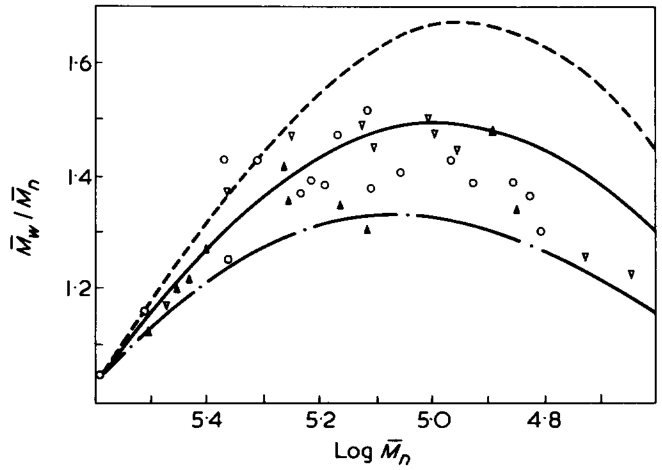

Figure 4 Polydispersity index $\bar{M}_w/\bar{M}_n$ against number-average molecular weight for degraded polystyrene 4.11 × 10^5: ▲, tetrahydrofuran — low ultrasonic intensity — microstyragel; ○, tetrahydrofuran — high ultrasonic intensity — styragel; ▽, toluene — low intensity — styragel. Simulated curves assuming random (— — — —), central (— · —) and intermediate rupture (———)

sity index. In all cases, as already reported in the literature, $\bar{M}_w/\bar{M}_n$ increases at first until it reaches a maximum value for $\bar{M}_n$ near 1.0 x 10^5; then, for lower molecular weights, the degraded samples become more homogeneous. Bimodal distributions from *Figure 3* correspond to samples whose polydispersity indices are situated in the upward part of the curve.

Quite comparable behaviour can be seen with polystyrenes 2.0 x 10^5 and 8.6 x 10^5 but the more heterogeneous sample 1.55 x 10^5 shows a continuous decrease in polydispersity from the initial value 2.56 to values below 1.5. During this time, the number-average molecular weight decreases from 1.55 x 10^5 to 4.5 x 10^4.

Various types of chain scission were tested by the computer simulation program[22]. Some of them were included in *Figure 4*. The highest simulated polydispersity values arise from the random scission (for $M_i > M_e$), the lowest from the central rupture. As expected from the chromatograms obtained with microstyragel columns, experimental plots do not fit with the random scission but the central rupture is also not verified. Most of the experimental plots are situated below a curve assuming a linear decrease in the probability of scission from the centre to the ends of the molecules, that is to say, this decrease is more pronounced. We have also tested the possibility of a mode of chain scission which evolves from a random to a central rupture with ultrasonication time. This type of rupture suggested by Fukutomi[26] and Booth[27] for mechanical degradations could explain the intermediate location of experimental plots, but simulated curves so obtained do not show bimodal distributions experi mentally observed in the early stages of the reaction (*Figure 3*).

These results suggest that, if the breakage does not occur exclusively near the centre of the chain, the probability of rupture decreases very rapidly away from the central part of the molecule. This conclusion confirms the results found by Glynn *et al.*[6–8] from the study of distribution curves.

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