# Ultrasonic degradation of polymer solutions: 2. The effect of temperature, ultrasound intensity and dissolved gases on polystyrene in toluene

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Solutions of polystyrene in toluene have been studied as part of a comprehensive study of the parameters affecting the degradation of polymers under irradiation with high-intensity ultrasound. Results are reported which demonstrate the molecular weight dependence of the process and the effect of solution temperature, ultrasound intensity and the nature of dissolved gases on the rate and extent of degradation over a considerably wider range than previously studied. They demonstrate that the limiting molecular weight and polydispersity of the materials can be controlled by suitable manipulation of the experimental conditions. The effects are explained in terms of the influence that each of the parameters has on the shear gradients generated around cavitation bubbles in the solution. The possibility of using the ultrasound process in the control of polymer structure and for the preparation of block copolymers is discussed.

**(Keywords: ultrasonic degradation; polymer solutions; polystyrene)**

## INTRODUCTION

The past decade has seen a considerable rise in the applications of high-intensity ultrasound in chemistry[1-3], particularly in organic and organometallic synthesis, where great improvements in rate and yield as well as changes in reaction mechanism can be achieved. However, the best-known effect in polymer chemistry, that of the degradation of chains when irradiated in solution[4,5], originates from the 1930s, when the reduction in viscosity of solutions of starch and agar was reported[6,7]. There has been a recent resurgence of interest in the process due to improved analytical methods for polymers and also to the more widespread availability of ultrasound equipment, particularly for operating on a larger scale, with pilot-plant type equipment now commercially available[8]. The major feature of the process which makes it potentially useful is that, unlike thermal or photochemical degradations, the chain cleavage is non-random with breakage occurring preferentially near the middle of the chain. Thus, it is akin to the shear degradation produced in flow fields[9,10].

The passage of the longitudinal sound wave through a liquid can be described in terms of the acoustic pressure in the liquid, $P_A$, represented by:

$$P_A = P_M \sin(2\pi\nu t) \tag{1}$$

where $\nu$ is the sound frequency and $P_M$ the maximum pressure generated, i.e. the amplitude of the wave. Most sonochemical effects are attributed to cavitation, or the growth and rapid collapse of microscopic bubbles as the alternate rarefaction and compression phases of the longitudinal sound wave pass through a liquid and $P_M$ is sufficient to overcome the intermolecular forces in the solution. Although many sonochemical effects can be explained by consideration of an electrical discharge due to charge separation on the bubbles[11], most workers interpret their results in terms of the high temperatures and pressures generated during bubble collapse. Treating the collapse as an adiabatic process leads to the following for the maximum values of temperature, $T_{max}$, and pressure, $P_{max}$, generated during cavitation:

$$T_{max} = TP_M(\gamma - 1)/P \tag{2}$$

and

$$P_{max} = P[P_M(\gamma - 1)/P]^{[\gamma/(\gamma-1)]} \tag{3}$$

where $T$ is the ambient temperature, $P$ the pressure in the bubble before collapse (often taken to be the saturated vapour pressure of the liquid) and $\gamma$ is the polytropic ratio (the ratio of the specific heat capacities at constant pressure and constant volume) of the solvent vapour or any dissolved gases that enter the bubble. These equations predict values in the region of several thousand Kelvin and several hundred atmospheres, depending on the system. This treatment of cavitation, originally suggested by Noltingk and Neppiras[12,13], has recently received experimental support from the work of Suslick[1,14]. In addition to these extreme conditions, which occur on a microsecond timescale, movement of solvent molecules around the bubbles sets up large shear fields and it is these that are primarily responsible for the degradations.

As well as a technique for molecular weight control, ultrasound offers the possibility of producing functionalized materials. The primary result from the chain cleavage is a macromolecular radical which can react with a second species. A number of workers have sonicated a mixture of two polymers in a common solvent, combination of

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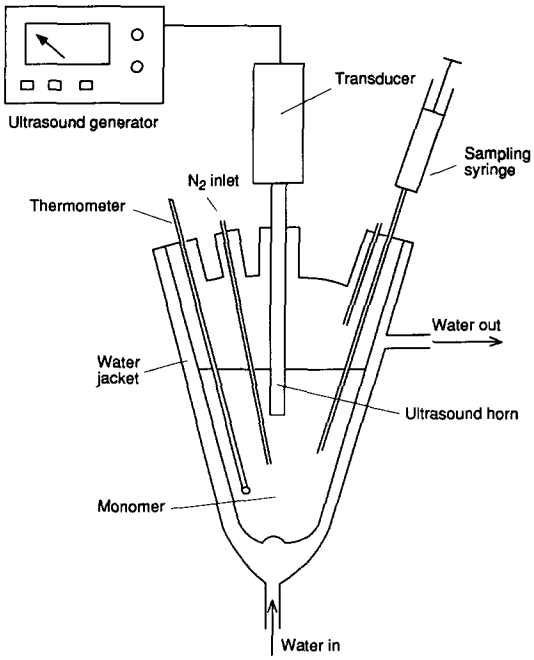


**Figure 1** Schematic diagram of sonication apparatus

the radicals giving a block copolymer. However, in this method the copolymer is difficult to recover and the control of the block length is also difficult. Our approach has been to sonicate a polymer in a solution containing a second monomer[15]. Our models and study of the degradation of homopolymers will allow us to control the molecular weight of the degradation product while manipulation of the properties such as the monomer concentration will give control over the second block length.

The achieve this, the precise effect of a number of parameters on the degradation must be known. While many papers dealing with the process have been published[4,5], there are few in-depth studies on one well-defined polymer system. We have commenced our study using polystyrene as a model system to allow accurate characterization, primarily by g.p.c., and this paper deals with the effect of the ultrasound intensity, the solution temperature and the nature of any dissolved gases on the degradation.

## EXPERIMENTAL

Irradiation of the polystyrene solutions was performed in an apparatus shown schematically in *Figure 1*. The glass cell, designed and constructed in our laboratory, consisted of a pear-shaped flask, surrounded by a jacket through which thermostatted water was circulated, modified by an indentation at the apex to assist the mixing caused by ultrasonic streaming. This obviated the need for additional stirring. Two versions were used: a 50 $cm^3$ capacity cell with a 'Sonics and Materials' VC50 sonicator, which was used for the majority of work described here, and a 100 $cm^3$ capacity cell with a VC600 sonicator from the same manufacturer. The latter apparatus gives access to a wider range of powers and was used for the variable intensity study. The intensities were measured calorimetrically in the usual manner[16].

Throughout the work, solutions of polystyrene in toluene (ACS Grade, Aldrich Ltd) at a concentration of 5 $g\,dm^{-3}$ (0.5% w/v) were used. The required volume was placed into the cell and, where appropriate, saturated with a gas by bubbling for 45 min. Periodically, small samples (approximately 0.25 $cm^3$) were removed for g.p.c. analysis. Polymer molecular weights were measured using a Bruker LC21/41 chromatography system with a refractive index detector. H.p.l.c. grade toluene (BDH Ltd) was used as the mobile phase at a flow rate of 1.0 $cm^3\,min^{-1}$ through two 'PL Gel' Linear 30 cm columns calibrated using low polydispersity standards (Polymer Laboratories Ltd) over the range 1020–$1.4 \times 10^6$.

The wider distribution polystyrenes used were secondary standards from Aldrich Ltd. That used for the temperature study had a number average molecular weight of 145 000 and a polydispersity of 3.1, while that used for the remainder of the work had $M_n = 122\,000$ and polydispersity of 2.4. The precise conditions used for each experiment are recorded in the following sections.

## RESULTS AND DISCUSSION

The basic effects of the ultrasonic degradation are shown in *Figure 2*, which illustrates the variation in molecular weight for four polystyrene standards with polydispersities of approximately 1.05 in toluene at $25.0 \pm 0.5$°C. Clearly, the degradation proceeds more effectively at high molecular weights and approaches a limiting value, $M_{lim}$, below which no further degradation takes place, in this case approximately 30 000. Polymers with this value, or lower, are unaffected by ultrasound under these conditions. The molecular weight dependence has implications for the polydispersity of the material as demonstrated by *Figure 3*. For an initially narrow sample, the distribution widens somewhat before reducing while the polydispersity of a broad sample with the same initial number average molecular weight falls throughout the sonication.

A number of different models have been proposed to account for the rate of degradation. We have applied these to our results and they will be the subject of a future paper, only the most successful being applied to the work described here. Building on earlier work by Schmid, Ovenall *et al.*[17] proposed that the rate of bond cleavage was first order, but depended on the chain length in excess of $M_{lim}$, conditions which lead to the following expression

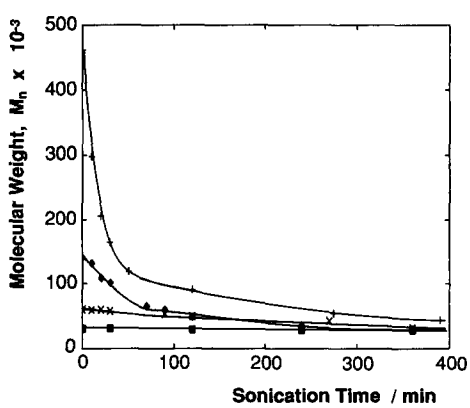


**Figure 2** Ultrasonic degradation of narrow polydispersity polystyrenes in toluene: (■) 30 000; (×) 68 000; (◆) 140 000; (+) 460 000. (Experimental conditions: 50 $cm^3$ of 0.5 wt% solution irradiated at $I = 17.4\,W\,cm^{-2}$ at 25°C)

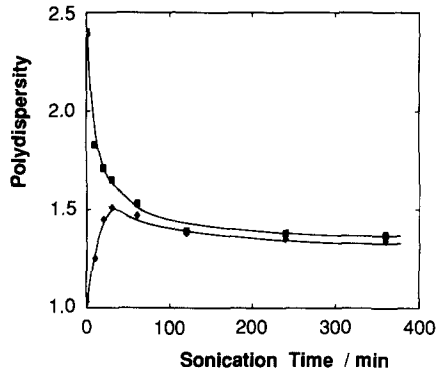


**Figure 3** Effect of degradation on the polydispersity of polystyrene of initial $M_n = 240\,000$. (Experimental conditions as in *Figure 2*)

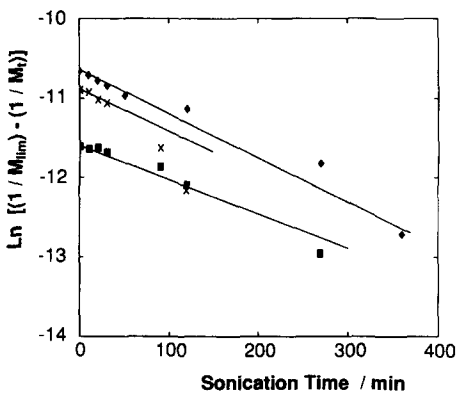


**Figure 4** Kinetic rate plot for Ovenall treatment of results from *Figure 2*

for the molecular weight, $M_t$, of the polymer at time, $t$, during the degradation:

$$\ln\left(\frac{1}{M_{\text{lim}}}-\frac{1}{M_t}\right)=\ln\left(\frac{1}{M_{\text{lim}}}-\frac{1}{M_i}\right)-k\left(\frac{M_{\text{lim}}}{cm_0}\right)t \qquad (4)$$

so that a plot of $\ln(1/M_{\text{lim}} - 1/M_t)$ *versus* $t$ should produce a linear relationship, the gradient of which, knowing the solution concentration, $c$, and the monomer molecular weight, $m_0$, yields the rate constant $k$. An alternative treatment was provided by El'tsefon and Berlin[18] who, on the basis of their work with polystyrene solutions in benzene, predicted that the degradation obeyed the equation

$$M_t = M_i(1 + M_i^2 kt)^{-1/2} \qquad (5)$$

where the variables have the same meaning as above so that again the rate constant can be found from the slope of an appropriate plot of the data.

The appropriate plots for the results from *Figure 3* are given in *Figures 4* and *5* and the rate constants are listed in *Table 1*, which also shows the initial rate of degradation, defined as the average reduction in $M_n$ over the first 10 min. The Berlin model gives a good linear fit to the data. The Ovenall expression fits well for the results at short degradation times, but large deviations occur at longer times. We feel that this arises for two reasons: first, deficiencies in the model such as the assumption of monodisperse samples and neglect of changes in polydispersity are not accounted for. Second, the derivation assumes a simple linear chain-breakage process. However, after a certain period other processes may occur such as the degraded chain, which initially takes the form of a macromolecular radical, grafting onto other chains giving branched materials. In addition, as the molecular weight approaches the limiting value, the experimental error in the values becomes increasingly large. Hence, the rate constants quoted refer only to the initial part of the degradation.

The aim of our work is to correlate the values of $M_{\text{lim}}$ and $k$ with the various experimental parameters. In addition to the results presented here, the effect of solution concentration and solvent properties has been described elsewhere[19].

*The effect of the ultrasound intensity*

The degradation of polystyrene in toluene at four intensities is shown in *Figure 6*. As might intuitively be expected, the process is faster and proceeds further at

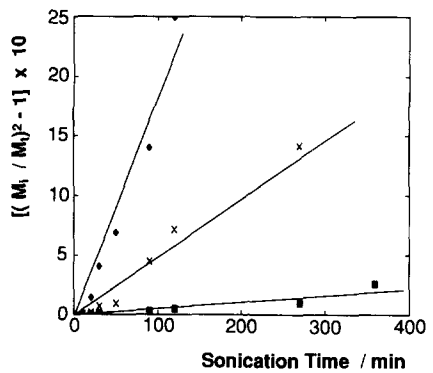


**Figure 5** Kinetic rate plot for El'tsefon and Berlin treatment of results from *Figure 2*

**Table 1** Properties of the ultrasonic degradation of toluene solutions of narrow polydispersity polystyrenes of varying initial molecular weight. (Experimental conditions as in *Figure 2*)

| | | | Rate constants | |
|---|---|---|---|---|
| Initial $M_n$ | $M_{\text{lim}}$ | Initial rate ($\text{min}^{-1}$) | Ovenall ($\times 10^8\ \text{dm}^3\ \text{min}^{-1}$) | Berlin ($\times 10^3\ \text{min}^{-1}$) |
| 68 000 | 35 000 | 80 | 2.7 | 2.25 |
| 140 000 | 35 500 | 1300 | 7.4 | 53.3 |
| 460 000 | 37 500 | 9900 | 9.7 | 285.0 |

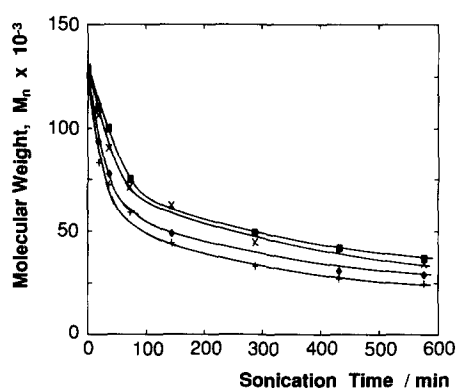


**Figure 6** Effect of ultrasound intensity on molecular weight during degradation of polystyrene in toluene. Intensities ($\text{W cm}^{-2}$): (■) 183.7; (×) 144.1; (◆) 89.8; (+) 48.9. (Experimental conditions: 100 $\text{cm}^3$ of 0.5 wt% solution irradiated at 25°C)

**Table 2** Effect of the ultrasound intensity on the ultrasonic degradation of polystyrene in toluene. (Conditions as in *Figure 6*)

| Intensity ($W\ cm^{-2}$) | $M_{lim}$ | Final polydispersity | Rate constants: Ovenall ($\times 10^6\ dm^3\ min^{-1}$) | Rate constants: Berlin ($\times 10^2\ min^{-1}$) |
|---|---|---|---|---|
| 48.9 | 24 750 | 1.34 | 1.02 | 2.71 |
| 89.8 | 28 950 | 1.33 | 1.13 | 3.19 |
| 144.1 | 34 320 | 1.24 | 1.63 | 4.93 |
| 183.7 | 36 830 | 1.19 | 1.34 | 4.71 |

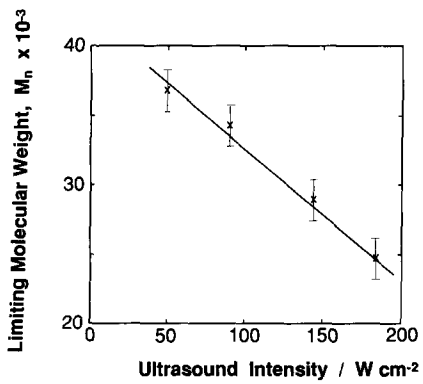


**Figure 7** Effect of ultrasound intensity on the limiting molecular weight during degradation of polystyrene in toluene. (Experimental conditions as in *Figure 6*)

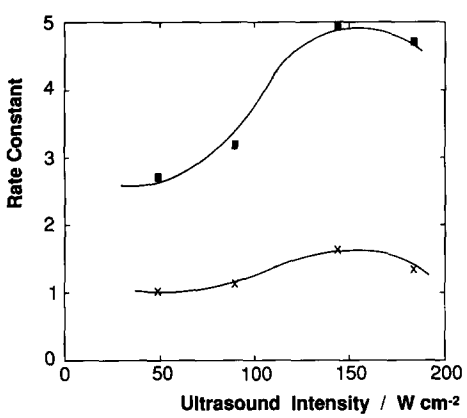


**Figure 8** Effect of ultrasound intensity on the rate constants during degradation of polystyrene in toluene: (■) Ovenall model; (×) Berlin model. (Experimental conditions as in *Figure 6*)

high intensity. The properties of the final polymers are shown in *Table 2* and demonstrate that, at the highest intensities available here, limiting polydispersities in the range of 1.1–1.3, comparable to those from ionic polymerizations, can be obtained. The limiting molecular weight is a linear function of the applied intensity, as shown by *Figure 7*, the results fitting the expression

$$M_{lim} = 41\,800 - 90.8 \times I(W\ cm^{-2})$$

with a correlation coefficient of 0.996. As the results suggest, the rate constant increases with rising intensity although, as *Figure 8* shows, the rise does not continue indefinitely and there is some optimum value, approximately $145\ W\ cm^{-2}$ under these conditions, where the rate constant has a maximum value.

A number of systems which show this rise in $k$ with increasing intensity have been described[4,5] although relatively few workers have attempted to quantify the effects. Mostafa[20] and Jellinek[21], using the same polymer–solvent combination as studied here, found a linear relation between $k$ and $I$, although over a much smaller range of intensities than considered in this work. Several groups[22,23] have suggested that $M_{lim}$ was independent of intensity, although this is clearly not the case here. Our results can be explained by consideration of the effect of the ultrasound intensity on the cavitation process.

Noltingk and Neppiras[12,13] showed that, above the cavitation threshold, the maximum radius reached by a bubble, $R_m$, is proportional to the square root of the intensity. Hence an increase in $I$ leads to larger bubbles and therefore higher shear forces on collapse so that a lower $M_{lim}$ is reached. Additionally, it would give rise to a large number of cavitation bubbles per unit volume of solution, so that the degradation would be faster. However, above a certain value of $I$, the increased number of bubbles means that the ultrasound field does not pass through the solution as efficiently, reducing cavitation. There is also insufficient time between consecutive rarefaction cycles for complete bubble collapse to take place. Thus, the efficiency of the process falls at very high intensity.

### *Effect of temperature*

The majority of chemical processes are accelerated by an increase in temperature. However, the opposite effect is often seen for mechanical processing. Indeed, this negative 'temperature coefficient' has often been cited as proof that a solution process is mechanical in origin. Sonochemical reactions often display faster rates at lower temperatures, and at least the primary sonochemical step of the reaction is usually more efficient at low temperatures. This is the case for ultrasonic degradation as shown in *Figure 9*. The effect of temperature is remarkably large and was considerably greater than the variation due to the ultrasound intensity. The temperature effect is also greater than that found for shear degradation in extensional flows[9]. A much wider range of limiting molecular weights was obtained and, as shown in *Figure 10*, the values were a linear function of the temperature. Treatment of the rate constants is more difficult in this case since the values calculated using the Ovenall model did not give consistent results although the usual Arrhenius treatment of the Berlin model gave a linear relation, albeit with a negative apparent activation energy of $-17.3\ kJ\ mol^{-1}$. Clearly, this bears no relation to the bond-breakage process, the activation energy for which in thermal degradation experiments is

$+167.4\,kJ\,mol^{-1}$. The interpretation of these negative values in sonochemical systems is open to question but can qualitatively be explained in terms of the effect on the solvent.

At increased temperatures, the solvent vapour pressure will clearly be higher and so vapour will enter the cavitation bubble. This effectively 'cushions' the collapse, so that the movement of solvent molecules is slowed down and the shock waves lessened. The same effect has been noted by other workers[22,24] and can also be achieved by using different solvents with a range of vapour pressures[4,5,14]. Malhotra *et al.*[25–27] also found accelerated degradation at lower temperatures and suggested that, in addition to the vapour effects, the increased viscosity leads to better transmission of the ultrasound through the liquid. While this may play a part, we feel that the vapour pressure is dominant, since using solvents with a range of viscosity[15] has little effect on the rate or extent of the degradation.

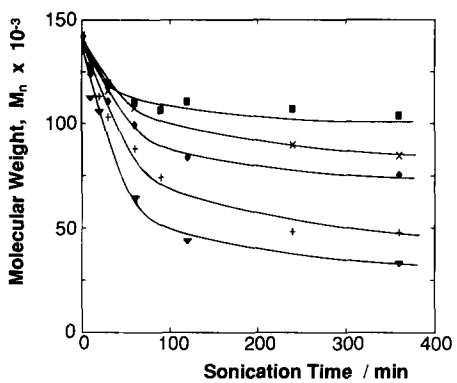


**Figure 9** Effect of temperature on molecular weight during degradation of polystyrene in toluene. Temperatures (°C): (■) 61; (×) 50; (◆) 40; (+) 5; (▲) −10. (Experimental conditions as in *Figure 2*)

*The effect of dissolved gases*

As is clear from equations (2) and (3), the extent of sonochemical effects will depend on the properties of dissolved gases in solution, two factors being of importance. First, diffusion of gas into the bubble will have the same effect as solvent vapour in the preceding section so that the solubility and diffusivity of the gas will be important. Second, the polytropic ratio of the gas in the bubble will determine the final conditions during cavitation and hence the magnitude of shear fields around collapsing bubbles. The degradation of polystyrene in solution saturated with six different gases is shown in *Figure 11*. Again, significant differences can be seen for the different gases. The properties of the gases[28,29] together with those of the resulting polymers are shown in *Table 3*.

Equations (2) and (3) show that the highest temperatures and pressures should be generated in cavitation bubbles with gases of high $\gamma$ and this heat would be transferred into the liquid in systems with high thermal conductivity. Hence it would be expected that the greatest degradation would be achieved by saturating with monatomic gases such as argon and the least with gases such as carbon dioxide. However, notwithstanding that the least degradation was obtained under carbon dioxide, consideration of the results in *Table 3* shows there to be little or no systematic correlation of the degradation

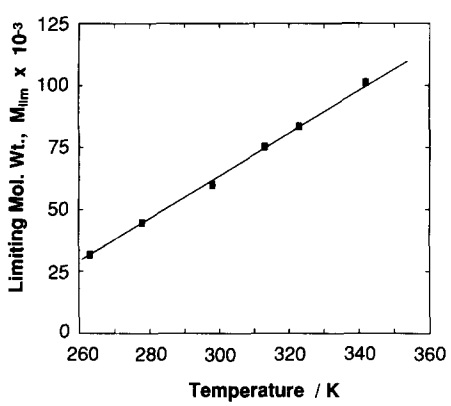


**Figure 10** Effect of solution temperature on the limiting molecular weight for degradation of polystyrene in toluene. (Experimental conditions as in *Figure 2*)

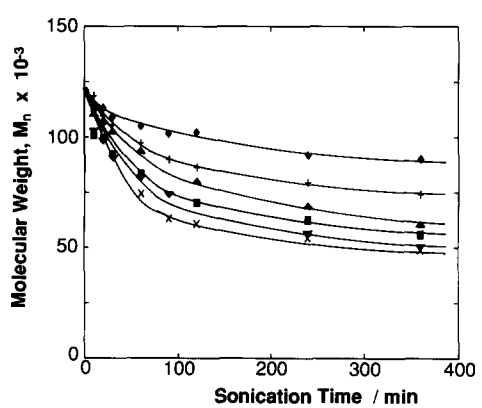


**Figure 11** Variation of molecular weight during degradation of polystyrene in toluene under different gases: (◆) $CO_2$; (+) $CH_4$; (▲) Ar; (■) $N_2$; (▼) CO; (×) $O_2$. (Experimental conditions as in *Figure 2*)

**Table 3** Effect of the physical properties of dissolved gases at 25°C on the ultrasonic degradation of polystyrene in toluene. (Conditions as in *Figure 11*)

| Gas | Thermal conditions ($mW\,m^{-1}\,K^{-1}$) | Mole fraction solubility | $\gamma$ | Initial rate ($min^{-1}$) | $M_{lim}$ |
|---|---|---|---|---|---|
| Carbon dioxide | 16.5 | 99.0 | 1.3 | 350 | 90 000 |
| Methane | – | 23.7 | – | 495 | 74 000 |
| Carbon monoxide | 25.0 | 7.1 | 1.4 | 980 | 51 000 |
| Nitrogen | 25.6 | 5.4 | 1.4 | 950 | 56 000 |
| Oxygen | 26.4 | 9.2 | 1.4 | 920 | 48 000 |
| Argon | 17.7 | 11.1 | 1.7 | 630 | 61 000 |

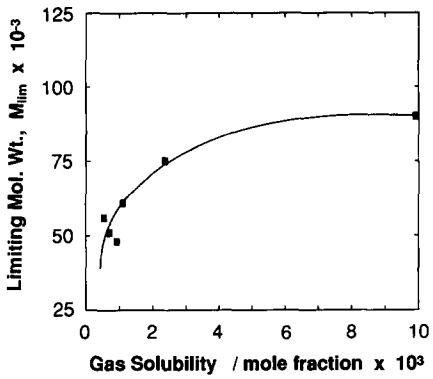


**Figure 12** Effect of solubility of dissolved gases on the limiting molecular weight for degradation of polystyrene in toluene. (Experimental conditions as in *Figure 2*)

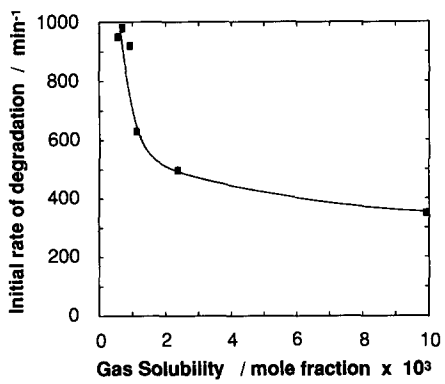


**Figure 13** Effect of solubility of dissolved gases on the initial rate of degradation of polystyrene in toluene. (Experimental conditions as in *Figure 2*)

rate or $M_{lim}$ with either of these properties, again demonstrating that the process is not thermal in origin. The major determining factor seems to be the gas solubility, as shown in *Figures 12* and *13*. Lower limiting molecular weights were obtained for gases with lower solubility. Consideration of the degradation rate is not straightforward as none of the various models gave rate constants which correlated sensibly with any of the gas properties, even though the rate plots were satisfactorily linear. However, the initial rate of degradation (measured by the reduction in $M_n$ over the first 30 min of sonication) followed the same dependence on gas solubility.

In both of these plots oxygen gave somewhat anomalous results. This is due to the chemical characteristics of the gas rather than its physical properties. Oxygen is reactive towards radicals and so would react very rapidly with the macroradical formed on chain cleavage, thereby preventing any recombination and/or grafting processes. The same will apply, although to a lesser extent, with carbon monoxide. The other gases are more inert and hence the radical would have a longer lifetime, increasing the likelihood of these processes and slowing the reduction in molecular weight.

The dependence on dissolved gas can be explained since the gas would act in a similar fashion to the solvent vapour in entering the cavitation bubble and cushioning its collapse. Systems with higher gas solubilities will therefore have more gas entering the bubbles, causing less shear force on the polymer chains and reducing the degradation. This dependence on solubility was suggested some time ago by Jellinek and Brett[21,30,31] but there has been little experimental study of this parameter. A second factor is that the presence of large amounts of dissolved gas will reduce the cavitation threshold[32], again making the degradation less efficient.

## CONCLUSIONS

Our results described here show that by suitable manipulation of the experimental conditions the ultrasonic degradation of polymer solutions can be varied to a large extent with consequent control over the molecular weight and polydispersity of the resulting materials. The effect of the various experimental parameters can be explained in terms of a large shear gradient effect around collapsing cavitation bubbles and this allows correlation, at least in a qualitative manner, of all the published results in this area. A more quantitative model is under development and will appear shortly.

At its most straightforward level it could be used for molecular weight control during synthesis and/or processing of suitable polymer systems by removing high molecular weight material. However, our main interest is to use the resulting macroradical to produce block copolymers, and so the results described here, together with those investigating other experimental parameters, will allow control of one of the block lengths. This work will be described in detail in a future paper.

## ACKNOWLEDGEMENT

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