Ultrasonic degradation of water-soluble polymers

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The ultrasonic degradation of the water-soluble polymers pullulan, poly(ethylene oxide) and polyvinylpyrrolidone was studied at a frequency of 500 kHz. The apparent degradation rate constants are 0.030 for pullulan, 0.076 for poly(ethylene oxide) and 0.032 min^{-1} for polyvinylpyrrolidone. The degradation mechanism was analysed by using Glynn's model. The water-soluble polymers used here are degraded with a Gaussian probability by ultrasonic irradiation.

(Keywords: ultrasonic degradation; water-soluble polymers; cavitation)

INTRODUCTION

The first reported investigation of the degradation of polymers by high-power ultrasound was carried out by Schmid and Rommel[1]. Since then, many studies have been carried out and reported in the literature[2-6]. It is well known that the irradiation of sound waves into a solution produces cavitation bubbles. The formation and collapse of the bubble plays an important role in the degradation of polymers in solution. The ultrasonic degradation of polymers was observed in the frequency range of 20 kHz to 1 MHz in various solvents. A number of investigations on ultrasonic degradation have been carried out, but quantatative comparison of the experimental results reported by various workers is difficult, since no standardization of the experimental conditions has been established. In general, the ultrasonic degradation process is a non-random process and the scission of polymer chains in solution occurs at a preferential position[2-6]. However, details of the degradation process are still obscure. Glynn *et al.* have investigated the ultrasonic degradation mechanism of polystyrene in solution and proposed a general model for the prediction of the molecular weight distribution of degraded polymers[7,8].

The ultrasonic degradation of water-soluble polymers has been studied by several workers. Basedow and co-workers have investigated dextran[9,10] and poly(ethylene glycol)[11], Ohta *et al.* dextran[12] and pullulan[13], whilst Keqiang *et al.* have studied hydroxyethylcellulose and poly(ethylene oxide) (PEO)[14]. However, little information was given on the problem of polydispersity (M_w/M_n). The value of M_w/M_n is a useful quantity which can shed light on the degradation mechanism. In addition, it is important to investigate various polymers under the same experimental conditions to elucidate the ultrasonic degradation mechanism. Unfortunately, it is difficult to compare the results obtained by different investigators. The purpose of this work is to investigate the ultrasonic degradation of three water-soluble polymers, pullulan, PEO and polyvinylpyrrolidone (PVP), which are well characterized. The degradation mechanism of the water-soluble polymers is discussed on the basis of Glynn's model. In this work, special care has been taken in setting up the experimental apparatus in order to obtain reproducible results.

EXPERIMENTAL

Sound waves were irradiated into a cylindrical sample cell, as shown in *Figure 1*. The cell was made of Pyrex glass and the sample volume was 20 cm^3. The oscillator was immersed in a water bath regulated at 4 ± 0.1°C. The position of the sample cell relative to the oscillator was fixed so that the ultrasonic power was effectively transmitted into the solution. For this purpose, the concentration of the nitrate ion, which was produced in water saturated with air, was used as a measure of the ultrasonic energy applied to the solution. The concentration of the nitrate ion was determined by the method proposed by Wood *et al.*[15]. A concave PZT transducer (diameter 50 mm) was used as an ultrasonic source and the operating frequency was 500 kHz. The effective irradiation of sound waves into solution was attainable by using a concave transducer (*Figure 1*). The ultrasonic generator could be used continuously up to 80 W output power. In this work, an output power of 80 W was used and the rate of the nitrate ion concentration produced in water under ultrasonic irradiation was $9.58 \times 10^{-4}\,\mathrm{mol\,dm^{-3}\,h^{-1}}$. An increase in solution temperature by continuous ultrasonic irradiation was not observed.

Standard samples of pullulan and PEO with a narrow molecular weight distribution were obtained from Showa Denko Ltd and Tosoh Co. Ltd, respectively. The samples were used without further purification. The molecular

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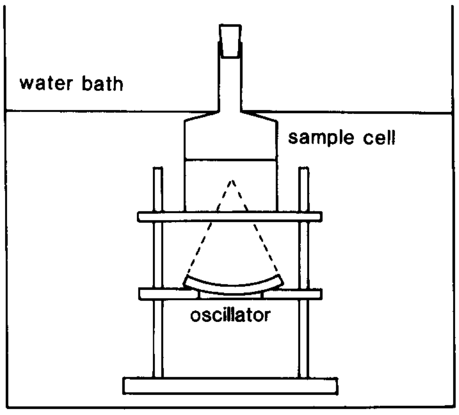

Figure 1 Ultrasonic irradiation system

weight of the pullulan used for ultrasonic irradiation was 10×10^4 ($M_w/M_n = 1.10$) and that of PEO was 8.6×10^4 ($M_w/M_n = 1.02$). PVP was purchased from Nakari Chemicals Co. and was purified by fractional precipitation using a water–acetone mixture as the solvent–non-solvent system[16]. The molecular weight of the PVP used was 8.2×10^4 ($M_w/M_n = 1.15$). The polymer concentration in solution was 0.1 wt%.

The molecular weight distribution was estimated from the gel permeation chromatogram. A CCPD model (Tosoh Co. Ltd) was used as the high pressure solvent delivery pump. A differential refractometer was used as the detector, with TSK-GEL G300PW and G5000PW as the columns (Tosoh Co. Ltd). The calibration curves for pullulan and PEO were obtained using Pullulan Shodex standard and TSK standard PEO samples, respectively. An aqueous solution of NaCl (0.1 mol dm^{-3}) was used as the solvent for all samples. Fractionated PVP samples were used to obtain the calibration curve.

RESULTS

Figure 2 shows the molecular weight distribution of pullulan as a function of sonication time. The molecular weight sharply decreased in a few hours and thereafter the degradation proceeded slowly. The molecular weight of pullulan approached a constant value of a few thousands after sonication for 36 h, as shown in *Figure 3*, where the molecular weight is calculated from the g.p.c. curve. The result for the low molecular weight sample ($M_w = 5.8 \times 10^3$) is also shown in *Figure 3*. The final molecular weight for the low molecular weight sample after a long irradiation time is nearly equal to that of the high molecular weight sample. Ohta *et al.*[13] suggested that the final molecular weight obtained by ultrasonic degradation at a frequency of 20 kHz is 3×10^3–5×10^3. In our work, the final molecular weight estimated from g.p.c. is $\sim 2 \times 10^3$–3×10^3. *Figure 4* shows a plot of M_w/M_n *versus* sonication time. A maximum is shown, the position of which depends on the initial molecular weight. After a long irradiation time the final value of M_w/M_n is independent of the molecular weight within experimental error.

Figures 5A and *B* show the molecular weight distribution of PEO and PVP, respectively, as a function of sonication time. The ultrasonic degradation of PEO and PVP chains is recognized to be like that of pullulan. The molecular weight distribution of the PVP sample gradually shifts to the low molecular weight region, but

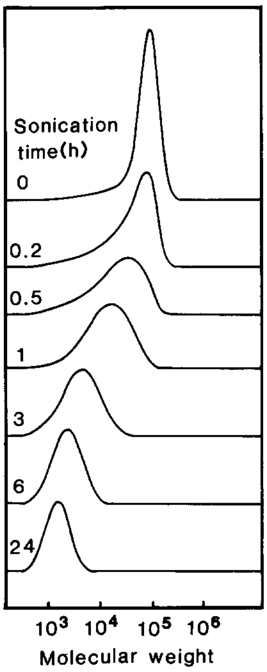

Figure 2 Molecular weight distribution of pullulan as a function of sonication time

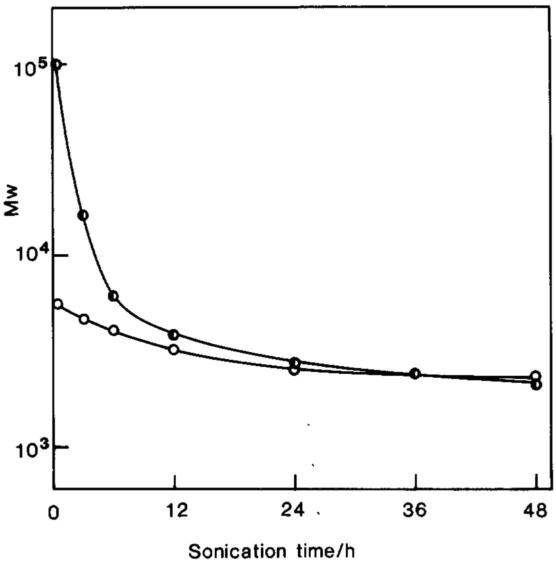

Figure 3 Molecular weight of pullulan as a function of sonication time: (◐) 1×10^5; (○) 5.8×10^3

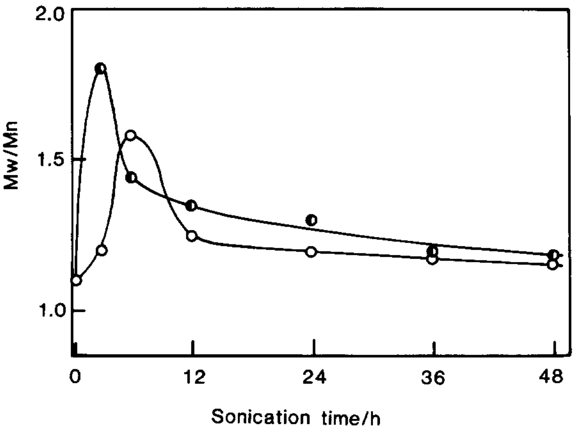

Figure 4 Plot of M_w/M_n as a function of sonication time for pullulan: (◐) 1×10^5; (○) 5.8×10^3

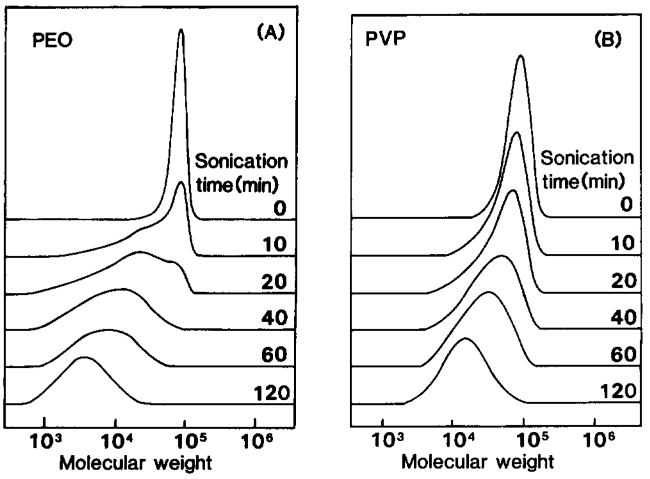

Figure 5 Molecular weight distribution of (A) PEO and (B) PVB as a function of sonication time

in the case of PEO, a large change in the molecular weight distribution is observed after a short irradiation time (10 min). This means that the PEO chain is scissile in comparison to pullulan and PVP.

DISCUSSION

The ultrasonic degradation process should be represented by a multi-step reaction. If the ultrasonic degradation in a short sonication time is assumed to be a first-order reaction, the apparent rate constant can be estimated. Note should be taken of the molecular weight at the maximum of the g.p.c. curve of the non-irradiated sample. The change in concentration of the fixed molecular weight is represented by:

$$\frac{dC(M_i)}{dt} = -kC(M_i) \tag{1}$$

where $C(M_i)$ is the concentration of the fixed molecular weight of M_i and k is the apparent degradation rate constant. *Figure 6* shows a plot of $\ln[C(M_i)]$ *versus* sonication time, where M_i is the value at the maximum of the molecular weight distribution of the non-irradiated sample. The apparent degradation rate constant defined in equation (1) can be estimated from the slope of the plot in *Figure 6*. The values of k are 0.076, 0.032 and 0.030 min^{-1} for PEO, PVP and pullulan, respectively. The molecular weight dependence of k for dextran and pullulan was reported by Basedow and Ebert[9] and Ohta *et al.*[13]. The k value of pullulan with a molecular weight of 10×10^4, which is estimated from the molecular weight dependence of the apparent rate constant given by Ohta *et al.*[13], is $\sim 0.03\ \text{min}^{-1}$, which is in good agreement with our result. The molecular weights of pullulan, PVP and PEO investigated in our work are not the same. The results of Basedow *et al.* and Ohta *et al.* indicate that k increases with molecular weight. It is expected that the k values for PEO and PVP with the same molecular weight as the pullulan used here are larger than that estimated from *Figure 6*. It is conceivable that the difference between the k values for PEO, PVP and pullulan is increased. The high value of k for PEO means that scission of the polymer chain occurs more easily in comparison with the other two polymers.

The bond energies for the C–O and C–C bonds are 357 and 345 kJ mol^{-1}, respectively. The difference in the rate constants is not correlated to the bond energy. Pullulan consists of the glucose unit but PEO is in the form of a simple linear chain. PEO is more flexible than pullulan. As PVP has the pyrrolidone group as its side group, its flexibility is lower than that of PEO. The conformation of flexible polymers is easily changed by applied force and flexible polymers are fully extended in a relatively short time in comparison with rigid polymers. Therefore, the flexibility of the polymer chain will be one of the most important factors in determining the degradation rate.

The rate equations for the depolymerization process of linear polymer chains are formulated by Simha[17]. The analytical solution is given and can be solved in special cases. Thermal degradation occurs randomly[18] and the preferential breaking at the chain ends occurs in the degradation of cryogenic crushing[19]. These reactions are well simulated by Simha's model. However, calculation of the non-random process, such as ultrasonic degradation, is difficult. Glynn *et al.* proposed a general model for prediction of molecular weight distributions of degraded polymers[7,8]. They indicated that ultrasonic degradation proceeds with a certain degradation probability. In this work, the probability of choosing a molecule for rupture $P(t, x)$ and the probability of rupture $Q(y, x)$ are used.

$$P(t, x) = A(t)xf_n(t, x) \tag{2}$$

and

$$Q(y, x) = [ry(2\pi)^{1/2}]^{-1} \exp[-(x - y/2)^2/2(ry)^2] \tag{3}$$

where t is the time of scission, x is the degree of polymerization, ry is the standard deviation of the Gaussian distribution function, $Q(y, x)$. Details are given in the literature[7,8]. If r is very large ($\gg 1$), the distribution approaches a random one and if r is very small ($\ll 1$), scission near the midpoint of the chains occurs. The $f_n(0, x)$ can be calculated from the initial molecular weight distribution and, successively, $f_n(1, x)$ is obtained. Three cases are simulated: random breakage, centre breakage and Gaussian breakage. The centre breakage process gives a molecular weight distribution showing a few sharp peaks. In the case of random breakage, scission of the polymer chain occurs with equal probability independent of the chain length and leads to a rapid increase in the low molecular weight sample. In our study, as shown in *Figures 3* and *5*, the molecular weight distribution by ultrasonic degradation gradually shifts to low molecular

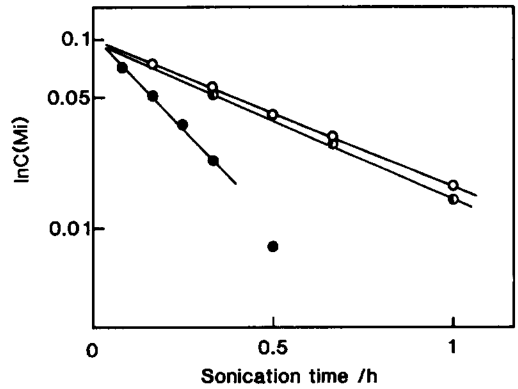

Figure 6 Plot of $\log[C(M_i)]$ *versus* sonication time: (○) pullulan; (●) PEO; (◐) PVP

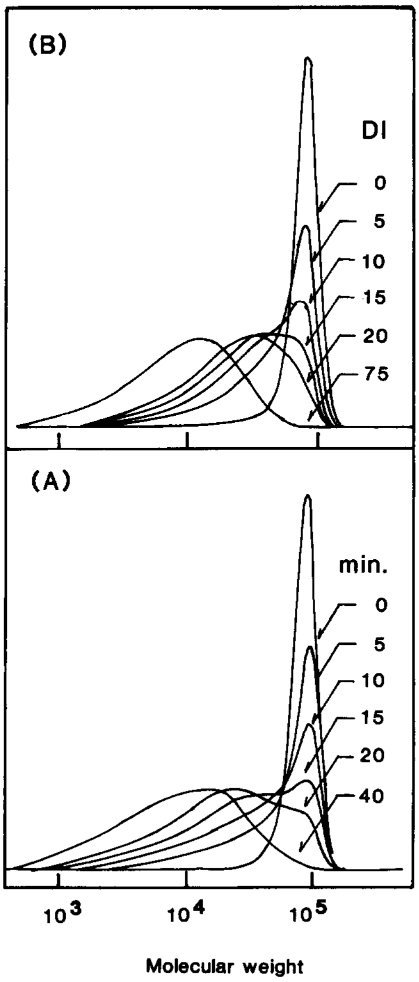

Figure 7 Molecular weight distribution of PEO: (A) observed result; (B) calculated result using Glynn's model and equation (3) with $r = 0.4$

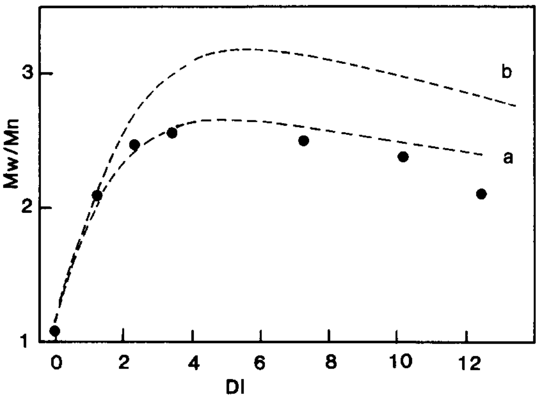

Figure 8 Plot of M_w/M_n *versus* DI for PEO. The symbols represent the M_w/M_n of PEO. The broken lines (a) and (b) are the calculated results using a Gaussian probability and random probability, respectively

weight. This behaviour is only reproduced by the Gaussian breakage process. As examples, *Figures 7* and *8* show $f_n(t, x)$ and M_w/M_n for PEO in aqueous solution as a function of the degradation index (DI). Similar results are obtained for pullulan and PVP. In general, DI, which describes the extent of degradation, is defined as:

$$\mathrm{DI} = \frac{M_n(0)}{M_n(t)} - 1 \tag{4}$$

where $M_n(0)$ is the molecular weight of the original polymer and $M_n(t)$ that of the degraded sample after t breaks. The calculated results of M_w/M_n for the random breakage process are also shown in *Figure 8*. Random scission leads to a broad molecular weight distribution. It is reasonable that the change in the molecular weight distribution of pullulan, PEO and PVP is reproduced with a Gaussian probability. The parameter, r, which gives the width of the Gaussian distribution, is 0.15 for pullulan, 0.3 for PVP and 0.4 for PEO. The PEO sample degrades at a very fast rate and consequently with a broad Gaussian probability. Scission of the pullulan sample by ultrasonic irradiation occurs with a narrow Gaussian probability. In other words, most of the pullulan chains degrade near the centre. The degradation rate of pullulan is almost the same as that of PVP as described above but the scission of PVP with its side group proceeds with a wider Gaussian probability than pullulan. This result suggests that the parameter r may depend not only on the degradation rate but also on the molecular structure. In order to elucidate the relationship between the degradation rate and the parameter r, further experiments will be required.

In conclusion, under ultrasonic irradiation water-soluble polymers degrade with a Gaussian probability and the degradation rate depends on the molecular structure and flexibility of the polymer. The width of the Gaussian distribution may be related to the degradation rate.

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