



# THE LIFE TIME OF A DISSOLVING POLYMERIC PARTICLE†

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**Abstract**—The life time of a dissolving polymeric particle in a hydrodynamic field is predicted by building up a model that includes the phenomenon of reptation of the macromolecules, disengagement of these molecules from the gel–liquid interface and also diffusion in the boundary layer surrounding the gel–liquid interface. The model predictions have been verified through some preliminary experiments. A striking experimental observation is that below a critical particle size, the dissolution time does not depend on the particle dimension, a finding that is in sharp contrast to the dissolution of ordinary low molecular weight systems. The minimum time for dissolution in the particle size independent region is shown to satisfy the prediction emanating from scaling theories. The implications of the findings in engineering practice have been discussed.

## INTRODUCTION

We have been investigating the diffusion–reaction problems in polymeric media for sometime now (Shah *et al.*, 1990; Vyavahare *et al.*, 1990a; Vyavahare *et al.*, 1990b; Kulkarni *et al.*, 1992). An important problem on which we have focused attention recently pertains to the case of dissolution of solid polymeric particles in solvents. This is a technologically important problem. Thus, in polymer modification reactions, the polymer is dissolved in a good solvent, before carrying out the modification reaction such as grafting or crosslinking. Drag reducing polymers need to be dissolved in a solvent, before injecting them in long distance pipe lines. In the manufacture of photoresists, the final pattern is formed by dissolving away a polymer in a solvent. Solid polymeric flocculents are dissolved in water before using them in waste water treatment. In all such cases, an understanding of the basic transport processes involved in the dissolution of polymers is essential.

At first sight, the problem of polymer dissolution may appear to be trivial, since there exists a comprehensive body of information on the theory and practice of dissolution of particles of low molecular weight. However, as we will show later, there are fundamental differences in the process of dissolution of low-molecular-weight and high-molecular-weight polymeric systems.

The process of dissolution of a glassy polymer begins with the ingress of a solvent in the glassy matrix by diffusion followed by some morphological changes within the polymer. Some incisive contribution in explaining this phenomenon have been made by Astarita and his coworkers (see e.g. Astarita and Sarti, 1978; Astarita and Joshi, 1978; Astarita, 1987; Occone and Astarita, 1987; Astarita *et al.*, 1989; Kalospiros *et al.*, 1991). As the solvent penetrates inside the polymer matrix, the glassy region becomes rubbery. There

is a sharp boundary separating the glassy region, (where the solvent concentration is almost negligible), from a rubbery region (in essence a swollen gel region), where the solvent concentration is fairly high. The molecules in the rubbery region adjacent to the polymer–solvent interface have high internal mobility and the movement of the polymer molecules in the solvent essentially starts from this region.

The problem of dissolution of polymers in solvent has been treated in the past by extending the conventional theories of diffusion and dissolution of ordinary solutes (Tu and Ouano, 1977). Many others have also studied the problem of polymer swelling and dissolution theoretically and experimentally (Burkley and Berger, 1962; Ueberreiter and Asmussen, 1962; Lapcik and Valko, 1971; Rossi and Mazich, 1991). However, the first attempts to focus attention on the molecular level events linked to the long-chain nature of the polymer molecules was made by Brochard and de Gennes (1983). In a significant paper, they evolved scaling concepts for dissolution of a drop containing a semi-dilute polymer solution. They proposed that when a droplet of semi-dilute polymer solution is placed in a solvent, the process of dissolution of the droplet comprises two steps. The first is the swelling of the polymer network by cooperative diffusion of the polymer chains and the second is the reptation of the polymer chains out of the swollen polymer network. These two steps are chiefly controlled by the cooperative diffusion coefficient,  $D_{COOP}$  and the reptation time,  $t_{rep}$  (De Gennes, 1971; De Gennes, 1979; Doi and Edwards, 1986). Brochard and De Gennes showed that an optimum droplet size of the order of  $\sqrt{D_{COOP}t_{rep}}$  may exist, below which the dissolution time will be equal. The time of dissolution in this case being equal to the reptation time and it is independent of particle size. This observation is in sharp contrast to that in the case of dissolution of a non-polymeric particle, where this time depends strongly on the particle size (Sherwood *et al.*, 1975).

Brochard and De Gennes were careful enough to warn that a direct extrapolation of their work to the

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dissolution process of solid polymers may be erroneous. Nevertheless, the basic physical arguments given by these authors do have direct relevance to the dissolution of a solid polymer, since at some stage, the macromolecules will take a certain minimum time to reptate and disentangle themselves, before moving into the bulk of the solvent.

Another interesting study focusing on the micro-mechanics of the problem of polymer dissolution was published by Herman and Edwards (1990). They analysed the contribution of the free energy and the chemical potential of the polymer and the solvent due to the non-random distribution of orientations induced by the penetration of the solvent and the subsequent swelling.

The question of the prediction of the dissolution time of a polymer and its dependence on the size of the particle has remained unanswered so far. In this paper, we propose a comprehensive model for describing the process of dissolution of a polymeric particle, which will take into account all the main molecular level processes. Ours is probably the first study aimed at making a prediction of the lifetime of a dissolving polymeric particle by considering all these processes together. We will bring out the unusual feature of particle size independent dissolution of polymeric particles through our model and verify it experimentally.

#### A PHYSICAL MODEL FOR DISSOLUTION OF POLYMERIC PARTICLES

The events that occur during the process of dissolution of a solid polymer have been shown schematically in Fig. 1. Initially, the solvent diffuses into the glassy polymer inducing transition of the glass into a rubbery state (which resembles a mildly swollen gel). This gel is held together by the physical crosslinks provided by entangled structure. The continuous swelling of the network is followed by the dissolution of the polymer chains from the gel-liquid interface. However, a polymer chain requires a certain minimum time to reptate out of the entangled swollen network and disengage itself from the interface. This minimum time will be assumed to equal the reptation time ( $t_{rep}$ ) of the polymer molecules. The reptation time will essentially depend on the structure of the polymer and the molecular weight. The physics of reptation and the scaling relationships for reptation time have been elucidated in the literature (De Gennes, 1971; Doi and Edwards, 1986).

The mobility of the polymer chains at the interface of the swollen gel phase is high. These chains will tend to disengage from the interface and move to the solution phase by travelling through the diffusion boundary layer. For low-molecular-weight solids, the dissolution process has been envisaged as one that involves two steps: detachment of molecules from the solid surface followed by the diffusion of the species through an external mass transfer film into the bulk liquid (Gallily and Friedlander, 1965; Rosner, 1969).

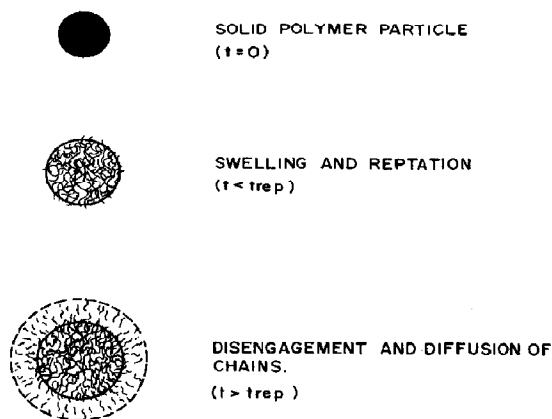


Fig. 1. Schematic representation of the mechanistic events in the dissolution of a polymeric particle.

Polymer chains, being long and mutually entangled, will be inhibited from entering the liquid phase due to the dynamic friction between the chains. We propose that the rate at which the chains disengage themselves from the gel-liquid interface is one of the factors controlling the dissolution rate in polymeric systems. There is a considerable indirect experimental evidence, supporting the concept of disengagement in related problems. For example, in the studies of Lee and Fuller (1984), polymer chains were absorbed under stagnant conditions. It was observed that a portion of the polymer chains was attached to the surface and entangled with the other chains. The remaining portion of the chain extended away for the surface as dangling ends. Any shearing action arising out of the imposition of a hydrodynamic field is assumed to result in loosening and tearing away of individual macromolecules from their neighbours, who form the entangled mass. It is interesting to draw a parallel with a similar situation that has been described by Barham and Keller (1990). They have studied "topological adsorption entanglement layer formation" in polymers, which represents mutual entanglement of the flowing solutions and that of the adsorbed layer along the surface. Barham and Keller postulated that on increasing the shear stress, these entanglements at the surface get torn away. The physical picture of disengagement at the gel-liquid interface proposed by us is somewhat similar to this.

In addition to the disengagement process at the interface, there will be some mass transfer resistance at the surface due to a concentration gradient that will be set up between the interface of the swollen gel and the bulk liquid, which will drive this process. If the disengagement rate ( $k_d$ ) is relatively low, the resistance of the external boundary layer, quantified by the mass transfer coefficient ( $k_l$ ), can be neglected. However, if the surface disengagement and the subsequent transport of the disengaged chains occur at comparable rates, then, depending on the relative magnitude of the resistances at any instance, the dissolution process

may be disengagement limited or diffusion limited. Our mathematical model for dissolution of polymeric particle will incorporate all the features of reptation, disengagement and diffusion through the boundary layer that have been described above.

#### MATHEMATICAL FORMULATION OF THE MODEL

For simplicity, we assume that the glass-gel transition is rapid and neglect the details of the kinetics of the glass-gel transition process. A more comprehensive model incorporating the phenomenon of glass-gel transition kinetics has been already attempted (Ranade and Mashelkar, 1993). The results show that such an inclusion does not lead to any significant differences in the predictions. We now set up the swelling-dissolution problem for a polymeric particle with spherical geometry. The mass conservation equation for diffusion of small solvent molecules can be viewed in a stationary coordinate frame. In terms of solvent volume fraction this can be given as

$$\frac{\partial \phi_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_s \frac{\partial \phi_s}{\partial r} \right) - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v \phi_s) \quad (1)$$

$$t > 0, 0 < r < R(t).$$

Here,  $D_s$  is diffusivity of the solvent in the polymer (which is defined relative to a polymer fixed frame and is assumed to be constant in our work),  $\phi_s$  is the volume fraction of the solvent in the polymer,  $R(t)$  is the moving gel-liquid interface,  $t$  is time,  $r$  is the radial position and  $v(r, t)$  is the local swelling rate, with which the coordinates move. Since the local swelling rate is equal in magnitude but opposite in direction to the local flux of the solvent, we have

$$v = D_s \frac{\partial \phi_s}{\partial r}. \quad (2)$$

The relevant initial and boundary conditions pertinent to eq. (1) are

$$\phi_s = 0 \quad \text{at } t = 0, 0 < r < R_0 \quad (3)$$

$$\phi_s = \phi_{s,i} \quad \text{at } r = R(t), t > 0 \quad (4)$$

$$\frac{\partial \phi_s}{\partial r} = 0 \quad \text{at } r = 0, t > 0. \quad (5)$$

Here,  $R_0$  is the initial radius of the spherical polymer particle, and  $\phi_{s,i}$  is the equilibrium volume fraction of the solvent in the polymer, which is assumed to be constant as per convention. This solvent concentration is also assumed to be greater than the critical concentration required for disengagement.

The movement of the gel-solvent interface  $R(t)$  takes place as a result of the swelling due to the solvent ingress and the disengagement of the polymer chains at the surface. This can be described as follows:

$$\frac{dR}{dt} = \left( D_s \frac{\partial \phi_s}{\partial r} \right)_{r=R^-(t)} - \left( \frac{D_p}{\phi_{p,i}} \frac{\partial \phi_p}{\partial r} \right)_{R^+(t)}. \quad (6)$$

In the above equation, the first term on the right-hand side is due to the swelling of the polymer network and

the second is due to the dissolution. The obvious initial condition is

$$R = R_0 \quad \text{at } t = 0. \quad (7)$$

As the polymer chains disengage, the boundary erodes and the polymer molecules move out from the gel-like phase (entangled state) to the less viscous liquid solution (free state) through a diffusion boundary layer. For simplicity, we will perform pseudo-steady-state calculations. This approximation is valid if  $\delta^2/D_p \ll t_d$ , where  $\delta$  is the diffusion boundary layer thickness and  $t_d$  is the dissolution time. However, a more precise computation using an appropriate flow field showed only marginal differences in the predictions (Ranade and Mashelkar, 1993).

The flux of the disengaged polymer molecules at the liquid side of the gel-liquid interface needs some attention. As a polymer chain requires a certain time to disengage from the gel-liquid interface, the disengagement rate is initially zero. This rate does not become finite till the chains at the gel-liquid interface complete the reptation process resulting in a viscous yield of the transient polymer network. As this minimum time required for the first few of chains to disengage from the gel-liquid interface is equivalent to the reptation time, we assume the following boundary condition to exist at the liquid side of the gel-liquid interface,  $R^+(t)$ :

$$D_p \frac{\partial \phi_p}{\partial r} = 0 \quad \text{at } r = R^+(t), 0 < t < t_{rep}. \quad (8)$$

However, after the reptation process, the transport of the polymer chains may be disengagement limited or diffusion limited. Although some intermediate behaviour might apply at  $t = t_{rep}$ , for retaining the simplicity of the analysis, we have not invoked these complications at this stage. At small times, i.e. at times just greater than reptation time, the rate of diffusion is sufficiently high to carry away the disengaged chains and the flux at the interface is limited by the constant disengagement rate  $k_d$ . Hence, the following condition prevails at the liquid side of the gel-liquid interface,  $R^+(t)$ :

$$-D_p \frac{\partial \phi_p}{\partial r} = k_d \phi_{p,i} \quad \text{at } r = R^+(t), t > t_{rep}. \quad (9)$$

Here,  $k_d$  is the disengagement rate. As the disengagement of the polymer chains occurs, the concentration of the polymer outside the interface increases as long as  $\phi_p < \phi_{p,i}$  at  $R^+(t)$ . If the mass transfer coefficient is low, then the polymer volume fraction  $\phi_p$  becomes equal to  $\phi_{p,i}$  at  $R^+(t)$ , the rate of diffusion is not sufficient to carry away the disengaged chains and thereafter the polymer concentration at  $R^+(t)$  is maintained at  $\phi_{p,i}$ . Thus, the process is controlled by the resistance to mass transfer in the liquid and we have the following condition at the liquid side of the gel-liquid interface,  $R^+(t)$  as long as  $\phi_p = \phi_{p,i}$ :

$$-D_p \frac{\partial \phi_p}{\partial r} = k_l (\phi_{p,i} - \phi_{p,b}) \quad \text{at } r = R^+(t), t > t_{rep}. \quad (10)$$

Here,  $k_l$  is liquid side mass transfer coefficient and  $\phi_{p,b}$  is the polymer volume fraction in the bulk. At large times, however, as the particle dimension diminishes due to dissolution, the mass transfer coefficient increases. The process becomes disengagement limited when  $\phi_p$  becomes less than  $\phi_{p,i}$  at  $R^+(t)$ .

The disengagement rate  $k_d$  is somewhat difficult to estimate quantitatively. The mass transfer coefficient  $k_l$ , however, can be approximately estimated by using the conventional relationships. As an approximation, we use Ranz's correlation for single sphere to determine the mass transfer coefficient (Ranz, 1952):

$$Sh = 2 + 0.6(Re)^{1/2}(Sc)^{1/3}. \quad (11)$$

The exact dissolution time, ( $t_d$ ) of the polymer particle can be determined from the following relation:

$$\int_0^{t_d} 4\pi R^2 \left( -D_p \frac{\partial \phi_p}{\partial r} \right)_{r=R^+(t)} dt = \frac{4}{3} \pi R_0^3. \quad (12)$$

The above equations are dedimensionalised by using a suitable dimensionless time and radial position:

$$\tau = \frac{t}{t_{rep}} \quad (13)$$

$$\xi = \frac{r}{(D_s t_{rep})^{1/2}}. \quad (14)$$

The dimensionless equations and the boundary conditions then become

$$\frac{\partial \phi_s}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \phi_p \frac{\partial \phi_s}{\partial \xi} \right) \quad \tau > 0, \quad 0 < \xi < \xi_i \quad (15)$$

$$\phi_s = 0 \quad \text{at } \tau = 0, \quad 0 < \xi < \xi_0 \quad (16)$$

$$\phi_s = \phi_{s,i} \quad \text{at } \xi = \xi_i, \quad \tau > 0 \quad (17)$$

$$\frac{d\phi_s}{d\xi} = 0 \quad \text{at } \xi = 0, \quad \tau > 0 \quad (18)$$

$$\frac{d\xi_i}{d\tau} = \left( \frac{\partial \phi_s}{\partial \xi} \right)_{\xi=\xi_i^-} - \left( \frac{D_p}{D_s \phi_{p,i}} \frac{\partial \phi_p}{\partial \xi} \right)_{\xi=\xi_i^+} \quad (19)$$

$$\xi_i = \xi_0 \quad \text{at } \tau = 0 \quad (20)$$

$$\frac{\partial \phi_p}{\partial \xi} = 0 \quad \text{at } \xi = \xi_i^+, \quad 0 < \tau < 1 \quad (21)$$

$$-\frac{D_p}{D_s} \frac{\partial \phi_p}{\partial \xi} = \mu_d \phi_{p,i} \quad \text{at } \xi = \xi_i^+, \quad \tau > 1 \quad (22)$$

where

$$\mu_d = \sqrt{\frac{k_d^2 t_{rep}}{D_s}} \quad (23)$$

$$-\frac{D_p}{D_s} \frac{\partial \phi_p}{\partial \xi} = \mu_i (\phi_{p,i} - \phi_{p,b}) \quad \text{at } \xi = \xi_i^+, \quad \tau > 1 \quad (24)$$

where

$$\mu_i(\tau) = \sqrt{\frac{k_i^2 t_{rep}}{D_s}} = \frac{1}{\xi_i} \left( \frac{D_p}{D_s} \right) + \frac{\alpha}{\xi_i^{1/2}} \left( \frac{D_p}{D_s} \right)^{2/3} \quad (25)$$

$$\alpha = \frac{0.6}{\sqrt{2}} \left( \frac{u t_{rep}^{1/2} D_s^{1/2}}{\nu} \right)^{1/2} \left( \frac{\nu}{D_s} \right)^{1/3}. \quad (26)$$

Here,  $\alpha$  is a parameter which depends on the hydrodynamics and  $\nu$  is kinematic viscosity of the solvent.

Equations (15)–(26) were solved numerically using Crank–Nicolson scheme and the dissolution time  $\tau_d$  was determined as a function of initial particle dimension  $\xi_0$ . This time is dependent on dimensionless parameter such as  $\mu_d$ ,  $D_p/D_s$  and  $\alpha$  for any fixed initial particle dimension.

## EXPERIMENTAL

We conducted only preliminary experiments to verify the validity of the key deductions from our model. We studied the process of dissolution in two polymer–solvent systems, viz. polystyrene in cyclohexane at 35°C (i.e. just above the  $\theta$ -temperature) and poly(methyl methacrylate) in benzene at 30°C. Polystyrene samples (Polystron 666, Polystron 678, MCG 100) with varying molecular weights were obtained from Polychem Ltd., Bombay. Samples of poly(methyl methacrylate) (PMMA) of different molecular weights were procured from Gujarat State Fertilizer Company Ltd, Vadodara. The molecular weights of these polymers were determined by viscometric measurements using toluene at 25°C for polystyrene and benzene at 30°C for PMMA. The intrinsic viscosities and the molecular weights are tabulated in Table 1. Cyclohexane and benzene (AR grade) were used as solvents. The solvents were double-distilled before using them in the dissolution studies.

Beads of these polymer samples, after grinding, were sieved through metallic sieves (ASTM standard)

Table 1. Molecular weights of polymers used in this work

Polymer	Intrinsic viscosity, $\eta$ (dl/g)	$M_w$ (molecular weight)
<i>Polystyrene</i>		
Polystron 666	0.688	$1.647 \times 10^5$
Polystron 678	0.588	$1.328 \times 10^5$
MCG 100	0.550	$1.212 \times 10^2$
<i>Poly(methyl methacrylate)</i>		
PMMA 932 HR	0.505	$1.377 \times 10^5$
PMMA 876 G	0.430	$1.115 \times 10^5$
PMMA 8015	0.341	$0.824 \times 10^5$

and different fractions of solid polymer particles with as narrow a particle size distribution of each sample as possible, were collected. The average particle size was taken for the purpose of the calculation.

All the dissolution experiments were conducted in a jacketed cylindrical beaker made up of glass of 200 ml capacity (diameter = 5 cm, height = 10 cm). The outer jacket of the beaker was connected to a thermostat. Water maintained at the appropriate temperature was circulated through the jacket. Mild agitation conditions were imposed by using a Teflon coated needle and a magnetic stirrer arrangement, so that the particle aggregation could be avoided. A high-precision thermometer with accuracy of 0.05°C was inserted in the dissolving fluid so as to ensure proper temperature control during all the dissolution studies.

For conducting the dissolution experiments, 80 ml solvent was taken in the beaker. By water circulation through the outer jacket, the temperature of the system was brought to the appropriate temperature. 0.06 g of polymer was weighed accurately and added carefully to the solvent under the desired stirring conditions in a period of about 5 s. Utmost care was taken to ensure that the suspended polymer particles did not form agglomerates in solution. The time required for complete disappearance of suspended polymer particles in solution was recorded by using a stopwatch with a precision of 0.1 s. The time required for complete dissolution of different particle sizes of all polymer samples was noted by a visual observation. The readings were reproducible to within  $\pm 5$  s.

## RESULTS AND DISCUSSION

### Model predictions

From the dimensionless equations, it is clear that the process of dissolution will be controlled by disengagement rate if  $\mu_d$  is less than  $\mu_i(\tau)$  or by diffusion rate, if  $\mu_i(\tau)$  is less than the  $\mu_d$ . We can define another dimensionless parameter  $\lambda$  to bring out the relative significance of the reptation:

$$\lambda = \frac{R_0/(\mu_{av}\phi_{p,i}^{1/3})}{t_{rep}} \quad (27)$$

Here,  $\lambda$  is the ratio of apparent dissolution time (i.e. dissolution time excluding the reptation time) to the reptation time.  $\mu_{av}$  is average dissolution rate, which could be  $\mu_d$ , in an entirely disengagement controlled process, or  $\mu_i$ , in an entirely diffusion controlled process, or time-weighted average of both. Clearly, if  $\lambda \ll 1$ , i.e. the apparent dissolution time is much

smaller than the reptation time. The dissolution process will then be controlled by the reptation process and the dissolution time will approximately equal the reptation time ( $t_d \approx t_{rep}$ ). On the other hand, if  $\lambda \gg 1$ , then the process may be disengagement or diffusion controlled and the actual dissolution time will be the sum of the reptation time and the apparent dissolution time. These different controlling regimes of dissolution are summarized in Table 2.

Figure 2 shows the influence of diffusivity of the polymer in the solvent ( $D_p$ ) on the total dimensionless dissolution time ( $\tau_d$ ) of the polymer particle for different dimensionless particle size ( $\xi_0$ ). It can be seen that for larger particle size, the dissolution time decreases with a decrease in the particle size. However, in the smaller particle size range, the dissolution time does not vary significantly with the particle dimension and converges to  $\tau = 1$ , which corresponds to the reptation time. Also, as the diffusivity of the polymer increases, the dissolution time decreases obviously because the mass transfer rate is enhanced.

Figure 3 shows similar trends of dissolution time vs particle dimension for different values of  $\mu_d$ , which represents the disengagement rate. It is obvious that the decrease in the disengagement rate increases the dissolution time for a fixed particle dimension. It can be also noted that for very low value of  $\mu_d$ , in which case the dissolution process is entirely disengagement controlled, the dissolution time varies almost linearly

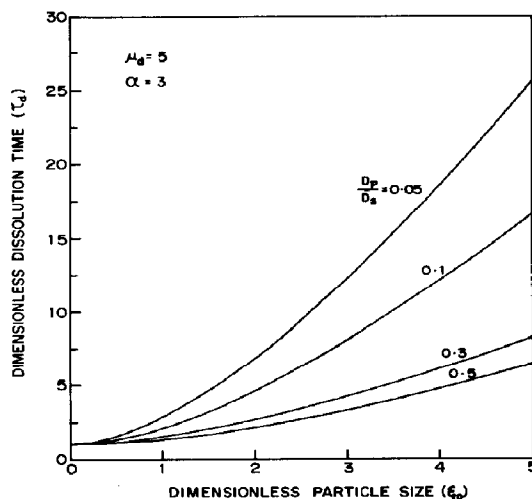


Fig. 2. Effect of the parameter  $D_p/D_s$  on the dissolution time for different particle dimensions.

Table 2

Different regimes of dissolution	Conditions	Particle size dependence of dissolution time
Reptation controlled	$\lambda \ll 1$ , for all $\mu(t)$ , $\mu_d$	Independent of particle size
Diffusion controlled	$\mu_i(t) < \mu_d$ , $\lambda \gg 1$	Dependent on particle size
Disengagement controlled	$\mu_d < \mu_i(t)$ , $\lambda \gg 1$	Dependent on particle size

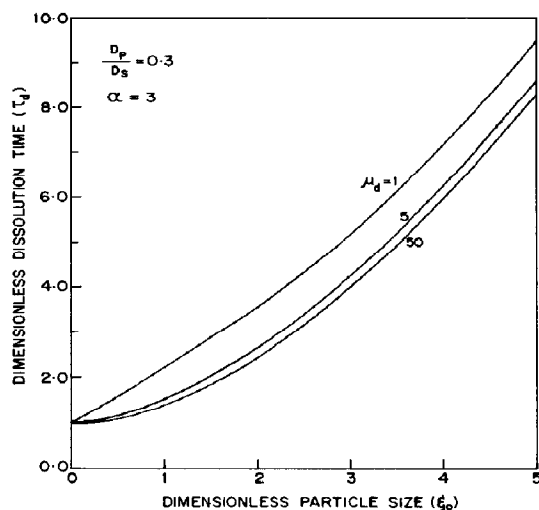


Fig. 3. Effect of the parameter  $\mu_d$  on the dissolution time for different particle dimensions.

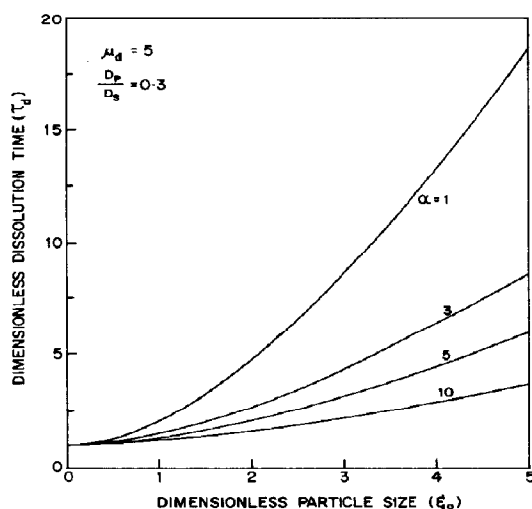


Fig. 4. Effect of the parameter  $\alpha$  on the dissolution time for different particle dimensions.

with particle dimension and the critical particle dimension does not really exist. Physically, disengagement controlled dissolution can occur in the dissolution of very high-molecular-weight polymeric particles or when the dissolution takes place in an intense hydrodynamic field.

In Fig. 4, we present the effect of the parameter  $\alpha$ , which depends on the external flow field or stirring condition. Here again with decreasing  $\alpha$ , the dissolution time for a given particle size increases. Also, for higher value of  $\alpha$ , i.e. in intense hydrodynamics fields, the dissolution time varies almost linearly with particle dimension, as the dissolution process becomes disengagement controlled. In all the cases, it can be seen that the dimensionless dissolution time converges to the minimum time of  $\tau = 1$ , around which the dissolution time does not vary substantially with particle dimension.

#### EXPERIMENTAL DATA

##### Effect of molecular weight on the dissolution time

In Fig. 5, we have plotted the experimental data on time for dissolution ( $t_d$ ) vs the average particle size ( $R_0$ ) of different fractions of solid polystyrene particles in cyclohexane. Dissolution curves for all the three molecular weights at the same temperature (35°C) and a constant rate of stirring are shown. It is seen that for large particles, the rate of dissolution decreases with an increase in the particle size. This is in accordance with the behaviour of small molecular weight compounds. However, as the particle size decreases, the curve of  $t_d$  vs particle size does not pass through the origin but ends with a finite intercept on the  $t_d$  axis. This observation is in contrast with the dissolution behaviour of low-molecular-weight solutes, where such a curve would go through the origin. It is also seen that the process of dissolution improves with a decrease in the molecular weight of the polymer.

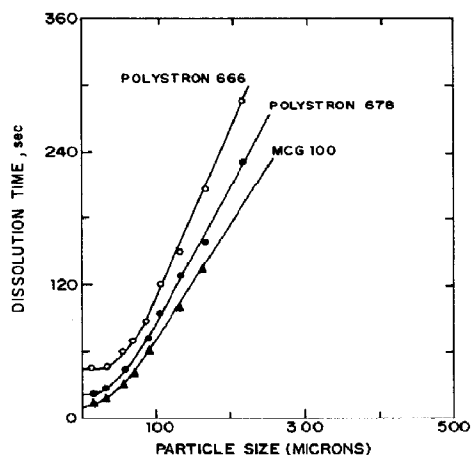


Fig. 5. Dissolution time as a function of the average particle size of polystyrene particles of different molecular weights in cyclohexane (temperature = 35°C, RPM = 230).

In order to substantiate these data with polystyrene-cyclohexane system, we present the dissolution curves obtained with PMMA-benzene system in Fig. 6. The trends here again confirm the same behaviour. It is thus seen that this behaviour is in qualitative agreement with the theoretical considerations summarized earlier.

##### Effect of a hydrodynamic field on the overall process of dissolution

The effect of changing the stirring speed on the process of dissolution is illustrated in Figs 7-9 for different polystyrene samples. The concentration of polymer was kept constant 0.075% (wt/vol) of polymer in cyclohexane at 35°C. Apart from an obvious conclusion that a higher rate of stirring leads to

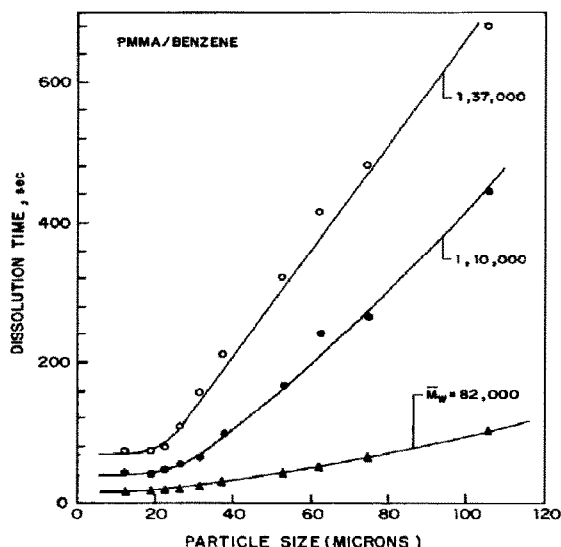


Fig. 6. Dissolution time as a function of the average particle size of PMMA particles of different molecular weights in benzene (temperature = 30°C, RPM = 150).

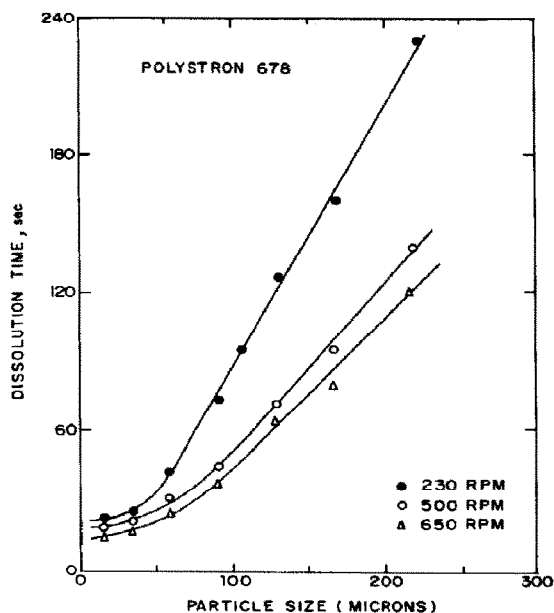


Fig. 8. Dissolution time as a function of the average particle size of polystyrene (Polystron 678) particles in cyclohexane at different stirring speeds (temperature = 35°C).

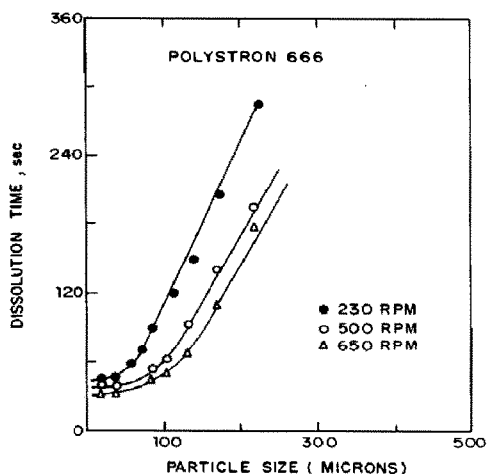


Fig. 7. Dissolution time as a function of the average particle size of polystyrene (Polystron 666) particles in cyclohexane at different stirring speeds (temperature = 35°C).

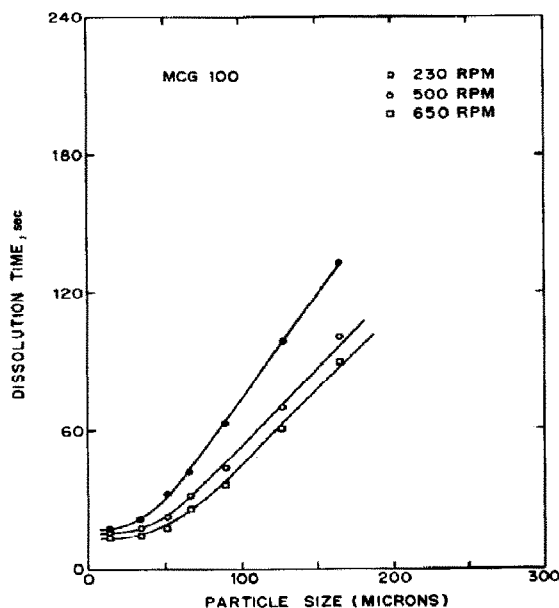


Fig. 9. Dissolution time as a function of the average particle size of polystyrene (MCG 100) particles in cyclohexane at different stirring speeds (temperature = 35°C).

slightly faster dissolution, an interesting observation is that there is an increase in the optimum particle size with increased rate of stirring. In other words, the characteristic particle size of a polymer, below which the time for dissolution does not change appreciably, increases with an increase in the rate of stirring. This observation is in line with the model predictions in Fig. 4, where an increase in the value of  $\alpha$  (which increases with the intensity of the hydrodynamic field) increases the critical particle size.

A semi-quantitative validation of the theoretical predictions will be now made by examining the dissolution data in the range of particle sizes below the

critical size. As shown earlier, the time for dissolution ( $t_d$ ) is approximately  $t_{rep}$  below this critical size. The molecular weight dependence of reptation time is estimated as  $t_{rep} \propto M_w^3$  based on simple scaling arguments due to De Gennes (1971, 1976) and  $t_{rep} \propto M_w^{3.4}$ , based on the experimental evidence and more refined theoretical calculations (Doi and Edwards, 1986). In

Fig. 10, we have plotted the reptation time ( $t_{rep}$ ) vs the molecular weight ( $M_w$ ) on a log-log scale. The slope of  $\log t_{rep}$  vs  $\log M_w$  curve is 3.2 in the case of polystyrene-cyclohexane system and 2.9 in the case of PMMA-benzene system. This is in close agreement with the exponent of 3 and 3.4 referred to earlier.

#### Verification of model prediction with experimental observations

We will now compare the experimental data with our model predictions in a quantitative way. The diffusivity of polystyrene in cyclohexane is calculated as  $3 \times 10^{-7}$  cm<sup>2</sup>/s at a temperature of 35°C, based on the work by King *et al.* (1973). The solvent diffusivity of cyclohexane in polystyrene has not been unfortunately reported. Therefore, looking at the structural similarity between cyclohexane and benzene, the

value for benzene ( $1 \times 10^{-6}$  cm<sup>2</sup>/s) reported by Zielinski and Duda (1992) at a temperature of 30°C was used. Similarly, the diffusivity of benzene in PMMA is estimated to be  $4 \times 10^{-6}$  cm<sup>2</sup>/s at 30°C by the Zielinski and Duda method (1992). The diffusivity of PMMA in acetone was used for calculation and is estimated to be  $2.2 \times 10^{-7}$  cm<sup>2</sup>/s (Ende, 1966). The reptation time was approximately estimated by extrapolating the experimental data to zero particle size. The slip velocities used in the Ranz's correlation were approximately estimated by the method suggested by Harriott (1962). In this method, the minimum mass transfer coefficient is initially estimated by using the terminal velocity of the particle in the Ranz's correlation. Using the minimum coefficient, the actual coefficient at any stirring speed was estimated using the correlation presented by Harriott. From the actual mass transfer coefficient, the slip velocity was calculated. Two parameters are difficult to estimate *a priori*. The first is the interfacial concentration of the solvent in the polymer ( $\phi_{s,i}$ ). Although measurements of  $\phi_{s,i}$  for other systems (such as methyl ethyl ketone in polystyrene) are available in the literature (Tu and Ouano, 1977), for our systems, the values were not available. Similarly, the disengagement rate ( $\mu_d$ ) is also difficult to estimate *a priori*. We, therefore, took them to be unknown parameters for the purpose of data fitting. Thus the present model, the way we have verified it, could be treated as a two-parameter model.

In Fig. 11, we have compared the prediction of the model for dissolution time vs particle dimension with the experimental data for polystyrene-cyclohexane system. It can be seen that the model prediction agrees reasonably well with the experimental data. A similar comparison is shown for PMMA-benzene system in Fig. 12. Here again the prediction compares reasonably well with the experimental data.

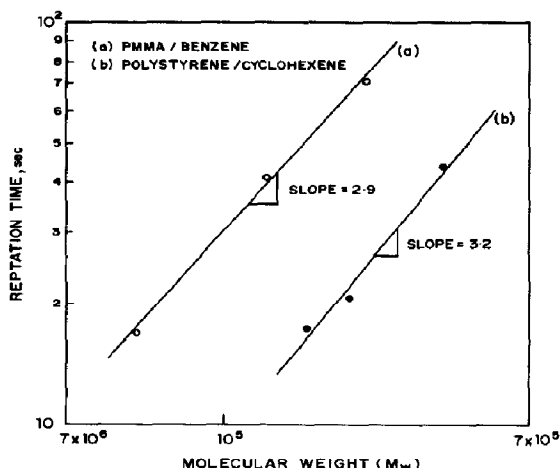


Fig. 10. Reptation time dependence on the molecular weight: validation of the scaling relationship.

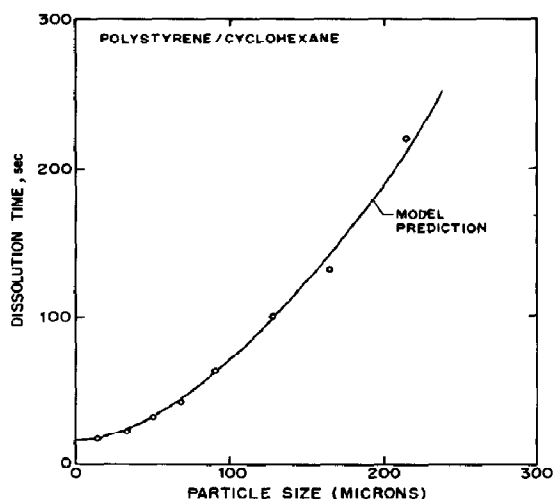


Fig. 11. Comparison of the model prediction with the experimental data for polystyrene-cyclohexane system.

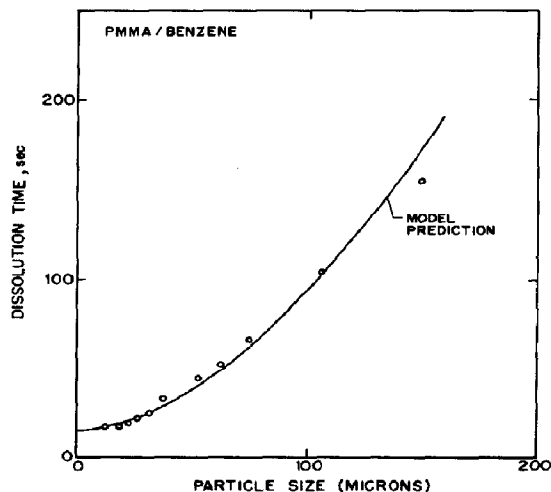


Fig. 12. Comparison of the model prediction with the experimental data for polymethyl methacrylate-benzene system.



## CONCLUDING REMARKS

We have developed a model for estimating the dissolution time of a polymeric particle in a hydrodynamic field. The model takes into account the process of reptation, disengagement from the gel-liquid interface and also diffusion through the boundary layer. By some preliminary experiments, we have demonstrated that there is a critical size of a polymer particle below which the time of dissolution of a solid polymer particle remains almost independent of the particle size. Although the experimental technique adopted in this work is not a sophisticated one, it still provides useful insights for further studies. The comparison between the semi-quantitative predictions and experimental observations is reasonably good.

For polymer technologists, our findings have obvious pragmatic implications. Our model defines a lower limit on the size to which a polymer particle should be reduced. Nothing will be gained in spending more energy to reduce this size further, since the dissolution time will remain independent of the particle size.

For rheologists, the polymer dissolution technique will provide a quick and easy way of obtaining the reptation time. All that one needs to do is to reduce the particle size continuously until a limiting constant dissolution time, independent of the particle size, is obtained. This time will equal the reptation time as per the model developed in this work.

**Acknowledgement**—It is a pleasure to dedicate this paper to Gianni Astarita, whose incisive and wide ranging contributions in transport phenomena in polymeric media over the past three decades have inspired one of us (RAM).

## NOTATION

$d_p$	diameter of the dissolving particle
$D_{\text{COOP}}$	cooperative diffusion coefficient of polymer chains
$D_p$	diffusivity of the polymer
$D_s$	diffusivity of the solvent
$k_t$	external mass transfer coefficient
$k_d$	disengagement rate
$M_w$	viscosity average molecular weight of the polymer
$r$	radial position
$R$	radius of the polymer particle
$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number
$t_d$	dissolution time of polymer particle
$t_{\text{rep}}$	reptation time for a polymer chain
$u$	slip velocity
$v$	local swelling velocity

## Greek letters

$\alpha$	defined by eq. (26)
$\eta$	intrinsic viscosity
$\lambda$	defined by eq. (27)
$\mu_{\text{av}}$	dimensionless average dissolution rate

$\mu_d$	defined by eq. (23)
$\mu_l$	defined by eq. (25)
$\nu$	kinematic viscosity
$\xi$	dimensionless radial position
$\tau$	dimensionless time
$\tau_d$	dimensionless dissolution time
$\phi$	volume fraction

## Subscripts

$b$	bulk
$i$	interface
$0$	initial value
$p$	polymer
$s$	solvent

## Superscripts

$-$	gel side of the interface
$+$	liquid side of the interface

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