Convective Diffusion from a Dissolving Polymeric Particle

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A comprehensive mathematical model for describing the process of dissolution of a spherical polymeric particle in a convective field is developed. It includes the process of glass transition, reptation of macromolecules, disengagement of these molecules from the gel-liquid interface, and diffusion in the boundary layer surrounding the gel-liquid interface. Different controlling regimes for the dissolution process are identified and quantitatively delineated in this moving boundary problem. Analytical solutions for the estimation of dissolution time for various limiting cases are presented. Key predictions from the model are verified by comparison with preliminary experimental data. A novel feature of a particle-size-independent dissolution of polymeric particles below a critical size brought out by the model is verified experimentally. The findings have pragmatic implications in diverse areas, such as polymerization, drag reduction, and microlithography.

Introduction

The process of dissolution of solid polymers in solvents is technologically important in various operations. These encompass a photoresist development (Greeneich, 1975), controlled release systems (Kulkarni and Mashelkar, 1992), and polymerization reactions (Mashelkar, 1984).

The phenomenon of dissolution of polymers has been studied both theoretically and experimentally (Burkley and Berger, 1962; Ueberreiter and Asmussen, 1962; Lapcik and Valko, 1971; Tu and Ouano, 1977; Lee and Peppas, 1987; Papanu et al., 1989; Rossi and Mazich, 1991). Molecular-level events accompanying polymer dissolution were addressed for the first time by Brochard and de Gennes (1983), and more recently by Papanu et al. (1989), Herman and Edwards (1990), and Devotta et al. (1994a,b).

Using scaling concepts Brochard and de Gennes (1983) looked at the closely analogous problem of the dissolution of a drop of a semidilute polymer solution. They postulated that an optimum droplet size of the order of $(D_{COOP}t_{rep})^{1/2}$ may exist, below which the dissolution time will be independent of the droplet size. Here D is the cooperative diffusion coefficient of the polymer network and t_{rep} is the reptation time. A very interesting study focusing on the micromechanics of the problem of polymer dissolution was published by Herman and Edwards (1990). They analyzed the contribution of the free energy and the chemical potential of the polymer and the solvent due to the nonrandom distribution of orientations induced by the penetration of the solvent and the subsequent swelling. When this contribution was sufficiently large compared to the ordinary mixing terms, they postulated that the system would undergo a phase separation into a gel-like concentrated solution phase and a dilute solution phase. Herman and Edwards showed with the help of simple model calculations that the presence of this gel-like phase can significantly slow down the dissolution process.

Devotta et al. (1994a) recently provided the first experimental evidence to show that when a polymer particle dissolves, a critical particle size exists, below which the dissolution time becomes independent of the particle size. This observation is in sharp contrast to what is observed in the case of nonpolymeric particles. These and other such interesting aspects of the dissolution process, coupled with the technological importance of the problem, has prompted us to launch a systematic investigation of the process of dissolution of a polymeric particle.

The elementary model set up by Devotta et al. (1994a) brought out some of the key features of the physical processes involved in the swelling-dissolving phenomena that accompany the disappearance of a polymeric particle. They showed that some fundamental differences in the process governing the dissolution of polymeric solids and nonpolymeric solids. Dis-

solution of particles of low-molecular-weight nonpolymeric materials is mainly governed by the mass-transfer resistance at the solid-liquid interface. For such materials the solid particles shrink as dissolution progresses. The time required for the complete dissolution (t_D) is therefore a strong function of the particle dimension. In contrast, the process of dissolution of a solid polymeric particle involves rather complicated processes. The dissolution proceeds through steps such as transition of the glassy polymer into a rubbery polymer, swelling of the rubbery polymer, disentanglement of the polymer chains from the surface of the swollen particle, and finally the movement of the free polymer chain into the bulk through the diffusion boundary layer surrounding the particle. Furthermore, unlike the case of dissolution of ordinary solutes, for polymeric systems, one cannot really assign any value for equilibrium solubility. In the case of an ordinary solute, the particle dimension continuously diminishes after the exposure to a solvent, whereas in the case of a polymeric particle, there is an increase in the dimension first due to swelling, which is followed by a reduction later.

Devotta et al. (1994b) recently studied the dynamics of the swelling-dissolution process in a rubbery polymer at a microscopic level using *in situ* nuclear magnetic resonance (NMR) measurements. They studied swelling and dissolution of polyisoprene and probed the change of mobility as a function of time. They observed an intermediate plateau in the mobility vs. time plot in this system that persisted for a surprisingly long time before any substantial dissolution would take place. Based on these microscopic studies, they developed a mathematical model that treated swelling and dissolution as distinctly decoupled processes.

The models proposed by Devotta et al. (1994a,b) are approximate. They did not include a number of issues (such as the progressive conversion of glassy phase into a rubbery phase), and a definition of various controlling regimes was not done quantitatively. A well-defined convective field was not assumed so that the full convective diffusion problem was not solved comprehensively. This article attempts to eliminate some of these lacunae and provide a more quantitative basis for this important problem.

Mathematical Model

Physical picture

First we discuss the essential physical ideas proposed by Devotta et al. The essence of the physics of the process of swelling-dissolution of a polymeric particle is shown in Figure 1. In the first step, the solvent diffuses into a glassy polymer, inducing the 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 the entangled structure. There is a sharp boundary separating the glassy region and the gel. As the solvent diffuses into the gel, swelling occurs. The molecules in the gel region have high internal mobility, and the movement of polymer molecules essentially starts from this region. These chains tend to disengage from the interface and diffuse into the bulk. A polymer chain may require a certain minimum time to reptate out of the entangled swollen network and disengage itself from the interface. Here we assume this minimum time is equal to the polymer molecules' reptation time (t_{rep}). The reptation time depends on the structure of the

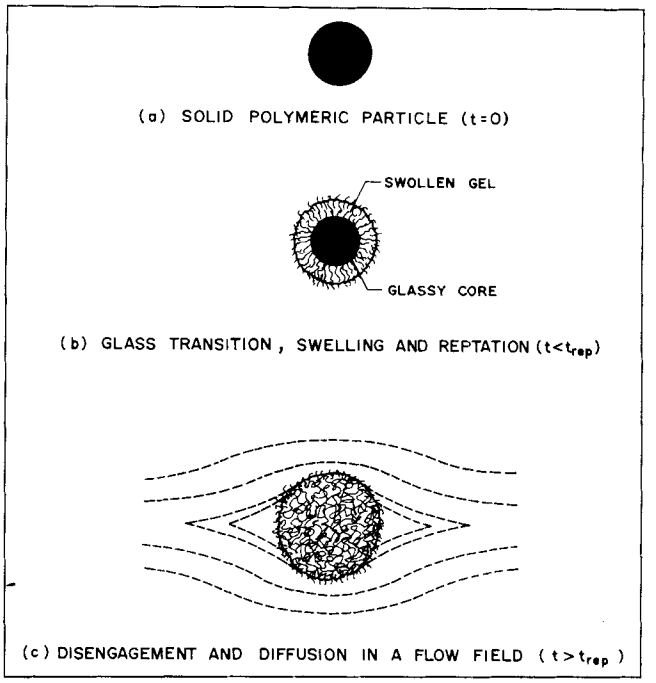

Figure 1. Mechanistic events in the dissolution of polymeric particle.

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 polymer chains on the gel side of the gel-solvent interface tend to disengage from the interface and move to the solution phase by traveling through the diffusion boundary layer. For low molecular weight solids, the detachment of molecules from the solid surface is usually rapid when compared to the diffusion of the molecules through an external boundary layer into the bulk liquid (Gallily and Friedlander, 1965; Rosner, 1969). We argue, however, that polymer chains being long and mutually entangled, are inhibited from entering the liquid phase due to the dynamic friction between the chains. Figure 1 depicts a possible feasible picture of the gel-liquid interface. The rate at which the chains disengage themselves from the gel-liquid interface (k_d) is one of the factors controlling the polymer dissolution. Some indirect experimental evidence, which supports the concept of disengagement in related problems associated with the adsorption layer development, is reported by Lee and Fuller (1984).

In addition to the disengagement process on the solvent side of the gel-solvent interface, there is also some mass-transfer resistance at the surface. A concentration gradient, set up between the interface of the swollen gel and the bulk, drives the process of the movement of the polymeric molecule. If the disengagement rate (k_d) is relatively low, the resistance through the external boundary layer [quantified by the reciprocal of the mass-transfer coefficient (k_{SL})] 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 magnitudes of the resistances, the dissolution process can become disengagement-limited or diffusion-limited.

Model equations

We consider the dissolution of a spherical polymeric particle placed in a uniform stream of solvent. Under these conditions, a two-dimensional transport equation in spherical geometry in a stationary coordinate frame represents the physical model of dissolution. In terms of polymer volume fraction (ϕ_p), we obtain

$$\frac{\partial \phi_p}{\partial t}+\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{\phi r}\right)+\frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}\left(N_{\phi\theta}\sin\theta\right)=S_\phi, \qquad (1)$$

where ϕ_p is the volume fraction of the polymer, $N_{\phi r}$ and $N_{\phi\theta}$ are the fluxes of polymer in the r and θ direction, and S_ϕ is the source term.

We will write the transport equations specific to each region described earlier while elaborating the physical model further.

The Glassy Region. In the early stage of the dissolution process there is a core of essentially pure polymer into which little solvent has penetrated, surrounded by the gel phase. The pure polymer region is not a distinct phase. However, the existence of a sharp boundary between this glassy region and the surrounding swollen gel phase is well established (Tu and Ouano, 1977; Astarita and Sarti, 1978; Thomas and Windle, 1982; Webb and Hall, 1991). In this analysis, we assume that the glassy region of the particle always contains a pure polymer ($\phi_p=1$). We are justified in assuming that the solvent diffusivity in the glassy region is close to zero. Therefore, no transport equations will be set up in the glassy region. It will, however, be necessary to model the movement of the boundary of the glassy region. The physics of the phenomenon suggest that diffusion (no matter how complicated) alone is not sufficient to predict the observed features. Two separate regions like two phases (glass and gel) do appear to exist and the phase transition needs to be considered and modeled appropriately, as shown by Astarita and Sarti (1978). The kinetics of phase transition was modeled either in terms of stress (stress difference with respect to critical stress level to initiate front movement, Papanu et al., 1989), or in terms of concentration (concentration difference with respect to threshold concentration level to swelling, Astarita and Sarti, 1978). In this article, we adopted the power law kinetic model proposed by Astarita and Sarti (1978), since it is able to incorporate all the essential features of the process of sorption of swelling solvents in glassy polymers. Following Astarita and Sarti (1978), movement of the boundary of the glassy region can be modeled as

$$\alpha\frac{dR_g}{dt}=k(\phi^*-\phi_g)^n, \qquad (2)$$

where R_g is the radius of the glassy region (located at the glass-gel interface), k and n are parameters in the glass transition kinetics, ϕ_g is the gel side volume fraction of the polymer at the glass-gel boundary, and ϕ^* is the polymer volume fraction corresponding to the threshold activity for glass transition. Here α is $(R_R/t_R U_R)$, and subscript R denotes the reference or characteristic values used for making the variables dimensionless. The choice of these reference variables would depend on the controlling step. We have deliberately formulated the equations in such a way that we can choose different reference variables for different limiting cases without changing the form of the equation.

The Gel Region. The solvent influx into the polymer matrix causes swelling and creates a gel-like phase between the glassy polymer and solvent phases. The existence of a gel phase around dissolving polymer particle was predicted thermodyamically (Herman and Edwards, 1990) and verified experimentally by many researchers (for example, Tu and Ouano, 1977; Thomas and Windle, 1982; Webb and Hall, 1991). This gel phase arises because of the anisotropic orientational distribution of polymer chains. Although the orientational stress due to swelling eventually relaxes, the gel phase was found to exist for times comparable to the dissolution time (Tu and Ouano, 1977; Devotta et al., 1994b). Tu and Ouano (1977) have used critical-angle illumination microscopy to identify different phases (solvent, gel, glass) and to measure the motion of phase boundaries. Recent *in-situ* measurements of mobility by Devotta et al. (1994b) using NMR also confirms the existence of a gel phase during the dissolution process.

If we assume that the particle swells uniformly in the θ direction, then only the first two terms of the lefthand side of Eq. 1 are of any consequence. The flux can now be written in terms of the convective part due to swelling and the diffusive part.

As the solvent diffuses into the polymer, it will swell at a rate corresponding to the local flux of solvent and polymer passing through that plane. The swelling rate or velocity, U_s, can be related to the diffusion of the solvent and the polymer in the gel phase as

$$U_s=\frac{1}{Pe_R}\left(D_{pg}\frac{\partial \phi_p}{\partial r}+D_s\frac{\partial \phi_s}{\partial r}\right), \qquad (3)$$

where D_{pg} and D_s are dimensionless diffusivities of the polymer and the solvent in the gel phase, respectively. The Peclet number Pe_R is given as $(R_R U_R/D_R)$. The total radial flux of polymer as seen by a stationary observer can be written as

$$N_{\phi r}=U_s\phi_p-\frac{1}{Pe_R}\left(D_{pg}\frac{\partial \phi_p}{\partial r}\right). \qquad (4)$$

Substituting this in Eq. 1 we get after some rearrangement

$$\alpha\frac{\partial \phi_p}{\partial t}=\frac{1}{Pe_R}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_{pg}\phi_s+D_s\phi_p\right)\frac{\partial \phi_p}{\partial r}\right]. \qquad (5)$$

The diffusivity of the polymer in the gel phase is much less than that of the solvent. Therefore $D_{pg}\phi_s \ll D_s\phi_p$. Thus, Eq. 4 simplifies to

$$\alpha\frac{\partial \phi_p}{\partial t}=\frac{1}{Pe_R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_s\phi_p\frac{\partial \phi_p}{\partial r}\right). \qquad (6)$$

For a given polymer-solvent pair and polymer molecular weight, it is reasonable to assume a unique value of interfacial polymer concentration at the gel-solvent boundary (Tu and Ouano, 1977; Papanu et al., 1989). The recent study of dynamics of swelling using *in situ* NMR measurements by Devotta et al. (1994b) shows the existence of an intermediate plateau in the mobility vs. time plot. Such a plateau does not occur if the interfacial polymer concentration varies significantly with time.

Therefore, the boundary condition for the gel-solvent boundary can be approximated as

$$r = R_p, \qquad \phi = \phi_B. \tag{7}$$

The boundary condition for the glass-gel boundary can be written as

$$r = R_g, \qquad \frac{1}{Pe_R}\left(D_s \frac{\partial \phi_p}{\partial r}\right) = \alpha(1-\phi_g)\frac{dR_g}{dt}. \tag{8a}$$

After the gel-glass interface has reached the center, the following normal boundary condition is used

$$r = 0, \qquad \frac{\partial \phi_p}{\partial r} = 0. \tag{8b}$$

Here ϕ_B is the polymer concentration at the gel-solvent interface. The two interfaces between the glass-gel and gel-solvent regions move with respect to time. Equation 2 describes the movement of R_g. The movement of the gel-solvent interface can be described as

$$\alpha \frac{dR_p}{dt} = -\frac{1}{Pe_R}\left(D_s \frac{\partial \phi}{\partial r}\right)_{r=R_p^-} - \frac{R_{\text{eff}}}{\phi_B}. \tag{9}$$

Here R_{eff} is the effective disengagement rate of polymer at the gel-solvent interface.

In the preceding equation, the first term on the righthand side is due to the swelling of the polymer network and the second is due to the dissolution. The obvious initial condition is

$$R_p = R_{po}, \qquad t = 0. \tag{10}$$

As the polymer chains disengage themselves, 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 the diffusion boundary layer.

The flux of the disengaged polymer molecules on the liquid side of the gel-liquid interface (R_{eff}) needs some attention. Since a polymer chain requires a certain amount of time to reptate, we assume that 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. Since the minimum time required for the first few of the chains to disengage from the gel-liquid interface is equivalent to the reptation time, we assume that the following boundary condition exists on the liquid side of the gel-liquid interface, $R_p^+(t)$.

$$R_{\text{eff}} = -\frac{1}{Pe_R}\left(D_p \frac{\partial \phi_p}{\partial r}\right)_{R_p^+} = 0, \qquad t < t_{\text{rep}}. \tag{11}$$

Here D_p is the diffusivity of polymer molecules in a solvent. After the reptation process, however, transport of the polymer chains might be disengagement limited or diffusion limited. At short times, that is, at times just longer than the reptation time, the rate of diffusion is reasonably high and the disengaged chains are easily carried away. The flux at the interface is then limited by the constant disengagement rate k_d. Hence, the following condition prevails on the liquid side of the gel-liquid interface, $R_p^+(t)$.

$$R_{\text{eff}} = -\frac{1}{Pe_R}\left(D_p \frac{\partial \phi_p}{\partial r}\right)_{R_p^+} = k_d \phi_B, \qquad t > t_{\text{rep}}. \tag{12}$$

A fundamental model for estimating the disengagement rate is not available in the literature. From the analysis provided by Papanu et al. (1989), however, it can be postulated that the disengagement rate is a function of polymer molecular weight and polymer concentration at the gel-solvent boundary. Therefore, for a given polymer-solvent pair and polymer molecular weight, it is reasonable to assume a unique value for the disengagement rate during the dissolution process. In principle the disengagement rate can be estimated from the dissolution experiments by designing experiments to eliminate diffusional limitations at the gel-solvent boundary. However, it would be necessary to use intense stirring. Unfortunately, the disengagement rate also differs for different external hydrodynamic conditions (due to the action of hydrodynamic forces on the polymer chains dangling into the liquid; Lee and Fuller, 1984). Further investigation into the microscopic physics of the gel-solvent boundary would be necessary to improve our current understanding of polymer disengagement. In this article, we treat the disengagement rate as an unknown parameter. As the disengagement of the polymer chains occur, the concentration of the polymer outside the gel-solvent interface continues to increase. If the rate of diffusion through the boundary layer is insufficient to carry away the disengaged chains, then the polymer concentration $R_p^+(t)$ is maintained thereafter at ϕ_B. Under these conditions, we have the following condition on the liquid side of the gel-liquid interface:

$$\phi_p|_{R_p^+} = \phi_B, \qquad R_{\text{eff}} = k_{SL}(\phi_B - \phi_{sb}), \tag{13}$$

where ϕ_{sb} is the amount of polymer in the bulk solvent phase and k_{SL} is the external mass-transfer coefficient. During the lengthy periods, however, as the particle size is reduced due to dissolution, the mass-transfer coefficient increases. Hence the dissolution can again become disengagement limited.

The Solvent Region. If the dissolving polymer particle is placed in a uniform stream of solvent moving with velocity U_∞, then the polymer concentration field will not be uniform in the r and θ directions. Under this condition, one needs to solve the transport equations in both r and θ directions. In terms of the external radial velocity component U and the θ directional velocity component V, Eq. 1 can be written as

$$\alpha\left(\frac{\partial \phi_p}{\partial t}\right) + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 U \phi_p) + \frac{1}{r \sin\theta}\frac{\partial}{\partial \theta}(V \sin\theta \cdot \phi_p) = \frac{1}{Pe_R}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_p \frac{\partial \phi_p}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(D_p \sin\theta \frac{\partial \phi_p}{\partial \theta}\right)\right\} + S_\phi. \tag{14}$$

The creeping flow solution, with slight modification in radial velocity (assuming θ independent swelling velocity, U_{sp}) due

due to swelling, can be used to estimate the external velocity field as

$$U=\left[1-1.5\left(\frac{r}{R_p}\right)+0.5\left(\frac{r}{R_p}\right)^3\right]\cos\theta+\frac{U_{sp}}{(r/R_p)^2} \quad (15)$$

$$V=-\left[1-0.75\left(\frac{r}{R_p}\right)-0.25\left(\frac{r}{R_p}\right)\right]\sin\theta, \quad (16)$$

where U_{sp} is the velocity of the gel-solvent interface and is given by Eq. 9.

The boundary condition for the gel-solvent interface was discussed earlier. The other boundary condition can be written as

$$r\to\infty \qquad \phi_p\to\phi_{sb}. \quad (17)$$

It should be noted that the solution of the two-dimensional transport equation results in nonuniform ($\partial\phi_p/\partial r$) with respect to θ on the solvent side of gel-solvent interface. If the dissolving polymer particle is held stationary in the flowing stream, the effective dissolution rate, R_{eff}, would also become nonuniform if diffusion through the boundary layer is one of the controlling steps. This would result in nonuniform swelling of the particle, which would no longer be spherical. In order to avoid this problem, we used some simplifications; for example, we formulated the equation for R_{eff} in terms of the average external mass-transfer coefficient (k_{SL}). The value of k_{SL} can be obtained from the solution of the detailed two-dimensional transport equation by averaging the local flux with respect to θ.

Solutions of model equations

We used the finite volume method with staggered grids (Patankar, 1980) to compute the unsteady dissolution process of a swelling polymer particle. The boundaries of the glass-gel and gel-solvent regions were placed at the nodes of radial velocity. The moving boundary conditions were treated using the front-following technique suggested by Murray and Laudis (1959). The numerical method for the solution of the two-dimensional equation for the solvent region was validated by using the results of Masliyah and Epstein (1972) for a nonswelling particle. Our preliminary computational results with the two-dimensional equation for the solvent region indicates that the magnitude of the swelling velocity and its contribution toward external mass transfer are almost negligible compared to that of the external solvent velocity U_∞. Under these conditions, it would be worthwhile to explore the possibility of using the correlations of external mass-transfer coefficients reported for nonswelling particles. Use of such correlations would drastically reduce the computational requirements, since then the whole problem of dissolution could be analyzed in a one-dimensional framework.

The steady-state Sherwood number valid for all Peclet numbers (Clift et al., 1978) is given as

$$Sh=1+(1+Pe)^{1/3}, \quad (18)$$

where Pe is the external Peclet number based on the external velocity and the diameter of the swollen particle.

When the disentanglement of the polymer molecules starts ($t=t_{\text{rep}}$), however, the Sherwood number would be higher than that described by the preceding equation, since the development of steady concentration profiles would require some time. The effective Sherwood number for this period can be obtained by using the following equation (Clift et al., 1978):

$$Sh=2R_{p_o}/\sqrt{\pi D_p t}. \quad (19)$$

This equation (which predicts a higher value of Sh for short periods when compared to the steady-state value) can be used in calculating Sh, until the steady-state value given by Eq. 18 is reached. As soon as this value is reached, Eq. 18 can be used for computations. Although this type of approximation underestimates the duration of the period of unsteady-state mass transfer, the resulting error in Sherwood number is not large as shown by Clift et al. (1978).

A typical comparison of the predicted Sherwood number derived from a detailed calculation of the two-dimensional unsteady-state mass-transfer problem based on Eqs. 14, 15, and 16 with that predicted by using correlations 18 and 19 is shown in Figure 2. These computations were carried out for the dissolution of a polymer particle of 200-micron diameter without considering the glass transition. The difference in the predicted values of the Sherwood number by these two methods is approximately 10%. The computation of the two-dimensional unsteady-state mass-transfer problem, however, required a much longer CPU time than the other method. Since the difference in the predicted value of dissolution time of a polymer particle is very small, the results described in the following section are based on the solutions of the one-dimensional equation using mass-transfer correlations.

When incorporating the glass transition phenomena into the numerical method, a slight modification in the initial condition is necessary to avoid excessively small time steps. The initial position (radius) R_p of the glass-gel boundary was set to 0.99

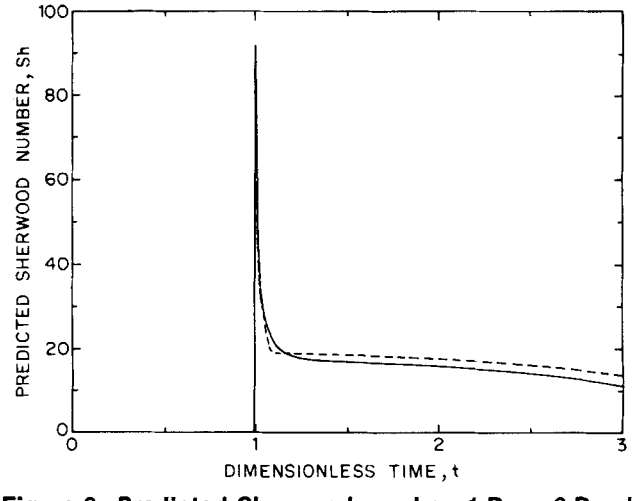

Figure 2. Predicted Sherwood number: 1-D vs. 2-D calculations (without considering glass transition).

$D_p/D_s=0.2$, $R_{po}=2$, $k_d=5$, $Re=0.1$, $Pe=5{,}000$, $\phi_B=0.5$. Curve, description; ——, two-dimensional calculations; ---, one-dimensional calculations.

R_{po} in all the computations. Furthermore, for our numerical calculations, we have defined the complete dissolution times as the time required to reduce the polymer content of the particle up to 0.1% of the original particle.

Results and Discussion

General solution of model equations

From the model equations it can be seen that the dissolution is mainly governed by the glass transition parameters, the specific value of ϕ_B, the reptation time, the disengagement rate (k_d), diffusivity of the solvent in the gel (D_s), diffusivity of the polymer in the solvent (D_p), and the external fluid velocity (U_∞). The numerical solution of the model equations can provide a wealth of information on the microscopic aspects of transition, swelling, and the disengagement phenomena.

Preliminary analysis of the computed results for a wide range of parameters suggests mainly that the value of reptation time, t_{rep}, and of the solvent diffusivity in the gel phase, D_s, govern the formation and swelling processes of the gel phase. Therefore, following Devotta et al. (1994a,b), we used the following reference variables: $t_R = t_{rep}$, $D_R = D_s$, $R_R = \sqrt{D_R t_R}$, $U_R = R_R/t_R$.

Figure 3 shows the typical movement of the glass-gel and the gel-solvent interface (in dimensionless form) during the dissolution process for two values of kinetic parameter of glass transition for $n=2$, $\phi^* = 1$ and $\phi_B = 0.5$. These results are obtained for the dimensionless initial particle radius of 2 with dimensionless external velocity equal to 250 (external particle Reynolds number $=0.1$, Peclet number $=5{,}000$). The radius of the glassy region decreases continuously. It can be seen that for times less than t_{rep}, the solid polymer particle only swells, while at times equal to t_{rep}, the polymer molecules start disengaging at the gel-solvent interface.

The results shown in Figure 3 were obtained by deliberately setting a high disengagement rate ($k_d = 5$) to highlight the role of mass transfer. Immediately after t_{rep}, the solvent surrounding the swollen particle contains no polymer. Therefore, initially the mass-transfer rate is high. This can be seen from the rapid decrease in the radius of the swollen particle immediately after t_{rep}. A steady state is reached within a short time, however, and there is a reduction in the rate at which the radius decreases. As time progresses, the swollen particle becomes smaller and smaller. Correspondingly, the mass-transfer rate per unit volume increases, which can be seen in the particle's progressively increasing rate of decrease with time.

It can be seen from Figure 3 that although glass transition kinetics influences the duration of the glassy phase in the polymer particle, the dissolution time remains almost unaffected. Thus, for instance, a 10-fold variation in kinetic parameters caused only a 6 percent change in the dissolution time. This is because of the high value of the kinetic constant of glass transition with respect to the external mass-transfer coefficient used in this simulation. Under such conditions (also see case 1 in the following subsection), there is a gel layer around the glassy region during the dissolution process, and glass transition kinetics does not significantly affect the dissolution rate.

A typical radial profile of the polymer volume fraction and intermediate time are shown in Figure 4. It can be seen that initially the swelling occurs relatively rapidly. As long as the glassy phase exists, the concentration profiles in the polymeric particle exhibit a discontinuity at the glass-gel interface. The

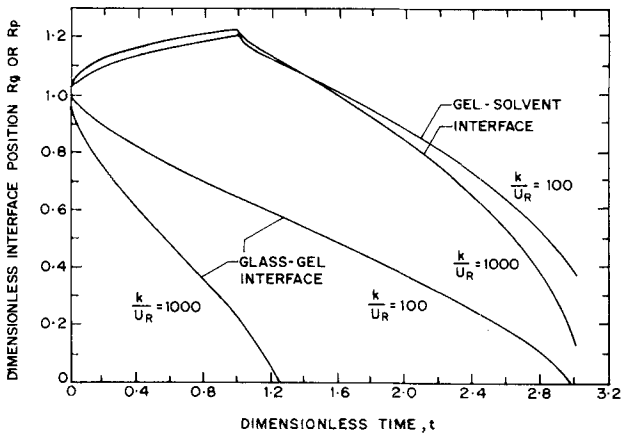

Figure 3. Movement of glass-gel and gel-solvent interfaces during the dissolution process.

$D_p/D_s = 0.2$, $R_{po} = 2$, $k_d = 5$, $Re = 0.1$, $Pe = 5{,}000$, $\phi_B = 0.5$.

profile for $t = 2.9$ does not show a glassy phase and the profile looks almost flat. This indicates that the particle is saturated with the solvent at a later stage of dissolution.

In the absence of the rate being limited by glass transition kinetics, the dissolution is mainly governed by three parameters, namely, the diffusivity of the polymer in the solvent, D_p, the external velocity, U_∞, and the disengagement rate, k_d. Figure 5 shows the influence of the diffusivity of the polymer, D_p, on the total dimensionless dissolution time (t_D) of the polymer particle for different dimensionless particle sizes, R_{po}. For larger particle sizes, the dissolution time decreases as the particle size decreases. However, in the smaller particle size range, the dissolution time does not vary significantly with the particle dimension and converges to $t_D = 1$, which corresponds to the reptation time. Also as the diffusivity of the polymer

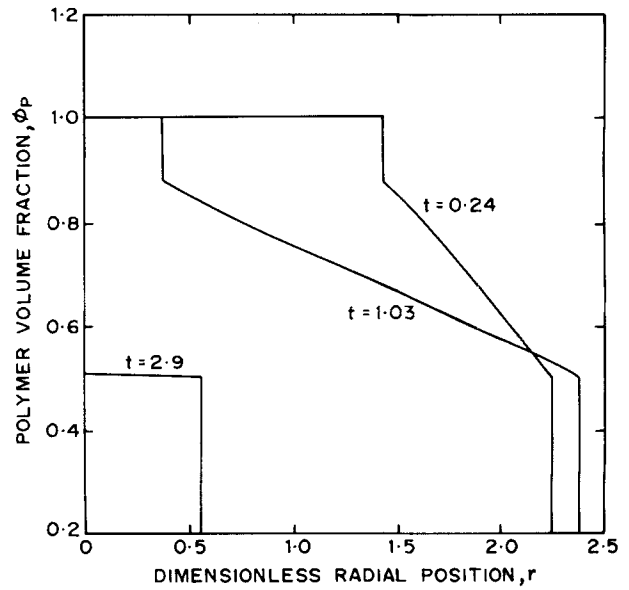

Figure 4. Radial profiles of polymer volume fraction during the dissolution process $k/U_R = 1{,}000$.

Other conditions are the same as in Figure 2.

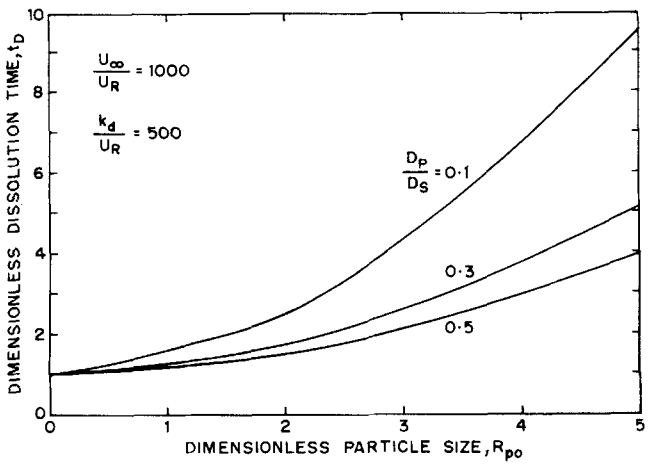

Figure 5. Effect of parameter D_p/D_s on the dissolution time for different particle sizes.

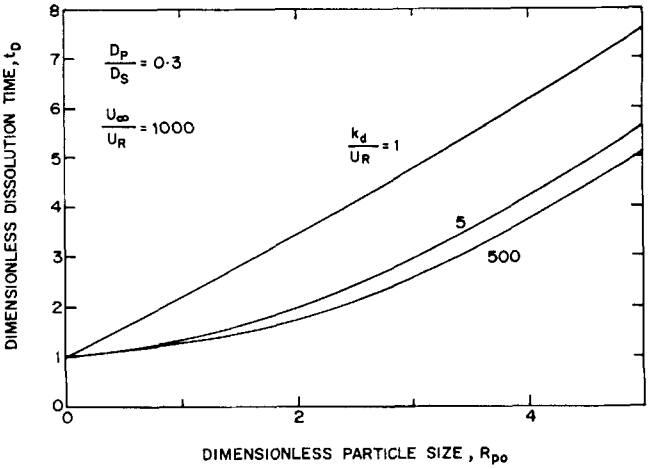

Figure 7. Effect of disengagement rate on the dissolution time for different particle sizes.

increases, the dissolution time decreases, obviously because of the enhanced mass-transfer rate.

Figure 6 shows a similar trend for the variation of the dissolution time as a function of the particle dimension for different values of external velocity. Here again, an increase in the external velocity, U_∞, causes a decrease in dissolution time. As the external velocity increases, the dissolution time tends to vary linearly with the particle size. As a limiting case, for very high external velocities, the dissolution process would become disengagement controlled and the dissolution time would vary linearly with the particle size.

In Figure 7, we present the influence of the disengagement rate on the relationship of the dissolution time and the particle size. When the disengagement rate is very slow (compared to external mass transfer), the dissolution process is not influenced by mass transfer. Instead, the dissolution time varies almost linearly with the particle size. Such behavior occurs when the dissolution of very high molecular weight polymeric particles is encountered or when the dissolution takes place in an intense hydrodynamic field.

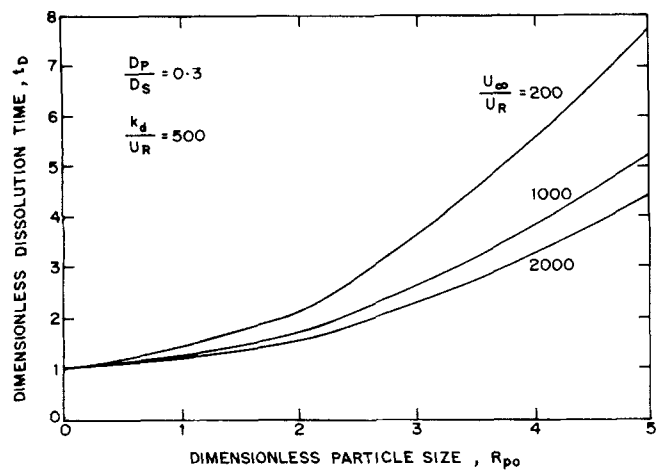

Figure 6. Effect of external velocity on the dissolution time for different particle sizes.

Limiting cases

For an engineer it is important to estimate the dissolution time of a polymeric particle. It is helpful to examine several limiting cases, so that the dissolution time can be estimated analytically.

Case 1: Glass Transition Process Controlling. When the glass transition process occurs very slowly compared to the process of disengagement or the process of external mass transfer, the gel layer is almost nonexistent. In such a case, the dissolution time is dictated by the glass transition kinetics. The dissolution time is equal to the time at which the radius of the glassy region R_g becomes zero. Under these conditions, we can assume that the profile of the volume segment in the gel phase is flat. Therefore, the polymer volume segment on the gel side of the glass-gel boundary can be set to ϕ_B. With this, Eq. 2 can be integrated to get the dissolution time as:

$$t_D = \frac{\alpha R_{po}}{k(\phi^* - \phi_B)^n}. \tag{20}$$

The conditions for this are expressed as:

$$\frac{k}{k_{SL}} \ll 1, \quad \frac{k}{R_{\text{eff}}} \ll 1, \quad \frac{(R_{po}/k)}{t_{\text{rep}}} \gg 1. \tag{21}$$

If the glass transition does become the controlling factor, then the choice of reference variables can be based on parameters k, ϕ^*, ϕ_B, and R_{po} (Astarita and Joshi, 1978). The dissolution time varies linearly with the particle size.

Case 2: Disengagement Process Controlling. When the glass transition process takes place rapidly, a gel layer is maintained at all times. In addition, if the external flow is rapid enough, then external mass-transfer limitations also do not arise, and the dissolution time is mainly governed by the disengagement rate. The dissolution time also depends on the extent of swelling of the polymer particle up to a time equal to t_{rep}. Since the swelling velocity is an exponentially decreasing function of time, its contribution to the dissolution process is almost negligible beyond the reptation time. Therefore, Eq.

9, after ignoring the first term on the righthand side and Eq. 12, can be used to predict the dissolution time.

The extent of swelling in the polymer particle up to t_{rep} can be estimated by using the ratios of characteristic swelling scales with particle radius. If the dimensionless particle radius is less than one, the particle can be assumed to be completely swollen at t_{rep}. Therefore,

$$R_p|_{t=t_{rep}} = \frac{R_{po}}{\phi_B^{1/3}}, \qquad R_{po} < 1. \tag{22}$$

Whereas for very large particles, $R_{po} \gg 1$, the swelling of a particle can be negligible up to t_{rep}. Therefore,

$$R_p|_{t=t_{rep}} = R_{po}, \qquad R_{po} \gg 1. \tag{23}$$

If the radius of a swollen particle is known at $t = t_{rep}$, and if only the disengagement process is controlling the dissolution procedure, then one can relate the dissolution time with the particle size as

$$t_D = t_{rep} + \frac{\alpha(R_p|_{t=t_{rep}})}{k_d}. \tag{24}$$

It can be seen that in this case also the dissolution time varies linearly with the particle size. As the interfacial value of the polymer volume fraction decreases, the dissolution time increases due to a higher degree of swelling. The value of ϕ_B decreases with an increase in molecular weight. The disengagement rate, k_d, decreases and also t_{rep} increases with an increase in the molecular weight. This suggests that higher molecular weight polymers take longer to dissolve.

Case 3: External Mass-Transfer Process Controlling. When glass transition and disengagement rates are fast enough to make the external mass-transfer process controlling, one can treat the dissolution of polymeric particles in a manner similar to nonpolymeric particles. Equation 9, after neglecting the contribution of the first term on the righthand side, and Eq. 13 can be used to estimate the dissolution time. Depending on whether the dimensionless particle size is less than or equal to one or far greater than one, values of the radius at $t = t_{rep}$ can be set according to Eq. 22 or 23. For polymeric systems, the diffusivity of the polymer in the solvent is usually very low. Therefore, the external Peclet numbers ($U_\infty R_{po}/D_p$) are usually quite large. In that case, the external mass transfer can be approximated by the asymptotic solution obtained for $Pe \to \infty$ (Levich, 1962) as

$$Sh = Pe^{1/3}. \tag{25}$$

If the influence of the higher extent of mass transfer in the unsteady period is neglected as an approximation (which is reasonable since the time required to attain the steady state is quite small compared to the dissolution time), then the dissolution time will be given as:

For $R_{po} < 1$

$$t_D = t_{rep} + \frac{3}{5}\frac{\alpha(2Pe_R)^{2/3}}{\phi_B^{4/3}}\frac{R_{po}^{5/3}}{D_p^{2/3}U_\infty^{1/3}}, \tag{26}$$

and for $R_{po} \gg 1$

$$t_D = t_{rep} + \frac{3}{5}\frac{\alpha(2Pe_R)^{2/3}}{\phi_B}\frac{R_{po}^{5/3}}{D_p^{2/3}U_\infty^{1/3}}. \tag{27}$$

In the last two cases, one can again choose reference variables based on reptation time and the solvent diffusivity, as done by Devotta et al. (1994a).

When external mass transfer is high, the dissolution time varies as $R_{po}^{5/3}$, which is unlike the previous two cases. Note also that as the radius of the polymer particle decreases due to dissolution, the value of the external Peclet number also decreases. The asymptotic solution underpredicts the mass-transfer coefficient for a smaller Peclet number. Incidentally, it is not possible to obtain an analytical solution using the more accurate correlation described by Eq. 18. However, we need to emphasize that for polymeric systems, there is no significant difference between the predicted dissolution times obtained by using Eq. 18 or Eq. 25.

The previous expressions were obtained by considering the same external velocity for all the particle sizes. Instead one can use the terminal settling velocity of each particle. Stokes' law can be used to predict the variation of the settling velocity with the particle radius. While equating the external solvent velocity to the terminal settling velocity, an analytical solution can be obtained using the following correlation for external mass transfer (which is closer to Eq. 18 for lower *Pe* than Eq. 25):

$$Sh = 1 + Pe^{1/3}. \tag{28}$$

Using this equation, the dissolution time can be obtained as

For $R_{po} < 1$

$$t_D = t_{rep} + \frac{R_{po}}{b\phi_B^{1/3}} + \frac{a}{b}\ln\frac{a}{a + (R_{po}/\phi_B^{1/3})}, \tag{29}$$

where

$$a = \frac{0.5D_p^{1/3}}{(R_R^3 g\Delta\rho/\mu D_R^{1/3})}, \qquad b = \phi_B D_p^{2/3}\left(\frac{D_R^2 g\Delta\rho}{\mu U_R^3}\right)^{1/3}. \tag{30}$$

For larger particles, the extent of swelling at $t = t_{rep}$ is insignificant, therefore $\phi_B^{1/3}$ in the preceding equation should be replaced by 1.

We can see that the third term in Eq. 29 is always negative. The term is significant for smaller particles compared to the dissolution time. The dissolution time will vary with the particle size with an exponent larger than one. However, for larger particles, the contribution of the negative third term to the dissolution time is insignificant. The dissolution time will then vary almost linearly with particle size. With the help of these analytical solutions of different limiting cases, a brief examination of the experimental data can give us a quick estimate of the relevant processes that control the process of dissolutions.

Case 4: Reptation Process Controlling. If the particle dimension is very small and if the disengagement rate and the rate of diffusion through the boundary layer are high, then

the dissolution time will be equivalent to the reptation time. The conditions under which the reptation process controls the dissolution of polymeric particles can be quantified by using the expression for the dissolution time discussed in earlier cases. If the magnitudes of the righthand side of Eq. 20 and the second terms from the righthand side of Eqs. 24 and 27 are much smaller than the value of the reptation time, then the dissolution is controlled by the reptation process. Then we have

$$\frac{\alpha R_{po}}{k(\phi^* - \phi_B)^n} \ll t_{\text{rep}} \tag{31}$$

$$\frac{\alpha R_{po}}{\phi_B^{1/3} k_d} \ll t_{\text{rep}} \tag{32}$$

$$\frac{3}{5}\frac{\alpha(2Pe_l)^{2/3}}{\phi_B^{4/3}}\frac{R_{po}^{5/3}}{D_P^{2/3}U_\infty^{1/3}} \ll t_{\text{rep}}, \tag{33}$$

and under these conditions,

$$t_D \sim t_{\text{rep}}. \tag{34}$$

Experimental validation of the model

It is useful to verify the predictions made here by comparing them with experimental data on particle dissolution. Although there is an abundance of data in the literature on the dissolution time of particles of ordinary solutions, there are no reported data on the dissolution time of polymeric particles of different sizes. There are also a number of publications on the dissolution of bioerodible hydrogels (Heller, 1978; Korsmeyer et al., 1986; Lee, 1987). However, the dissolution process of bioerodible hydrogels is essentially controlled by the molecular weight degradation rates. Since our present investigation deals with the physical process of the dissolution of a polymer particle (and not the dissolution by chemical erosion), these data are not directly useful in validating the present model. Papanu et al. (1989) and Wu and Peppas (1993) have reported experimental data for the dissolution of thin films. Their data indicate the possibility of dissolution through a crack mechanism. Our present model does not incorporate this mechanism. The only directly relevant data for the purpose of validation of the present model are provided by Ambeskar (1990) and Devotta et al. (1994a) and, therefore, these are used here.

Some typical experimental data of the dissolution time of polymeric particles obtained by these workers are shown in dimensionless form in Figures 8 and 9. We can see that when the polymer particle is less than a certain critical size, the time required for dissolution does not vary appreciably with the particle size. This observation is in contrast with the dissolution behavior of small molecular weight solutes, where the dissolution time vanishes as the particle size tends to zero.

We now compare these experimental data with our model predictions. It should be noted, however, that fluid mechanics in stirred vessels is extremely complex. Predicting the external fluid velocity for different particle sizes is particularly difficult. Therefore, for curve fit, we treated this external fluid velocity as an unknown parameter.

We selected polystyrene-cyclohexane and PMMA-benzene systems for this comparison. The diffusivity of polystyrene in cyclohexane is calculated as 3×10^{-7} cm^2/s at 35°C, based on the work by King et al. (1973). The solvent diffusivity of cyclohexane in polystryene was not known. Therefore, because of the structural similarity between cyclohexane and benzene, the value for benzene reported by Zielinski and Duda (1992) was used (1×10^{-6} cm^2/s at 30°C). Similarly, using the Zielinski and Duda (1992) method, we estimated the diffusivity of benzene in PMMA to be 4×10^{-6} cm^2/s at 30°C. The diffusivity of PMMA in acetone was estimated to be 2.2×10^{-7} cm^2/s (Ende, 1966). The reptation time (t_{rep}) was estimated approximately by extrapolating the expermental data reported in Figures 7 and 8 to the zero particle size ($t_{\text{rep}} = 18$ s for the polystyrene-cyclohexane system and $t_{\text{rep}} = 17$ s for the PMMA-benzene system).

For a quantitative prediction of the dissolution time the model still needs the value of the disengagement rate as well as the interface concentration (ϕ_B). However, the model pre-

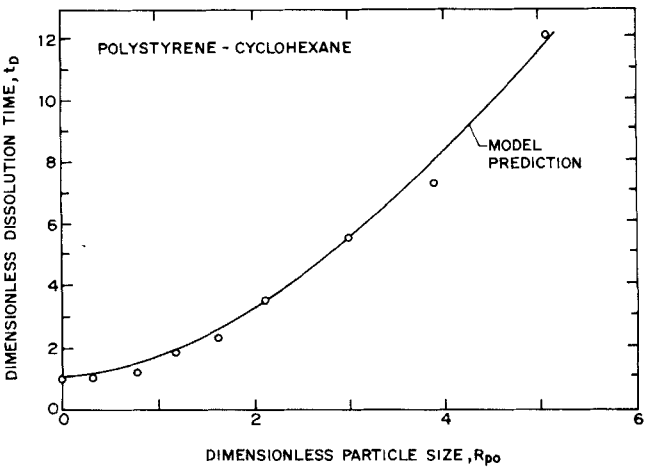

Figure 8. Typical experimental data for the dissolution of polystyrene in polystyrene ($M_w = 121{,}200$)/ cyclohexane system (from Ambeskar, 1990) vs. model predictions.

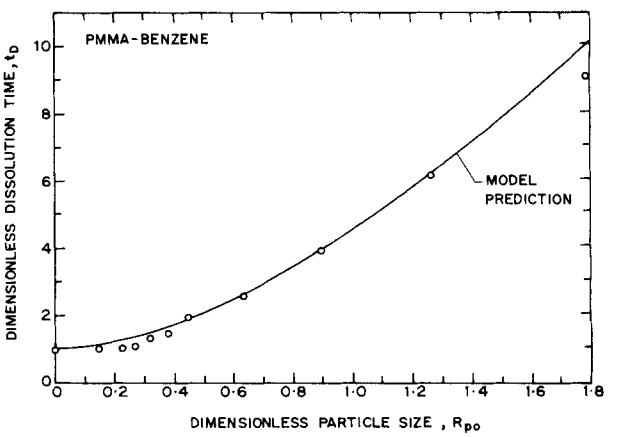

Figure 9. Experimental data for polymethylmethacrylate ($M_w = 82{,}000$)/benzene system (from Devotta et al., 1994a) vs. model predictions.

dictions will not be sensitive to the precise value of the disengagement rate if the dissolution process is mainly controlled by external mass transfer. For the present comparisons, the value of the disengagement rate was deliberately set to a high value so that predictions are not sensitive to the precise value. The value of ϕ_B is a function of molecular weight of the polymer. Using Tu and Onano's (1978) data as a guideline we used $\phi_B = 0.9$ for PMMA-benzene system ($M_w = 82{,}000$) and $\phi_B = 0.22$ for polystyrene-cyclohexane system ($M_w = 121{,}000$).

Model predictions were made on the basis of the solution of one-dimensional transport equations along with mass-transfer correlations (Eqs. 18 and 19). Predicted values of the dissolution time as a function of the particle dimension are compared with the experimental data in Figure 8 for the polystyrene-cyclohexane system and in Figure 9 for the PMMA/benzene system. It can be seen that the model predictions compare reasonably well with the experimental data. Of course, a more rigorous validation of the model would require more than such a preliminary comparison. However, considering that our studies encompass diverse and complex phenomena of reptation, disengagement, external diffusion, convection, and so on, in a single model, the comparison is probably adequate at this stage.

Conclusions

We have developed a model for estimating the dissolution time of a polymeric particle in a well-defined hydrodynamic field. The model takes various processes into account, such as glass transition, reptation, disengagement from the gel-liquid interface, and diffusion through the boundary layer. The comparison between the experimental observations and the model predictions is reasonably good.

Analytical solutions for estimating the dissolution time were presented for some limiting cases. These solutions can be used to interpret the experimental data and to identify the controlling steps in the dissolution process.

Our findings have obvious pragmatic implications for polymer technologists. Our model defines a lower size limit 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.

Our findings also have implications in microlithography. The rate at which the thin films of organic polymers dissolves becomes a critical parameter in microlithography. The difference in the rate of dissolution between the irradiated and the unexposed film, namely the resist, allows the production of a polymer mask, through which the various operations of doping, insulating and metallizing are carried out on the surface of a silicon wafer. In actual practice, for instance, one is concerned about the role of the dissolution of very thin (1-μm) films of various methacrylate polymers (Groele and Rodriguez, 1989). It is precisely in this range of dimensions that we predict that the dissolution process is reptation controlled. The guidelines given in the foregoing are useful in a more quantitative analysis of the dissolution process in microlithography.

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Notation

D_{COOP} = cooperative diffusion coefficient of polymer chains
D_p = diffusivity of polymer in solvent
D_{pg} = diffusivity of polymer in gel phase
D_R = reference diffusivity
D_s = diffusivity of solvent in gel phase
k = kinetic constant of glass transition
k_d = disengagement rate
k_{SL} = mass-transfer coefficient
M_w = molecular weight of polymer
n = order of glass transition kinetics
$N_{\phi r}$ = flux of ϕ_p in the r direction
$N_{\phi\theta}$ = flux of ϕ_p in the θ direction
Pe = Peclet number
Pe_R = Peclet number based on reference variables
r = radial direction
R_{eff} = effective disengagement rate
R_g = location of glass-gel interface
R_p = location of gel-solvent interface
R_{po} = initial particle radius
R_R = reference length scale
Sh = Sherwood number
t_D = dissolution time
t_R = reference time scale
t_{rep} = reptation time
U_∞ = velocity of solvent stream
U_R = reference velocity scale
U_{sp} = velocity of the gel-solvent interface, dR_p/dt

Greek letters

α = ratio of reference length scale to product of reference time and velocity scales ($R_R/t_R U_R$)
ϕ^* = polymer volume fraction corresponding to the threshold activity for the glass transition
ϕ_B = interfacial polymer volume fraction (gel/solvent)
ϕ_g = interfacial polymer volume fraction (glass/gel)
ϕ_p = polymer volume fraction
ϕ_{sb} = polymer volume fraction in the bulk solvent phase
μ = viscosity of solvent
Δ_ρ = difference in densities of polymer particle and solvent

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