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ROLE OF THERMODYNAMIC AND KINETIC FACTORS IN POLYMER DISSOLUTION IN MIXED SOLVENTS+

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ROLE OF THERMODYNAMIC AND KINETIC FACTORS IN POLYMER DISSOLUTION IN MIXED SOLVENTS[+]

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A model for polymer dissolution in mixed solvents has been developed with the purpose of explaining the hitherto unexplained maximum in the dissolution rate with the solvent composition. The variation of the interface concentration of both the solvents and the dissolution rate with the composition of the non-solvent in the dissolution medium is predicted. The model predicts an increase in dissolution rate with an increase in low molecular weight non-solvent content of the dissolution medium. However, further increase in the non-solvent content, decreases the dissolution rate. The relative role of kinetic and thermodynamic quality of the solvent is shown to be the reason for this unusual behaviour. The model also predicts reduction in swelling with an increase in non-solvent content of the dissolution medium. The implications of the work in designing mixed solvent systems for microlithography to meet the goal of maximum dissolution rate with minimum swelling are discussed.

Keywords: Polymer dissolution swelling; mixed solvents micro-lithography polymer gels

INTRODUCTION

Dissolution of polymer plays an important role in microlithography. It is important to select a solvent which dissolves the degraded/uncrosslinked portions of the pattern with absolutely minimal or no swelling of the unexposed/crosslinked portions. Both thermodynamic and kinetic factors come into play here. The thermodynamic factor is governed by large interaction between the solvent and the polymer molecules. The kinetic factors depend upon the relative rates of penetration of the solvent molecules into polymer based on their sizes (Asmussen and Ueberreiter, 1962). There are, thus, two

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conflicting demands. The solvent needs to be such that the rates of dissolution should be high. This means that the solvent should be kinetically 'good'. However, thermodynamically, if the solvent is good, then substantial swelling may take place. We need a solvent system so that minimum swelling should take place with maximum rate of dissolution. These conflicting requisites can be met by using a binary mixture of solvents. In this paper, we examine the dissolution of a polymer in a mixture of solvents. We develop a predictive theory for the rate of polymer dissolution in such systems. Hopefully, the results in this work will provide guidance for the selection of suitable solvents in microlithography.

Some limited experimental data on the dissolution in mixed solvents have been reported in the literature (Cooper *et al.*, 1986; Manjkow *et al.*, 1987). Figure 1 shows one such set of data with an interesting trend. An increase in the low molecular size non-solvent composition in the dissolving medium increases the dissolution rate. This is contrary to one's expectation. Interestingly, after a certain composition of non-solvent the dissolution rate decreases thus showing a maximum. This indicates that the criteria of higher dissolution rate with lesser swelling can be achieved by a particular composition of the non-solvent in the dissolution medium. We will build a theoretical framework now to explain the trends shown in Figure 1.

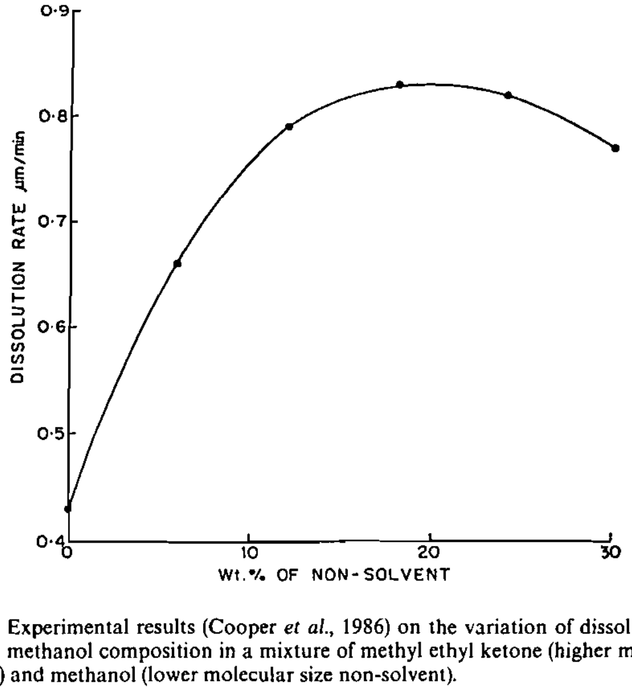

FIGURE 1 Experimental results (Cooper *et al.*, 1986) on the variation of dissolution rate of PMMA with methanol composition in a mixture of methyl ethyl ketone (higher molecular size good solvent) and methanol (lower molecular size non-solvent).

Let us briefly review some of the previous work in this area. Brochard and de Gennes (1983) predicted that the dissolution of semi-dilute droplets is controlled by stress relaxation. Herman and Edwards (1990) predicted the existence of two phases (gel-like concentration solution and dilute solution) when the contribution to the chemical potential due to the non-random distribution of orientation was sufficiently large campared to the contribution arising from the spatial variation in the concentration.

Tu and Ouano (1977) considered the dissociation of the chains at the interface and the external mass transfer resistance in their model. Papanu *et al.* (1989) developed a model for dissolution of glassy polymer with the kinetics controlled by the disentanglement rate. They also incorporated a model for concentration of the solvent at the gel-liquid interface. Lee and Peppas (1987) showed that the thickness of the gel layer was proportional to the square root of time. Peppas *et al.* (1994) developed a model by considering the polymer chain disentanglement time controlling the movement of the gel-liquid boundary. They predicted the effect of molecular weight of the polymer on its dissolution rate and the thickness of gel layer.

In our earlier work we have demonstrated experimentally the presence of a critical particle size of the polymer particle below which the dissolution time was independent of the particle size (Devotta *et al.*, 1994a). Ranade and Mashelkar (1995) developed a more comprehensive model for the dissolution of a polymer particle in a well defined convective field. In a very recent work (Devotta *et al.*, 1995), the process of disengagement dynamics incorporated in our models earlier (Devotta *et al.*, 1994a, 1994b) was put on sound mechanistic footing. A key feature of the model was the incorporation of a kinetic model to relate the disengagement rate to the swelling rate, through the changing mobility of the disengaging macromolecule at the gel-liquid interface. The model predicted substantial increase in dissolution rate with a marginal increase in residual solvent content in line with the experimental data of Ouano (1982). Our experimental results showed the presence of an intermediate plateau in the dissolution curve for low molecular weight polymer under stagnant condition as predicted by the model. In this work, we will focus our attention on the dissolution of the polymer in a mixed solvent medium.

MODEL DEVELOPMENT

We consider the swelling-dissolution problem of a slab as shown in Figure 2. Therefore, the problem will be set up as a one dimension diffusion problem. The key focuss in this work is on explaining the feature of maximum, since the other basic features of the swelling-dissolution problem have been already comprehensively highlighted in earlier papers (Devotta *et al.*, 1994a; 1994b; 1995; Herman and Edwards, 1990; Tu and Ouano, 1977; Lee and Peppas, 1987; Papanu *et al.*, 1989; Astarita and Sarti, 1978, Peppas *et al.*, 1994). For simplicity, we will assume that the kinetics of dissolution is completely controlled by the process of disengagement of chains from the gel-liquid interface. We can easily show the feature of maximum even if the process was partially controlled by diffusion in the boundary layer.

The diffusion of the two solvents into the polymer film can be described by the following conservation equations.

$$\frac{\partial \phi_1}{\partial t} = \frac{\partial}{\partial x}\left(D_1 \frac{\partial \phi_1}{\partial x}\right) + \frac{\partial}{\partial x}(v\phi_1) \tag{1}$$

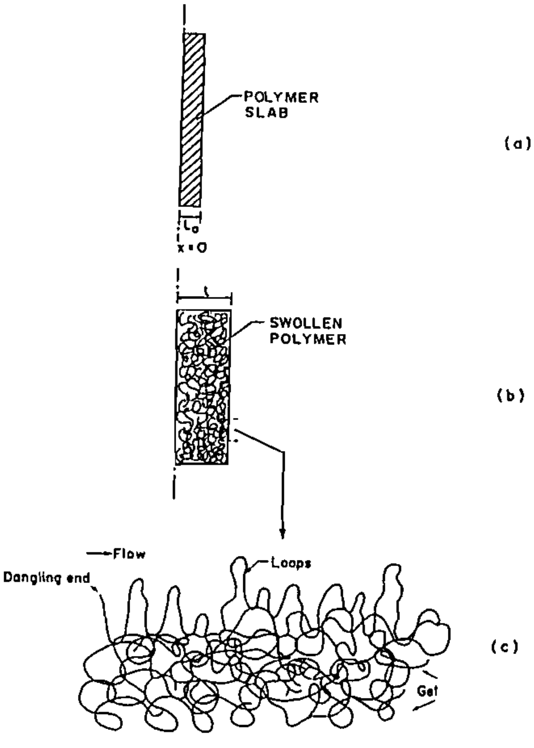

FIGURE 2 (a) Polymer slab with an initial thickness L_0; (b) Swollen gel and (c) Disengagement process with dangling ends and loops of the polymer segments at the surface of the swollen gel.

$$\frac{\partial \phi_2}{\partial t} = \frac{\partial}{\partial x}\left(D_2 \frac{\partial \phi_2}{\partial x}\right) + \frac{\partial}{\partial x}(v\phi_2) \tag{2}$$

Here, v is the swelling velocity which is related to the diffusion of both the solvents as follows

$$v = D_1 \frac{\partial \phi_1}{\partial x} + D_2 \frac{\partial \phi_2}{\partial x} \tag{3}$$

The diffusivities of the two solvents will depend on their sizes and may be related to the free volume of the gel phase by the following expressions.

$$D_1 = A_{d1} \exp\left(-\frac{B_{d1}}{f_g}\right) \tag{4}$$

$$D_2 = A_{d2} \exp\left(-\frac{B_{d2}}{f_g}\right) \tag{5}$$

Here, A_d and B_d are parameters which depend on the size of the diffusing species, f_g is the free volume of the gel phase. Assuming additivity of free volumes, f_g can be evaluated from the following relation:

$$f_g = f_p \phi_p + f_1 \phi_1 + f_2 \phi_2 \tag{6}$$

Here, f_p, f_1 and f_2 are the free volume fraction of the polymer and the two solvents, respectively.

The initial and the boundary condition for equation (1) and (2) are as follows:

$$\phi_1 = \phi_2 = 0 \quad \text{at } t = 0 \tag{7}$$

$$D_1 \frac{\partial \phi_1}{\partial x} = D_2 \frac{\partial \phi_2}{\partial x} = 0 \quad \text{at } x = 0 \tag{8}$$

$$\phi_1 = \phi_{1,s} \quad \text{at } x = l \tag{9}$$

$$\phi_2 = \phi_{2,s} \quad \text{at } x = l \tag{10}$$

Here $\phi_{1,s}$ and $\phi_{2,s}$ are the surface concentrations of the two solvents, which will depend on the composition of the two solvents in the dissolution medium.

As the solvent diffuses into the polymer film, its thickness increases and as the polymer chain leaves the interface, the thickness reduces. Assuming completely disengagement controlled dissolution kinetics, the net rate of movement of the gel-liquid interface can be described as follows:

$$\frac{dl}{dt} = D_1 \frac{\partial \phi_1}{\partial x}\Big|_{x=l} + D_2 \frac{\partial \phi_2}{\partial x}\Big|_{x=l} - k_d \tag{11}$$

Here, k_d is the time dependent disengagement rate of the polymer chains from the gel-liquid interface. The physics of this disengagement process has been elaborated by us in our previous work (Devotta *et al.*, 1994b; 1995) and is schematically shown in Figure 2(c).

In a recent analysis (Devotta *et al.*, 1995), we have related the disengagement rate to the instantaneous mobility of the disengaging chains. As the solvent penetrates, the chains in the gel phase disentangle themselves and become more mobile. If the solvent size is small, then it penetrates into the polymer rapidly, since its diffusivity is higher. Hence the mobility of the chain in the gel phase increases faster and such highly mobile chains disengage at the gel-liquid interface at a faster rate. Therefore, as per our earlier postulates (Devotta *et al.*, 1995), we can relate the disengagement rate directly to mobility as follows

$$k_d \propto m_p \tag{12}$$

Here, m_p is the time dependent mobility of the disengaging polymer chains. The mobility of the polymer molecules in the gel phase changes with the extent of disentanglement. As explained in our earlier work (Devotta *et al.*, 1995), the mobility of the chain in the gel phase is assumed to vary according to the following kinetics.

$$\frac{dm_p}{\partial t} = K(m_{p,\infty} - m_p) \tag{13}$$

Here, K is a kinetic constant and $m_{p,\infty}$ is the maximum mobility that the polymer chain can attain at that concentration, when a state of maximum disentanglement is attained at large time. This mobility of the polymer molecules will depend on the concentration or the free volume and hence it is given by

$$m_{p,\infty} = A_d \exp\left(-\frac{B_d}{f_g}\right) \tag{14}$$

The next question to be addressed is the variation of the interface concentration of both the solvents with the composition of the dissolution medium. This can be evaluated by assuming a thermodynamic equilibrium at the interface and hence by equating the chemical potentials of each of the solvent in both the phases. i.e.

$$\mu_1^{\mathrm{L}} = \mu_1^{\mathrm{G}} \tag{15}$$

$$\mu_2^{\mathrm{L}} = \mu_2^{\mathrm{G}} \tag{16}$$

The chemcial potential of the solvent in the gel phase can be expressed using the Flory-Huggins theory, with appropriate modifications, which are based on the assumption of the equivalence of the physical entanglement in the gel phase to chemical crosslinks (Papanu *et al.*, 1989; Devotta *et al.*, 1995).

The difference in the chemical potential of the two solvents in the gel phase and the pure solvents is given by

$$\begin{aligned}\frac{\mu_1^{\mathrm{G}} - \mu_1^0}{RT} = {} & \ln(\phi_1) + (1 - \phi_1) - \phi_2\left(\frac{X_1}{X_2}\right) - \phi_3\left(\frac{X_1}{X_3}\right) + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) \\ & - \chi_{23}\left(\frac{X_1}{X_2}\right)\phi_2\phi_3 + \frac{V_1}{V_0}N_e\left(\frac{2}{\phi_3} - \phi_3\right)\end{aligned} \tag{17}$$

$$\begin{aligned}\frac{\mu_2^{\mathrm{G}} - \mu_2^0}{RT} = {} & \ln(\phi_2) + (1 - \phi_2) - \phi_1\left(\frac{X_2}{X_1}\right) - \phi_3\left(\frac{X_2}{X_3}\right) + (\chi_{21}\phi_1 + \chi_{23}\phi_3)(\phi_1 + \phi_3) \\ & - \chi_{13}\left(\frac{X_2}{X_1}\right)\phi_1\phi_3 + \frac{V_2}{V_0}N_e\left(\frac{2}{\phi_3} - \phi_3\right)\end{aligned} \tag{18}$$

Here, N_e represents the time dependent number moles of physical entanglements and is considered equivalent to the number of moles of crosslinks in a chemically crosslinked polymer. The concentration of the entanglements decrease as the matrix swells and the polymer molecules disentangle in the gel phase. Assuming a kinetics similar to eqn.(13), the rate of change of moles of entanglements is given by (Devotta *et al.*, 1995)

$$\frac{dN_e}{dt} = K(N_{e,\infty} - N_e) \tag{19}$$

Here, $N_{e,\infty}$ is the moles of entanglement at large time corresponding to the concentrated polymer solution at that concentration and is given by (Papanu *et al.*, 1989, Graessley, 1974)

$$N_{e,\infty} = V_o \rho_p \left(\frac{2\phi_p}{M_c} - \frac{1}{M} \right) \tag{20}$$

Here, M_c is critical molecular weight for entanglement and M is the molecular weight of the polymer.

The difference in the chemical potential between the solvents in the mixture and the pure solvent is given by

$$\frac{\mu_1^L - \mu_1^o}{RT} = \ln(\phi_1) + \left(1 - \frac{1}{X_2}\right)\phi_2 + \chi_{12}\phi_2^2 \tag{21}$$

$$\frac{\mu_2^L - \mu_2^o}{RT} = \ln(\phi_2) + (1 - X_2)\phi_1 + \chi_{12}X_2\phi_1^2 \tag{22}$$

In the above equation the presence of small amount of polymer in the solvent phase is neglected and the solvent phase is treated as a binary mixture of two solvents throughout the dissolution process. Thus, using condition (15) and (16) and using the equations (17)–(22) for chemical potential and the concentration of entanglements, we can evaluate $\phi_{1,s}$ and $\phi_{2,s}$ using multi-variable Newton-Raphson method.

A numerical solution to the above equation gives the concentration profile of the two solvents in the gel phase. From this the changing mobility of the chain in the gel phase and hence the disengagement rate can be evaluated.

RESULTS AND DISCUSSION

Before we analyse the variation of dissolution rate with solvent composition, it will be useful to predict the variation of surface concentration of both the solvents with the composition of the dissolution medium. Figure 3 shows this prediction. It can be seen that as the non-solvent composition of the solvent phase is increased, the interface concentration of the non-solvent increases and that of the good solvent decreases. Figure 3 also shows the volume fraction of polymer at the surface (i.e. $1 - \phi_{1,s} - \phi_{2,s}$), which increases with the non-solvent composition. This indicates lesser swelling of the polymer film with increase in non-solvent content of the solvent phase.

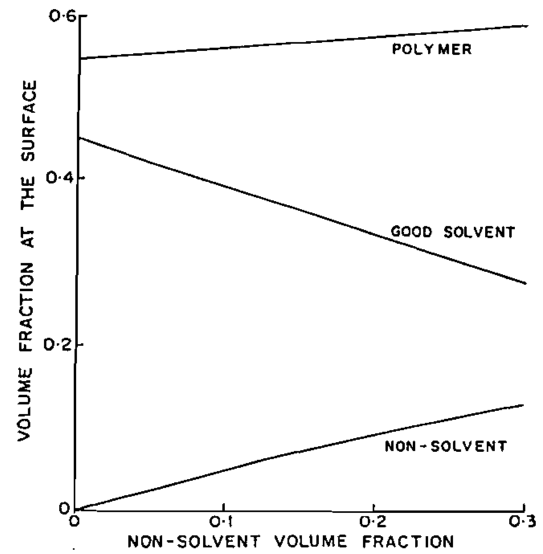

FIGURE 3 Predicted variation of initial interface concentration of the two solvents and the polymer with the composition of non-solvent in the dissolution medium.

The concentration profiles of both the solvents, which are diffusing at different rates within the polymer matrix are presented now. Figure 4 shows the profiles of the low molecular size non-solvent at different times. It can be seen that concentration profiles are almost flat even at small times and the concentrations are almost equal to the interface value throughout the matrix. This is because of the faster diffusion rates of the non-solvent, which is specifically chosen to be small is size. However, Figure 5 shows the concentration profiles (for the same time as in Fig. 4) of the good solvent, which diffuses at a slower rate compared to the non-solvent. It is seen clearly that the concentration varies appreciably within the polymer matrix. This is obviously because of the larger size of the good solvent which results in slower diffusive transport within the polymer matrix.

Figure 6 shows the predicted variation of normalised dissolution rate (normalised with respect of dissolution rate in a 100% good solvent) of the polymer film with the non-solvent composition. For this prediction, we have chosen a non-solvent with small molecular size (i.e. high χ_{23} and low B_{d2}) and 'good solvent' with relatively larger molecular size (i.e. low χ_{13} and large B_{d1}). Figure 6 shows that as the non-solvent composition of the solvent phase in increased, the dissolution rate is predicted to increase. This unusual behaviour is due to the 'kinetic goodness' of the dissolution medium. Since

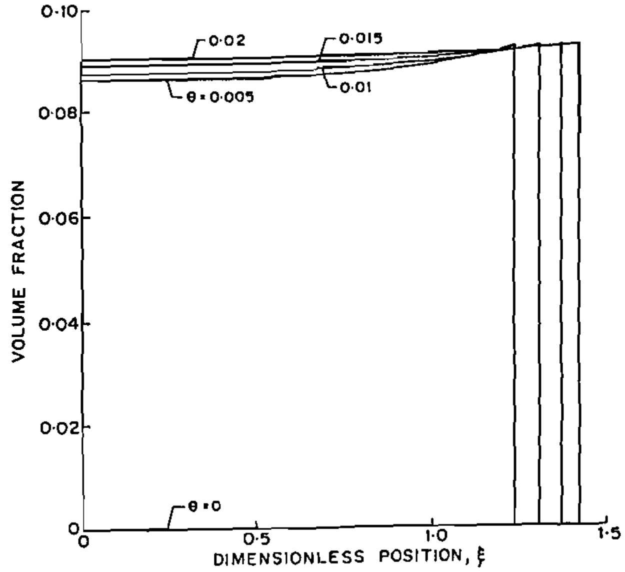

FIGURE 4 Concentration profiles of the low molecular size non-solvent in the gel phase.

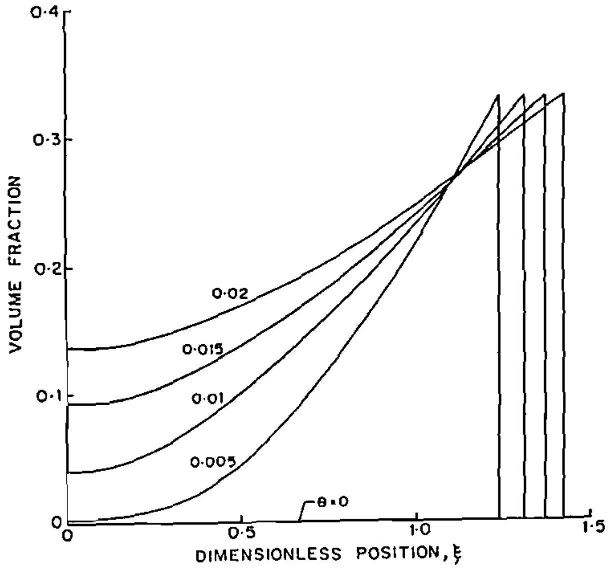

FIGURE 5 Concentration profiles of the higher molecular size good solvent in the gel phase.

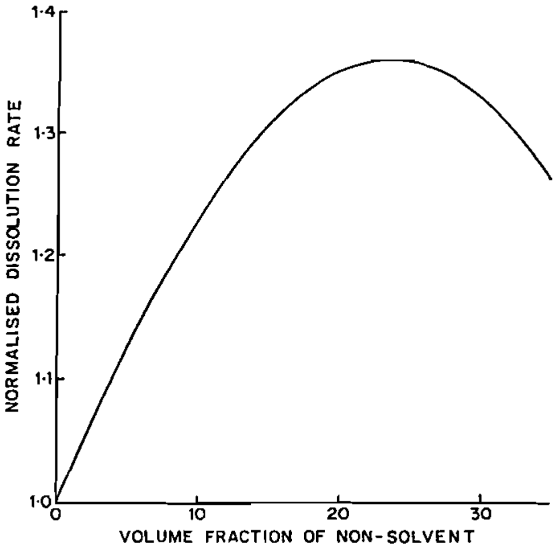

FIGURE 6 Predicted variation of normalised dissolution rates with the non-solvent composition in the dissolution medium.

the non-solvent is of smaller molecular size, it penetrates faster into the polymer, increasing the free volume faster. This enhances the diffusivities of both the solvents and also the mobility of the chains in the gel phase. Higher disengagement rates of the such chains result in higher overall dissolution rates. However, as the non-solvent composition is increased further, the dissolution rate decreases showing a maxima. This is because the dissolution medium becomes 'thermodynamically poor' resulting in reduced swelling. Although the non solvent penetrates fast, since the swelling is reduced, the mobility of the chains gets restricted resulting in a lower dissolution rate. This prediction is in line with the experimental observations (Fig. 1), where the dissolution rate of the polymer film initially increases and then decreases as the composition of the low molecular size non-solvent in the dissolution medium is increased.

CONCLUSIONS

A mathematical model for dissolution of polymer in mixed solvents has been developed by incorporating the kinetic and thermodynamic features of the solvents. An interesting prediction of increase in dissolution rate with increase in low molecular size non-solvent is observed in line with the experimental data reported in the literature. The model also predicts reduction in swelling with increase in non-solvent composition. The results have pragmatic implications in guiding a more quantitative design of solvent media with the requisites of higher dissolution rate and lower swelling.

NOTATION

B_d	free volume parameter in equation (4) and (5)
A_d	free volume parameter in equation (4) and (5)
D	diffusivity of the solvent
f	free volume fraction
K	kinetic constant
k_d	disengagement rate
l	swollen thickness of the film
M	molecular weight of the polymer
M_c	critical molecular weight for entanglement
m_p	mobility of the polymer chains
N_e	concentration of entanglements
R	gas constant
T	temperature
t	time
v	swelling velocity
V	molar volume
X	ratio of the molar volumes
x	distance from the center of the slab

Greek Symbols

ϕ	volume fraction
μ	chemical potential
μ^0	chemical potential of pure component
χ	Flory's interaction parameter
ρ	density

Subscript

1	solvent 1
2	solvent 2

3	polymer
p	polymer
s	surface value
g	gel phase
∞	value at large times

Superscript

L	liquid phase
G	gel phase

References

Asmussen, F. and Ueberreiter, K. (1962) "Velocity of dissolution of polymers" Part **II**, *J. Poly. Sci.*, **57**, 199.

Astarita, G. and Sarti, G. C. (1978) "A class of mathematical model for sorption of swelling solvents in glassy polymers", *Polym. Engg. Sci.* **18**, 388.

Brochard, F. and de Gennes, (1983) "Kinetics of polymer dissolution", *Physico Chemical Hydrodynamics*, **4**, 313.

Cooper, W. J., Krasicky, P. D. and Rodriguez, F. (1986) "Dissolution rates of PMMA films in mixed solvents", *J. Appl. Polym. Sci.*, **31**, 65.

Devotta, I., Ambeskar, V. D., Mandhare, A. B. and Mashelkar, R. A. (1994a) "Life time of a dissolving polymer particle", *Chem. Engg. Sci.*, **49**, 645.

Devotta, I., Premnath, V., Badiger, M. V., Rajmohanan, P. R., Ganapathy, S. and Mashelkar, R. A., (1994b) "Dynamics of mobilisation of swelling dissolving polymeric system", *Macromolecules*, **27**, 532.

Devotta, I., Badiger, M. V., Rajmohanan, P. R., Ganapathy, S. and Mashelkar, R. A. (1995) "The phenomena of anomalous retardation and enhancement in plymer dissolution: Role of disengagement dynamics", *Chem. Engg, Sci.*, in press.

Graessley, W. W. (1974) "The entanglement concept in polymer rheology" *Adv. Polym. Sci.* **16**, 1.

Herman, M. F. and Edwards, S. F. (1990) "Reptation model for polymer dissolution", *Macromolecules*, **23**, 3662

Lee, P. I. and Peppas, N. A. (1987) "Prediction of polymer dissolution in swellable controlled release systems", *J. Controlled Rel.*, **6**, 207.

Manjkow, J., Pappanu, J. S., Soong, D. S., Hess, D. W. and Bell, A. T. (1987) "An in situ study of dissolution and swelling behaviour of PMMA thin film on solvent/nonsolvent binary mixtures", *J. Appl. Phys.*, **62**, 682.

Ouano, A. C. (1982) Dissolution kinetics of polymers: Effect of residual solvent content, in "Macromolecular solution", Seymour, R. B. and Stahi, G. A., (Eds), Pergamon Press, USA.

Papanu, J. S., Soane, D. S., Bell, A. T. and Hess, D. W. (1989) "Transport models for swelling and dissolution of thin polymer films", *J. Appl. Polym. Sci*, **38**, 859.

Peppas, N. A., Wu, J. C. and Von Meerwall, E. D. (1994) "Mathematical modeling and experimental characterization of polymer dissolution", *Macromolecules*, **27**, 5626.

Ranade, V. V. and Mashelkar, R. A. (1995) "Convective diffusion from a dissolving polymer particle", *AIChEJ*, **41**, 666.

Tu, Y. and Ouano, A. C. (1977) "Model for the kinematics of polymer dissolution", *IBM J. Res. Dev.*, **21**, 131.