Model for Attachment of Active Species onto Gelular Polymer Bead

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SYNOPSIS

Equations for the equilibrium between the stresses and the degree of swelling, and also for the mass balance of substrate and functional groups, are proposed in order to analyze the attachment of active species onto gelular polymer bead. The asymptotic expansion technique was used to solve these equations when the relaxation rate of polymer in solvent is higher than the reaction rate and the reaction rate is much faster than the diffusion rate. It was shown that the interaction between solvent and polymer with attachment can be explained from the simulation. The equations proposed can be utilized to better understand the control of active species distributions in the polymer bead. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Recently considerable work has been done to overcome the disadvantages of homogeneous reactions, mainly devoted to the attachment of active species onto polymer supports. The attachment of active species on the polymer support is quite different from that on zeolites or on porous oxides. Zeolite or porous oxides involve well-defined rigid support structures in which the functional groups reside at specific locations within the solid particle and do not change the geometry during attachment. In polymer supports the functional groups are anchored at specific locations along the polymer backbone. However, as the polymer chains are mobile during the attachment of active species, the geometry of the polymer might change. And the mobility depends on the extent of crosslinking, the volume fraction of swollen polymer, the volume fraction of sorbed species, and the nature of solvents.

The morphology of commonly used polymer supports is of gelular or macroreticular form. Gelular polymer does not have pore networks in the dry state. When it contacts good solvents, the polymer matrices open up as solvents are sorbed into it. Macroreticular resin consists of agglomerates of microparticles of gelular polymer, separated by macropores. The attachment of bulky active species onto macroreticular resin is generally achieved on the surface of the gelular microparticles.[1,2]

The properties of polymer will change by attaching active species on the polymer, so the equilibrium swollen polymer volume fraction of the gelular polymer bead might change with extent of reaction. But little has been studied on the mathematical formalism concerning the attachment of active species onto swollen polymer bead. The objective of this work is to obtain mathematical formulas for the attachment of active species onto gelular polymer bead, and solve it in two cases: by asymptotic expansion technique when the reaction rate is much faster than the diffusion rate and by typical calculation in the other extreme case.

MATHEMATICAL FORMULATION

The local property of polymer along the radius of a bead might change during the attachment of active species onto gelular polymer bead, so the local swelling ratio of the polymer at a position in the bead will change to a new equilibrium state while the chemical reaction occurs. Suppose that the rate

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of change from an equilibrium swollen state to a new one is more rapid than that of chemical reaction. Then the gelular polymer swollen by solvent is always at equilibrium during chemical reaction. The equilibrium volume fraction of swollen polymer v is a function of position, which is formulated by force balance. The force balance consists of two elements such as force due to the Gibbs' free-energy change and elongation of polymer.

Valanis and Landel[3] have shown that the work function $W(\lambda_1, \lambda_2, \lambda_3)$ involved in a deformation that can be written as a sum of components, $W(\lambda_i)$, where λ_i is the extension ratio along the ith principal axis. The extension ratio is defined as the ratio of length of the deformed sample to that of the undeformed sample along the axis of deformation. The corresponding difference in stress along the axis i and j are

$$\sigma_i - \sigma_j = \lambda_i W'(\lambda_i) - \lambda_j W'(\lambda_j) \qquad (1)$$

or equivalently

$$\sigma_i = \lambda_i W'(\lambda_i) + P \qquad (2)$$

where σ_i is the force per unit area of the deformed sample along the ith principle deformation axis, $W'(\lambda_i)$ is the derivative of $W(\lambda_i)$ with respect to λ_i, and P is an arbitrary isotropic force and is related to the sum of the molar Gibbs free energy of dilution of polymer by solvent and hydrostatic force applied to the swollen polymer. For swollen polymer, eq. (2) can be modified as[4,5]

$$\sigma_i = \lambda_i v W'(\lambda_i) + P \qquad (3)$$

The phantom network expression can be employed to express the work function as follows:

$$W_{ph} = \frac{G(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)}{2} \qquad (4)$$

where G is the modulus of the elastomer and the subscripts 1, 2, and 3 represent the principle axis, r, θ, and φ, respectively. For the network with tetrafunctional crosslinks, Flory[6] has shown that the elastic modulus is simply expressed as

$$G = -\frac{\rho RT}{M_c}\left(1 - \frac{2M_c}{M_n}\right) \qquad (5)$$

In eq. (5) ρ is the density of the polymer in the unswollen state, R is the universal gas constant, M_c

is number-average molecular weight between the crosslinks, and M_n is the number-average molecular weight of the original uncrosslinked polymer, respectively. Generally the value of M_c/M_n is so small that this equation is simplified as follows:[5]

$$G = \frac{\rho RT}{M_c} \qquad (6)$$

The force balance for spherical polymer bead system can be expressed as follows:[7]

$$\frac{d\sigma_1}{dr} = \frac{2}{r}(\sigma_2 - \sigma_1) \qquad (7)$$

Considering the geometry of the polymer bead, the extension ratios along each of the three principle directions are expressed by the parameter λ_1, λ_2, and λ_3, respectively:

$$\lambda_1 = \frac{dr}{dr'} \qquad (8a)$$

$$\lambda_2 = \frac{r}{r'}\frac{d\theta}{d\theta'} = \frac{r}{r'} \qquad (8b)$$

$$\lambda_3 = \frac{r}{r'}\frac{\sin\theta}{\sin\theta'}\frac{d\varphi}{d\varphi'} = \frac{r}{r'} \qquad (8c)$$

where r' and r are the radial positions in the unswollen and corresponding swollen networks, respectively, and can be related by mass balance of polymer as follows:

$$r'^3 = 3\int_0^r r^2 v\, dr \qquad (9)$$

Then the formulas of eq. (8) are rewritten as

$$\lambda_1 = \frac{dr}{dr'} = \frac{1}{v}\frac{r'^2}{r^2} = \frac{1}{v\lambda_2^2} \qquad (10a)$$

$$\lambda_2 = \lambda_3 = \frac{r}{r'} \qquad (10b)$$

The relation between the equilibrium swelling and the principal stress in a pure homogeneous strain has been given by the Treloar.[7] As the hydrostatic pressure is not applied to the swollen polymer, the relevant relation is of the form:

$$\sigma_i = \frac{G_m}{V_0} + \lambda_i v W'(\lambda_i) \qquad (11)$$

where G_m is the molar Gibbs free-energy change of dilution of the polymer, and it will be assumed to be given by Flory–Huggins relation:

$$G_m = RT[\ln(1 - v) + v + \chi v^2] \qquad (12)$$

where χ is an interaction parameter that is specific to the particular polymer–liquid system considered.

Differentiating eq. (11) and then comparing it with eq. (7) results in the following expression for the gradient of the equilibrium volume fraction of swollen polymer, v:

$$\frac{dv}{dr} = \frac{2v(\lambda_2^2 - \lambda_1^2) + 4\left(\dfrac{\lambda_1}{\lambda_2^2} - \dfrac{1}{\lambda_2}\right)}{\dfrac{M_c}{\rho V_0}\left(2\chi - \dfrac{1}{1 - v}\right)v - \lambda_1^2} \frac{1}{r} \qquad (13)$$

Its boundary condition is

$$r = R \qquad \sigma_1 = 0 \qquad (14)$$

where R is the particle radius of swollen bead at equilibrium.

Now consider the chemical reaction of substrate with the functional groups on the polymer bead. The mathematical balance equations for substrate and reacted functional groups on the polymer bead are given by

$$\frac{\partial C}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r} D_e r^2 \frac{\partial C}{\partial r} - \mathbb{R} \qquad (15a)$$

$$\frac{dC_f}{dt} = \mathbb{R} \qquad (15b)$$

where D_e is effective diffusivity, C and C_f are the concentration of substrate and reacted functional group, and $\mathbb{R}$ is the reaction rate of substrate with functional groups on the polymer. Generally, but not always, the chemical reaction is second order.

$$\mathbb{R} = kC_{p0}C\left(1 - \frac{C_f}{C_{p0}}\right)v(1 - v) \qquad (16)$$

where k is the reaction rate constant and C_{p0} is the concentration of functional group at dry state on the polymer that could react with substrate.

Gelular polymer does not have pores for the substrate to penetrate in the dry state.[8] But swollen by sorbed solvent, the polymer matrix opens up as solvent is sorbed into it and substrates will penetrate

into the polymer matrix by counter diffusion with solvent. Accordingly, the effective diffusivity is given as follow:

$$D_e = D(1 - v) \qquad (17)$$

where D is the diffusivity of substrate in a given solvent.

The boundary and initial conditions are

$$C[r, 0] = 0 \qquad (18a)$$

$$C_f[r, 0] = 0 \qquad (18b)$$

$$\frac{\partial C[0, t]}{\partial r} = 0 \qquad (18c)$$

$$C[R, t] = C_0 \qquad (18d)$$

By defining dimensionless parameters and variables,

$$\tau = \frac{Dt}{R_0^2} \qquad \Psi = \frac{C_0}{C_{p0}} \qquad \phi^2 = \frac{kC_{p0}R_0^2}{D} \qquad (19a)$$

$$\mathbb{C} = \frac{C}{C_0} \qquad \mathbb{C}_f = \frac{C_f}{C_{p0}} \qquad z = \frac{r}{R_0} \qquad (19b)$$

eqs. (13), (14), (15), and (18) become, respectively

$$\frac{dv}{dz} = \frac{2v(\lambda_2^2 - \lambda_1^2) + 4\left(\dfrac{\lambda_1}{\lambda_2^2} - \dfrac{1}{\lambda_2}\right)}{\dfrac{M_c}{\rho V_0}\left(2\chi - \dfrac{1}{1 - v}\right)v - \lambda_1^2} \frac{1}{z} \qquad (20a)$$

$$\frac{\partial \mathbb{C}}{\partial \tau} = \frac{1}{z^2}\frac{\partial}{\partial z} z^2(1 - v)\frac{\partial \mathbb{C}}{\partial z}$$
$$- \phi^2 \mathbb{C}(1 - \mathbb{C}_f)v(1 - v) \qquad (20b)$$

$$\frac{\partial \mathbb{C}_f}{\partial \tau} = \Psi\phi^2 \mathbb{C}(1 - \mathbb{C}_f)v(1 - v) \qquad (20c)$$

$$\mathbb{C}[z, 0] = 0 \qquad (21a)$$

$$\mathbb{C}_f[z, 0] = 0 \qquad (21b)$$

$$\frac{\partial \mathbb{C}[0, \tau]}{\partial \tau} = 0 \qquad (21c)$$

$$\mathbb{C}[Z, \tau] = 1 \qquad (21d)$$

$$\sigma_1[Z, \tau] = 0 \qquad (21e)$$

The rate of reaction and distribution of active species on the polymer bead will be obtained by solving eqs. (20a) through (21e).

ASYMPTOTIC APPROXIMATION FOR TWO EXTREME CASES

The preceding governing equations could be rather easily analyzed for two extreme cases; one under no diffusion limitations ($\phi^2 \ll 1$) and the other with strong diffusion limitations ($\phi^2 \gg 1$).

Case I: $\phi^2 \ll 1$

In this restriction the rate of diffusion of the substrate through the polymer bead is much faster than that of the chemical reaction. So the concentration of substrate and reacted functional groups in the polymer bead is almost uniform throughout the bead. The equation of swelling and reaction will be reduced simply as follows:

$$\frac{M_c}{\rho V_0} [\ln(1 - v) + v + \chi v^2] + \lambda_1^2 v = 0 \quad (22a)$$

$$\frac{\partial C_f}{\partial \tau'} = (1 - C_f)v(1 - v) \quad (22b)$$

$$C_f[z, 0] = 0 \quad (22c)$$

where $\tau' = \tau / \Psi \phi^2 C$.

In order to obtain a numerical solution of eqs. (22), the following values of the parameters for polystyrene and benzene were chosen, which were considered to be the most typical.[9]

$$\rho = 1050 \text{ kg/m}^3 \qquad V_0 = 8.94 \times 10^{-2} \text{ m}^3/\text{mol}$$

At a temperature of 298 K the value of modulus for the unswollen polymer, $\rho RT/M_c$, is 1.1088 MN/m² when M_c has the value of 2346 kg/mol. It is assumed that additional crosslinking does not occur during the chemical reaction. The modulus will change little by the immobilization of active species, while the polymer–solvent interaction parameter, χ, might change. The χ value was used as a measure of the extent of these interactions between solvent and polymer. The value of χ decreases with increase of the compatibility between polymer and solvent, which ranges from 0.0 to 0.5, commonly reported values for many solvent–polymer systems.[4,10] The change of interaction parameter with reaction was estimated by group contribution as follows:

$$\chi = \chi_{\text{unreacted}} + C_f \chi_{\text{reacted}} \quad (23)$$

The value of $\chi_{\text{unreacted}}$ and χ_{reacted} were chosen as 0.5 and 0.0 in the case of expanding, and 0.0 and 0.5

in the case of shrinking of polymer during reaction, respectively. Figures 1 and 2 show that the volume fraction of polymer and the concentration of reacted functional group changed with time.

Case II: $\phi^2 \gg 1$

It is important to recognize that the chemical reaction and equilibrium swelling condition are coupled; that is, the equilibrium polymer volume fraction v depends on the extent of reaction. In order to find out the simple relationship between the equilibrium polymer volume fraction and extent of reaction, assuming a two-phase (i.e., the outer phase is totally reacted and the inner remains unreacted) system of homogeneous polymers in contact with each other. A sharp discontinuous phase boundary is considered. Figures 3 and 4 show that the equilibrium volume fraction of swollen polymer depends on not only the position of polymer–polymer interface but also a radial position. The volume fraction of polymer strongly depends on the extent of reaction (C_{mf}) and local conversion at a position (C_f), but is nearly independent of the radial position as long as it is in the same phase. Figures 5 and 6 represent the mean equilibrium swollen ratio ($1/v$) of two phases with the extent of reaction. It can be assumed that the mean swollen ratio is nearly linear to the extent of reaction. So the volume fraction of polymer is simplified as

$$1/v [C_f = 0] = a C_{mf} + b \quad (24a)$$

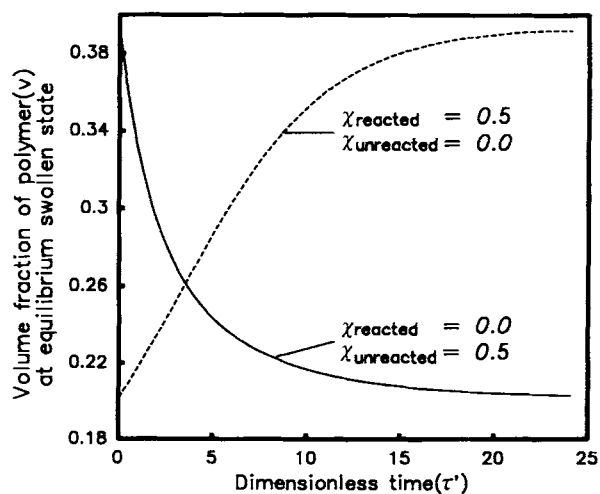$$1/v [C_f = 1] = a' C_{mf} + b' \quad (24b)$$

Figure 1 Equilibrium volume fraction of polymer as a function of dimensionless time: solid line: $\chi_{\text{unreacted}} = 0.5$, $\chi_{\text{reacted}} = 0.0$; dashed line: $\chi_{\text{unreacted}} = 0.0$, $\chi_{\text{reacted}} = 0.5$.
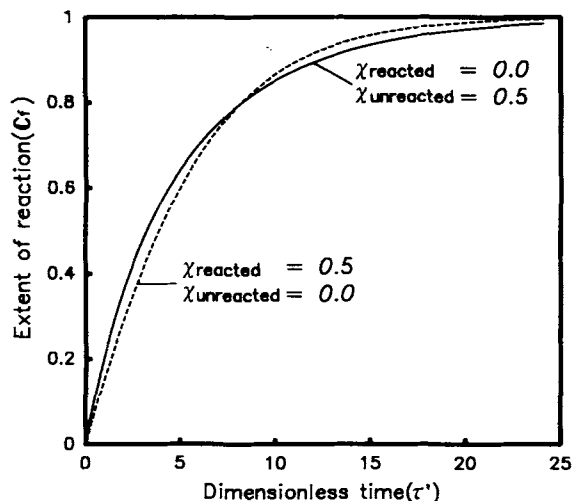
Figure 2 Extent of reaction as a function of dimensionless time: solid line: $\chi_{unreacted} = 0.5$, $\chi_{reacted} = 0.0$; dashed line: $\chi_{unreacted} = 0.0$, $\chi_{reacted} = 0.5$.
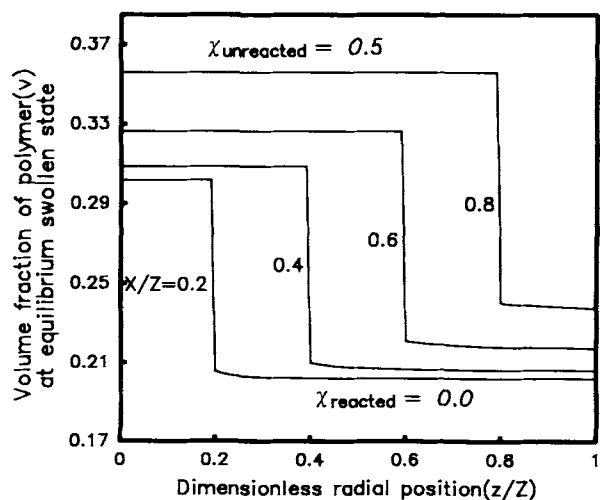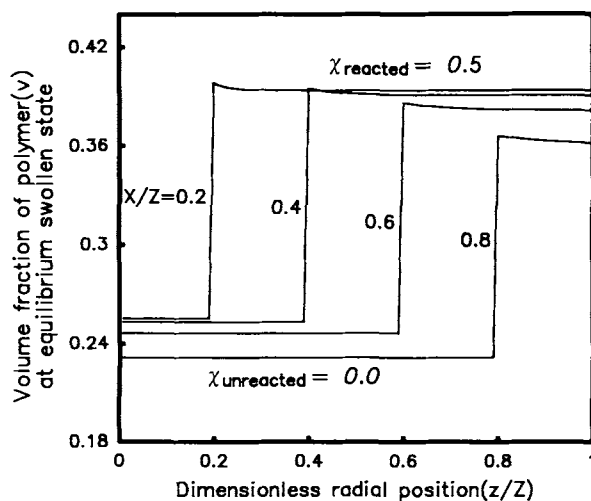

Figure 4 Equilibrium volume fraction of polymer as a function of polymer–polymer interface position. ($\chi_{unreacted} = 0.0$, $\chi_{reacted} = 0.5$).

$$1/v = 1/v \, [\mathbb{C}_f = 0]$$
$$+ (1/v \, [\mathbb{C}_f = 1] - 1/v \, [\mathbb{C}_f = 0])\mathbb{C}_{mf} \quad (24c)$$

where $v \, [\mathbb{C}_f = 0]$ and $v \, [\mathbb{C}_f = 1]$ are the swollen polymer volume fraction at the unreacted and reacted part in the polymer bead, respectively. The extent of reaction ($\mathbb{C}_{mf}$) is given by

$$\mathbb{C}_{mf} = \oint \mathbb{C}_f v d\mathcal{V} \Big/ \oint v d\mathcal{V} \quad (25)$$

The dimensionless position of polymer–solvent interface Z is evaluated by mass conservation of polymer.

$$\int_0^Z v r^2 \, dr = v \, [\mathbb{C}_{mf} = 0]/3 \quad (26)$$

Since the rate of reaction is higher than that of diffusion ($\phi^2 \gg 1$), the time scale of equations must

Figure 3 Equilibrium volume fraction of polymer as a function of polymer–polymer interface position. ($\chi_{unreacted} = 0.5$, $\chi_{reacted} = 0.0$).
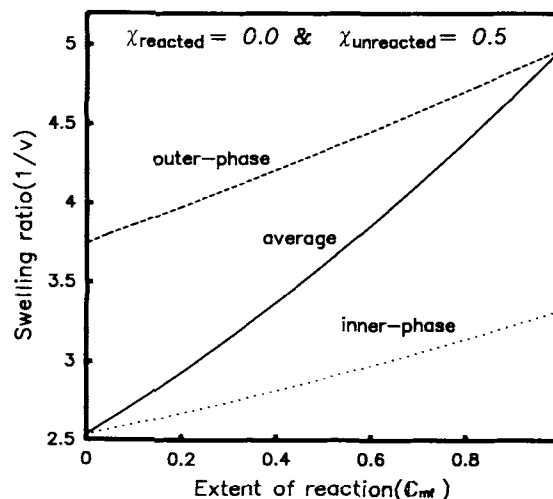

Figure 5 Swelling ratio as a function of conversion: dashed line: mean swelling ratio of reacted polymer of outer phase, dotted line: that of unreacted polymer of inner phase, solid line: average value ($\chi_{unreacted} = 0.5$, $\chi_{reacted} = 0.0$).
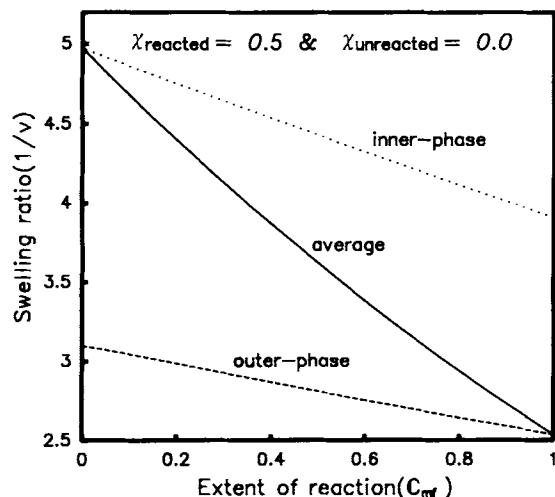
Figure 6 Swelling ratio as a function of conversion: dashed line: mean swelling ratio of reacted polymer of outer phase, dotted line: that of unreacted polymer of inner phase, solid line: average value ($X_{\text{unreacted}} = 0.0$, $X_{\text{reacted}} = 0.5$).

be rescaled to observe transient behavior of the system starting from the initial conditions.

$$T = \tau \phi^2 \qquad (27a)$$

$$\frac{\partial C}{\partial T} = \frac{\mu^2}{z^2} \frac{\partial}{\partial z} z^2 (1 - v) \frac{\partial C}{\partial z}$$

$$- C(1 - C_f) v(1 - v) \qquad (27b)$$

$$\frac{\partial C_f}{\partial T} = \Psi C(1 - C_f) v(1 - v) \qquad (27c)$$

where $\mu = 1/\phi \ll 1$.

In most, if not all cases, the value of parameter Ψ is small. The time scale T is too fast to observe any change in the concentration of substrate in the polymer bead. The proper time scale to observe the concentration profile in the polymer bead is much slower than the real one, and it is given by

$$T' = \Psi \mu^2 T \qquad (28a)$$

Then eqs. (25b) and (25c) are rewritten as

$$\Psi \mu^2 \frac{\partial C}{\partial T'} = \frac{\mu^2}{z^2} \frac{\partial}{\partial z} z^2 (1 - v) \frac{\partial C}{\partial z}$$

$$- C(1 - C_f) v(1 - v) \qquad (28b)$$

$$\mu^2 \frac{\partial C_f}{\partial T'} = C(1 - C_f) v(1 - v) \qquad (28c)$$

Applying the perturbation technique to eq. (28), there are two outer and one inner solutions that are valid in the subdomain $I_1 = [0, X)$, $I_2 = (X, Z]$ and $I_3 = (X)$, where X is the time-dependent radial position of polymer–polymer interface. To obtain these outer solutions, it is assumed that C, C_f, and C_{mf} possess the following asymptotic expansions in the form of a series in ascending powers of μ^2:

$$C = C_0[z, T'] + \mu^2 C_1[z, T'] + O(\mu^2) \qquad (29a)$$

$$C_f = C_{f0}[z, T'] + \mu^2 C_{f1}[z, T'] + O(\mu^2) \qquad (29b)$$

$$C_{mf} = C_{mf0}[z, T'] + \mu^2 C_{mf1}[z, T'] + O(\mu^2) \qquad (29c)$$

By eqs. (28) and (29), an infinite sequence of subproblems can be obtained. The first two are

$$O(1): \quad C_0(1 - C_{f0}) v(1 - v) = 0 \qquad (30)$$

$$O(\mu^2): \frac{1}{z^2} \frac{\partial}{\partial z} z^2 (1 - v) \frac{\partial C_0}{\partial z}$$

$$- \{ C_0 C_{f1} + C_1(1 - C_{f0}) \} v(1 - v) = 0 \quad (31a)$$

$$\frac{\partial C_{f0}}{\partial T'} = \{ C_0 C_{f1} + C_1(1 - C_{f0}) \} v(1 - v) = 0 \quad (31b)$$

$O(1)$ is called the leading-order equation or sometimes the degenerate equation in the literature. There are two solution to $O(1)$; the first one is

$$C_0 = 0 \quad \text{and} \quad C_{f0} \neq 1 \qquad (32)$$

which is valid in the subdomain $I_1 = [0, X)$. The second one is

$$C_0 \neq 0 \quad \text{and} \quad C_{f0} = 1 \qquad (33)$$

which is valid in the subdomain $I_2 = (X, Z]$.

Combining eqs. (31a) and (31b), we obtain

$$\frac{\partial C_{f0}}{\partial T'} = \frac{1}{z^2} \frac{\partial}{\partial z} z^2 (1 - v) \frac{\partial C_0}{\partial z} \qquad (34)$$

Solving this equation in inner-phase $I_1 = [0, X)$, by substituting eq. (32) and then integrating the result with respect to time T' with eq. (21b), which is the initial condition, eq. (35) was obtained.

$$C_{f0} = 0 \qquad (35)$$

This is consistent with our physical intuition, that is, the functional groups did not react in the inner core of polymer $[0, X)$, and the substrate concentration is virtually at zero level.

For the outer-phase of the polymer particle (X, Z], eqs. (33) and (34) give the following equation:

$$\frac{1}{z^2}\frac{\partial}{\partial z}z^2(1-v)\frac{\partial \mathbb{C}_0}{\partial z} = 0 \qquad (36)$$

The penetration of substrate species into the polymer bead is governed by a diffusion process. Since eq. (36) is only valid in the outer subdomain (X,Z], then boundary conditions must be imposed on the boundaries, $z = X$ and $z = Z$. The boundary condition at $z = Z$ (i.e., at the interface of polymer-solvent) is given in eq. (21d). Based on the fact that $\mathbb{C}_0$ is absolutely zero in the inner-phase $[0, X)$, the boundary condition at $z = X$ for eq. (36) must be chosen as

$$z = Z \qquad \mathbb{C}_0 = 1 \quad \text{and} \quad z = X \qquad \mathbb{C}_0 = 0 \qquad (37)$$

The integration of the eq. (36) with boundary condition is

$$\mathbb{C}_0 = -\frac{ZX}{Z-X}\frac{1}{z} + \frac{Z}{Z-X} \qquad (38)$$

where Z is the position of solvent-polymer interface and will be found out from eq. (26).

The velocity of the moving polymer-polymer interface, reaction zone, is balanced by the substrate flux at that interface. In terms of dimensional variables, it becomes

$$vC_{p0}\frac{dw}{dt} = -(1-v)D\frac{\partial C}{\partial r}\bigg|_{r=w} \qquad (39)$$

where the w is the position of polymer-polymer interface.

By defining the dimensionless parameters and variables,

$$T' = \frac{C_0}{C_{p0}}\frac{Dt}{R_0^2} \qquad X = \frac{w}{R_o} \qquad (40a)$$

$$Z = \frac{r}{R_0} \qquad \mathbb{C} = \frac{C}{C_0} \qquad (40b)$$

eq. (39) becomes

$$\frac{dX}{dT'} = -(1-v)\frac{\partial \mathbb{C}}{\partial z}\bigg|_{z=X} \qquad (41)$$

The right-hand side of this equation is approximated by using eq. (38).

$$\frac{dX}{dT'} = -(1-v)\frac{Z}{X(Z-X)} \qquad (42a)$$

The position of polymer-solvent interface is obtained by mass balance of polymer.

$$Z^3 = \left(\frac{1}{b} - \frac{X^3}{a\mathbb{C}_{mf}+b}\right)(a'\mathbb{C}_{mf}+b') + X^3 \qquad (42b)$$

The extent of reaction is obtained from eq. (25)

$$\mathbb{C}_{mf} = \frac{1}{\left(\dfrac{a'\mathbb{C}_{mf}+b'}{a\mathbb{C}_{mf}+b}\right)\left(\dfrac{X^3}{Z^3-X^3}\right)+1} \qquad (42c)$$

The solutions of eqs. (42) with boundary conditions (18) are simply solved by numerical analysis. The results are given in Figs. 7–11.

Suppose the condition that the reacted polymer is more compatible with solvent than is the unreacted one (Case A: $\chi_{unreacted} > \chi_{reacted}$), the polymer expands during the chemical reaction as shown in Fig. 7. In another condition (Case B: $\chi_{unreacted} < \chi_{reacted}$), the polymer shrinks during the chemical reaction (Fig. 8). Therefore, the reacted domain in case B is smaller than that in case A under the same extent of reaction by shrinking. The diffusion of substrate from the polymer-solvent interface to polymer-polymer interface (i.e., reaction zone) depends on the distance between two interfaces and the polymer volume fraction affecting on effective
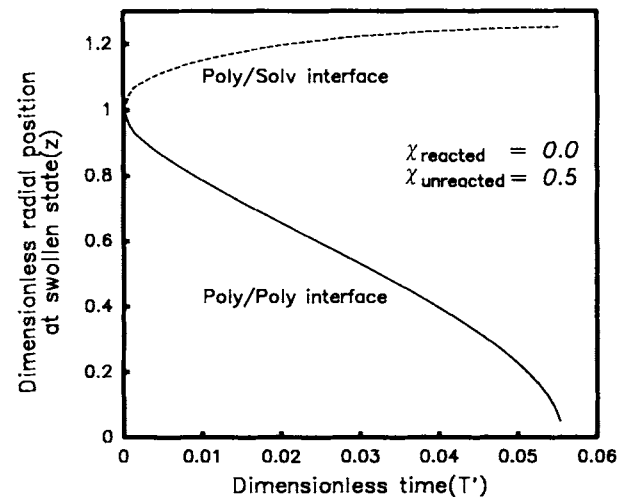

Figure 7 Dimensionless position of polymer-polymer interface (solid line) and polymer-solvent interface (dashed line) as a function of dimensionless time ($\chi_{unreacted}$ = 0.5, $\chi_{reacted}$ = 0.0).
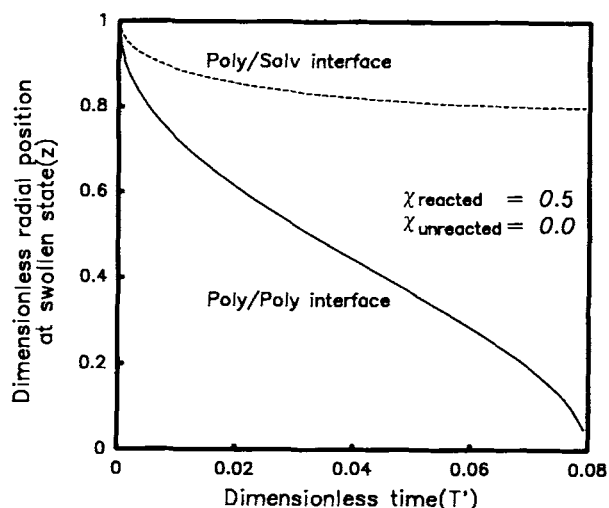
Figure 8 Dimensionless position of polymer–polymer interface (solid line) and polymer–solvent interface (dashed line) as a function of dimensionless time ($X_{unreacted}$ = 0.0, $X_{reacted}$ = 0.5).

Figure 10 Position of polymer–polymer interface at swollen state as a function of dimensionless time: solid line: $X_{unreacted}$ = 0.5, $X_{reacted}$ = 0.0; dashed line: $X_{unreacted}$ = 0.0, $X_{reacted}$ = 0.5.

diffusivity. Though the distance in case B is shorter than that in case A at same reaction time, the reaction rate in case B is lower than that in case A (Fig. 9). It might be explained from this result that the change of polymer volume fraction played a more important role than the change of the distance between two interfaces to the diffusion of substrates from the polymer–solvent interface to the polymer–polymer interface. The movement of polymer–polymer interface toward the center of polymer bead is slower in case A than in case B at the beginning of the reaction (Fig. 10). But based on the dry state,
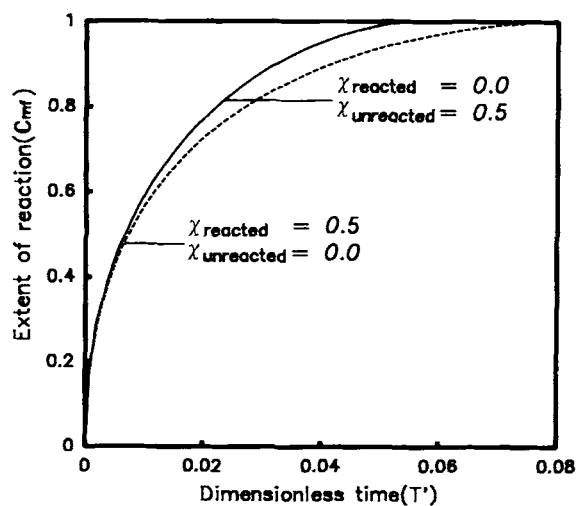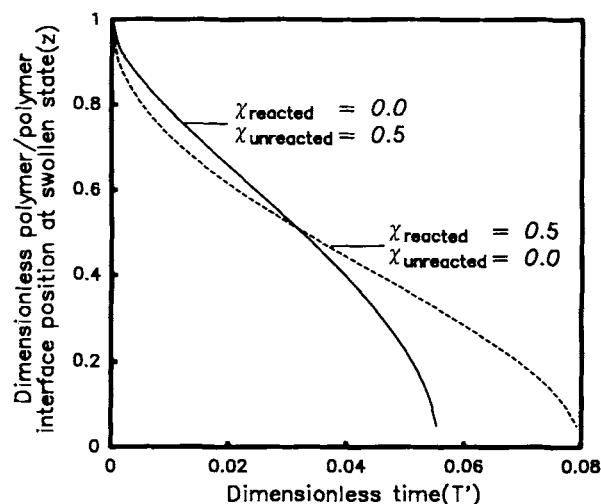
the radial positions of the polymer–polymer interface in both cases are nearly the same (Fig. 11). It might be attributed to the expanding or the shrinking of polymer during the reaction, that is, the expanding of the inner-phase polymer restricted the movement of the polymer–polymer interface toward the center of polymer bead in case A.

Since the transport properties of active species into gelular polymer bead are strongly dependent on the degree of swelling, the reaction rate of attachment depends on the interaction parameter, which

Figure 9 Extent of reaction as a function of dimensionless time: solid line: $X_{unreacted}$ = 0.5, $X_{reacted}$ = 0.0; dashed line: $X_{unreacted}$ = 0.0, $X_{reacted}$ = 0.5.

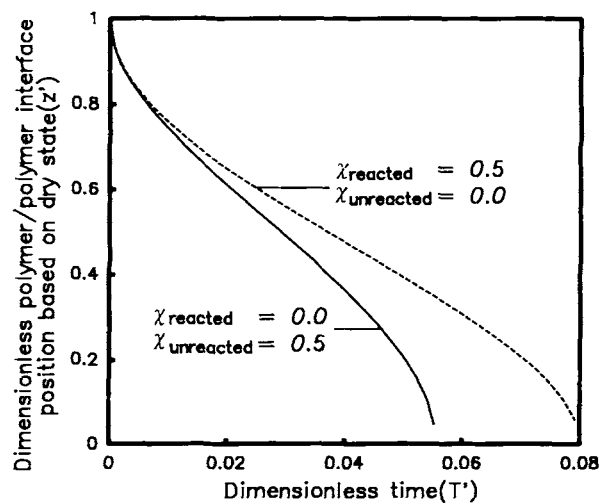**Figure 11** Position of polymer–polymer interface based on dry state as a function of dimensionless time: solid line: $X_{unreacted}$ = 0.5, $X_{reacted}$ = 0.0; dashed line: $X_{unreacted}$ = 0.0, $X_{reacted}$ = 0.5).

represents the degree of compatibility of solvent with polymer network. In view of the transport properties, the solvent that is more compatible with the unreacted polymer network than with the reacted one may be useful to control effectively the distribution of active species in the gelular polymer bead.

CONCLUSIONS

A model has been proposed to predict the reaction rate of the attachment and the distribution of active species in gelular polymer bead. The asymptotic solution of this model was obtained in the two extreme cases wherein the reaction rate is much faster or slower than the diffusion rate. In the case that the reaction rate is much faster than the diffusion rate ($\phi^2 \gg 1$), it is shown that the attachment rate of active species and movement of reaction zone (polymer–polymer interface) are influenced by the expanding or the shrinking of polymer bead during the reaction. Solvent that is more compatible with unreacted polymer network than reacted one may be useful to effectively control the distribution of active species in the gelular polymer bead.

NOTATION

C	concentration of substrate
$\mathbb{C}$	concentration of substrate, dimensionless
C_{p0}	initial concentration of functional group at dry state on the polymer
C_f	concentration of functional group has reacted
$\mathbb{C}_f$	concentration of functional group has reacted, dimensionless
$\mathbb{C}_{mf}$	extent of reaction
D	diffusivity of substrate
D_e	effective diffusivity of substrate
G	modulus of polymer
G_m	molar Gibbs free energy
k	reaction rate constant
M_c	number-average molecular weight between the crosslinks
M_n	number-average molecular weight
R	universal gas constant
R_t	radius of polymer bead at swollen state
R_0	initial radius of polymer bead at swollen state
$\mathbb{R}$	reaction rate

r	radial position variable
T	absolute temperature
t	time variable
T, T'	time variable, dimensionless
v	equilibrium swollen polymer volume fraction
V_0	molar volume of solvent
X	polymer–polymer interface position, dimensionless
$\mathcal{V}$	domain of swollen polymer bead
W	work function
w	polymer–polymer interface position
Z	polymer–solvent interface position, dimensionless
z	radial position variable, dimensionless

Greek Symbols

σ_i	stress along the ith principle axis
λ_i	extension ratio along the ith principle axis
ρ	density of polymer
χ	polymer–solvent interaction parameter
τ, τ'	time variable, dimensionless
Ψ	parameter, dimensionless
ϕ	Thiele modulus
θ	colatitude variable
φ	azimuth variable
μ	$1/\phi$

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