A MULTI-PHASE STEFAN PROBLEM DESCRIBING THE SWELLING AND THE DISSOLUTION OF GLASSY POLYMER*

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Abstract: In the swelling and the dissolution of certain glassy polymers, three distinctive regimes are present. They are (1) the liquid solution wherein the disassociated polymer molecules are carried away by diffusion, (2) the gel layer of rubbery polymer containing large solvent concentration, and (3) the glassy phase of the polymer where there is very little solvent penetration. The gel/liquid interface that separates the diffusion of the disassociated polymer in the liquid solution from that of the solvent in the polymer is characterized by a constant disassociation concentration. The position of this gel/liquid interface is described explicitly either by a relationship between diffusion processes, or by the rate of disassociation at the interface in addition to the diffusion processes, depending on whether the disassociation rate exceeds the diffusion capability in removing the disassociated polymer molecules at the interface.

The glassy phase is characterized by a sharp decrease in several orders of magnitude of the diffusion coefficient of solvent in gel-like and glassy polymers. The position of the glass/gel transition, however, has to be determined implicitly from the diffusion problem. The existence of the glass/gel transition presents some unique features in the Stefan problem requiring special numerical considerations.

1. Introduction. One of the lithographic techniques in the fabrication of large-scale integrated circuits is the use of polymers as electron beam resist materials. When a region of a polymer film is exposed to an electron beam, it dissolves many times faster than areas which have not experienced electron bombardment. By careful choice of solvents, a pattern can be developed in the polymer surface with very good resolution and contrast. The current direction of this technology is toward narrower lines and greater line density. It is important that the geometric integrity of the patterns generated during E-beam exposure be maintained during the development process. Consequently, a greater and deeper understanding of the nature of polymer dissolution is needed. As may be well understood, there are a variety of polymers which may serve as resist materials. The description of the phenomena given here and the following mathematical representation applies to a class of polymers for which diffusion is a predominant mechanism in the rate of dissolution. Other phenomena such as bubble formation and cracking may be of importance in other materials but these are excluded from this treatment.

The complexity observed in the diffusion of solvent in a glassy polymer was not believed explicable in terms of nonlinear concentration dependence of the diffusion coefficient alone [1]. The anomalous behavior was attributed to the stress fields that

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existed due to the nonhomogeneous swelling in the gel and in the glassy phase of a finite polymer specimen. In the analysis of Wang and Kwei [2], the stress effect was represented by a constant swelling rate independent of time as well as space in the gel layer of the polymer. The diffusion coefficient was assumed to be a constant in their analysis, and the constant swelling rate was regarded as a material property. The dissolution of the dissolving polymer into the liquid solution that is taking place simultaneously while the polymer is swelling was ignored in their analysis.

The nonlinear concentration dependence of the diffusion coefficient of the solvent in polymer is, however, well known to span 5 to 7 orders of magnitudes in the gel and in the glassy phase of the polymer. In considering simultaneously the swelling and the dissolution of glassy polymer in one dimension, the only stress field that may exist in the polymer is that of uniform hydrostatic pressure. Therefore, the kinematics of the swelling and the dissolution may be described analytically without complications. The coupling between the swelling of the polymer and the dissolution of the dissolving polymer in the liquid solution may then be investigated. In a rational manner, some material properties may be defined analytically, and, at the same time, they may be measured and verified experimentally. Accordingly, Tu and Ouano proposed a phenomenological model to describe the kinematics of polymer dissolution. The physical concept and the experimental verification of their model has appeared in [3]. The mathematical description consists of (*i*) the diffusion of solvent in polymer, (*ii*) the diffusion of dissolved polymer in liquid solution, and (*iii*) the characterization of the dissolution of polymer taking place at the interface separating the two diffusion processes. The equations constitute a multi-phase Stefan problem [4]. The mathematical derivations and the numerical methods used in the integration scheme are presented here.

2. Mathematical description of physical phenomena. When a glassy polymer is being dissolved in a solvent, three distinctive regimes exist: (*i*) liquid solution, (*ii*) gel layer of polymer and (*iii*) glassy phase of polymer. The physical phenomena occurring during the dissolution will be described by means of the following physical parameters:

- Disassociation concentration (denoted by c_F)—the volume concentration of the polymer at the gel/liquid interface, $0 < c_F < 1$.
- Disassociation rate (denoted by R)—the rate in cm/sec at which the disassociated polymer molecules are freed to diffuse into the liquid solution from the gel/liquid interface.
- Glass/gel interface concentration (denoted by c_G)—the volume concentration of the polymer at which diffusion coefficient of solvent undergoes a sharp decrease ($c_F < c_G < 1$).
- Nominal diffusion coefficient of solvent in polymer (denoted by D_s)—the diffusion coefficient of solvent in polymer at the gel/liquid interface (cm²/sec).
- Nominal diffusion coefficient of polymer in liquid solution (denoted by D_p)—the diffusion coefficient of polymer in dilute solution (cm²/sec).
- Gel/liquid interface (denoted by $y(t)$)—position of the gel/liquid interface at time t (*cm*).
- Glass/gel interface (denoted by $x_G(t)$)—position in the polymer where the volume concentration is c_G at time t, $y(t) < x_G(t)$.
- Boundary layer thickness (denoted by B)—thickness in the liquid solution, measured from the gel/liquid interface, at which the concentration of polymer may be taken to be zero.

It will be taken that the space coordinate x is directed into the polymer and $x = 0$ coincides with the gel/liquid interface at time $t = 0$. Thus $y(0) = 0$, (see the concentration profiles in Figs. 7a and 8a). c_F and R are dependent upon the molecular weight of the polymer, but they are independent from each other in the model.

When the polymer is developed in the lab, the liquid solution is stirred mechanically. A boundary layer exists between the surface of the polymer and the main stream of the liquid solution. Hence, the dissolved polymer is swept away within the boundary layer in the direction parallel to the surface. In this one-dimensional analysis, the boundary layer is represented so that the dissolved polymer is removed at the edge of the boundary layer in the direction of diffusion.

We introduce the following notation in addition to that defined above:

c—volume concentration of polymer, $0 < c < 1$;

c'—volume concentration of solvent, $c' = 1 - c$;

H_p—initial thickness of polymer film when $c \equiv 1$, i.e., polymer occupies the region $0 < x < H_p$ at $t = 0$;

$f_s(c)$—numerical factor for the diffusion coefficient of solvent in polymer. Hence the local diffusion coefficient of solvent in polymer is equal to $D_s f_s(c)$. $f_s(c) > 0$, $f_s(c_F) = 1$;

$f_p(c)$—numerical factor for the diffusion coefficient of dissolved polymer in liquid solution. Hence the local diffusion coefficient of polymer in liquid solution is equal to $D_p f_p(c)$. $f_p(c) > 0$, $f_p(0) = 1$;

$q(x, t)$—local flux of dissolved polymer in liquid solution, cm/sec;

$q'(x, t)$—local flux of solvent in polymer, cm/sec; and

$v(x, t)$—swelling rate of polymer at x and time t, cm/sec.

The local flux of solvent passing through any material point x in the polymer is given in terms of the concentration of solvent c' by

$$q'(x, t) = -D_s f_s(c)(\partial c'/\partial x), \quad x > y(t). \tag{1}$$

Similarly, the local flux of polymer in liquid solution is given by

$$q(x, t) = -D_p f_p(c)(\partial c/\partial x), \quad x < y(t). \tag{2}$$

1. The swelling of the polymer. As solvent diffuses into the polymer, the latter swells at the rate $v(x, t)$ equal in magnitude but opposite in direction to the flux $q'(x, t)$ of the solvent at x and t; hence

$$v(x, t) = -q'(x, t), \quad y(t) < x < H_p. \tag{3}$$

However, at the gel/liquid interface, $x = y(t)$, the interface position is determined by the equation

$$dy/dt = v(x = y^+(t), t) - q(x = y^-(t), t), \tag{4}$$

where $q(x = y^-(t), t)$ is the flux of dissolved polymer leaving the interface, and $y^\pm(t)$ indicate the gel and the liquid solution sides of the interface $y(t)$, respectively. The effect of swelling was investigated by Wang and Kwei [2] based on constant swelling rate, independent of x and t.

2. The diffusion of solvent in the polymer, $y^+(t) < x < H_p$. Observed from a coordinate moving with the swelling rate $v(x, t)$ of the polymer material at x, the local flux of solvent is q'. The absolute flux of solvent as seen by the stationary observer is, therefore, $q' + c'v$. Consequently, the conservation equation becomes

$$(\partial c'/\partial t) + (\partial/\partial x)[q' + c'v] = 0, \quad y^+(t) < x < H_p. \tag{5}$$

Since $c' = 1 - c$, the above conservation equation may be expressed in terms of c by means of Eqs. (1) and (3) in the form

$$(\partial c/\partial t) = D_s(\partial/\partial x)[f_s(c)(\partial c/\partial x)], \qquad y^+(t) < x < H_p . \tag{6}$$

Initially, $c' \equiv 0$; hence

$$c(x, t = 0) \equiv 1, \qquad y^+(0) = 0 < x < H_p . \tag{7}$$

At the gel/liquid interface, $x = y^+(t)$, the concentration is kept at constant c_F . For an impervious substrate at $x = H_p$, the flux vanishes. Thus, the boundary conditions for c are

$$\begin{aligned} c = c_F \quad &\text{at } x = y^+(t), \quad t > 0, \\ \partial c/\partial x = 0 \quad &\text{at } x = H_p , \qquad t > 0. \end{aligned} \tag{8}$$

At the glass/gel interface, both c and the flux $D_s f_s(c)(\partial c/\partial x)$ must be continuous.

3. The diffusion of dissolved polymer in the liquid solution, $x < y^-(t)$. The swelling of the polymer causes a bulk motion in the liquid phase (dilute solution) equal to the velocity of the gel/liquid interface given by Eq. (4). Observed from a coordinate moving with the liquid solution at velocity dy/dt, the local flux of polymer in the solution is q. The absolute flux of polymer in solution (as seen from a stationary coordinate) is therefore $q + c(dy/dt)$. Hence, the conservation equation becomes

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x}\left[q + c\frac{dy}{dt} \right] = 0, \qquad x < y^-(t). \tag{9}$$

Making use of Eq. (2), we derive the conservation equation in terms of c:

$$\frac{\partial c}{\partial t} + \frac{dy}{dt}\frac{\partial c}{\partial x} = D_p\frac{\partial}{\partial x}\left[f_p(c)\frac{\partial c}{\partial x} \right], \qquad x < y^-(t). \tag{10}$$

Initially

$$c(x, t = 0) \equiv 0, \qquad x < y^-(0) = 0. \tag{11}$$

At the gel/liquid interface, $x = y^-(t)$, the flux of dissolved polymer leaving the interface is computed according to

$$q(x = y^-(t), t) = -D_p f_p(c)(\partial c/\partial x) \quad \text{at } x = y^-(t), \quad t \geqq 0. \tag{12}$$

Depending on the condition at the gel/liquid interface, either of the following may take place:

(*i*) Starting from time $t = 0$, the flux given by Eq. (12) is limited by the disassociation rate R of the disassociated polymer molecules that are available from the gel/liquid interface. Hence,

$$-q(x = y^-(t), t) = D_p f_p(c) \frac{\partial c}{\partial x} = R \qquad \text{at } x = y^-(t), \qquad 0 < t < t_c , \tag{13}$$

for some t_c , provided $c < c_F$ at $x = y^-(t)$. Gradually, the concentration c at $x = y^-(t)$, which is zero at $t = 0$, increases as long as $0 < c < c_F$ at $x = y^-(t)$. During these times, the diffusion capability is always sufficient to carry away whatever dissolved polymer that is available at the interface.

(*ii*) In the end, $c = c_F$ at $x = y^-(t)$ for $t > t_c$, because the diffusion capability becomes insufficient to carry away the dissolved polymer molecules which continue to be available

at the disassociation rate R. Thereafter, the concentration c at $x = y^-(t)$ is maintained at c_F. Hence

$$c = c_F \quad \text{at } x = y^-(t), \quad t > t_c. \tag{14}$$

At $t = t_c$, both Eqs. (13) and (14) are satisfied.

When condition (13) is valid we shall call this "Source-Limited Analysis." When condition (14) prevails we shall call this "Flux-Limited Analysis."

The second boundary condition at the boundary layer is given by

$$c = 0 \quad \text{at } x = y^-(t) - B. \tag{15}$$

Since $f_p(0) = 1$, the rate of removal of dissolved polymer may be computed according to

$$q_B = -D_p \frac{\partial c}{\partial x}, \qquad x = y^-(t) - B. \tag{16}$$

Returning to the gel/liquid interface given by Eq. (4), its velocity may be expressed in terms of c by using (1), (2), and the condition $f_s(c_F) = 1$:

$$\frac{dy}{dt} = D_p f_p(c) \left. \frac{\partial c}{\partial x} \right|_{x=y^-(t)} - D_s \left. \frac{\partial c}{\partial x} \right|_{x=y^+(t)}. \tag{17}$$

3. The Stefan problem. Introducing the dimensionless time variable τ defined by

$$\tau = D_s t / H_p^2, \tag{18}$$

and normalizing all linear dimensions with respect to the initial film thickness H_p, we can define the following dimensionless parameters:

$$\begin{aligned} & y^*(\tau) = y(t)/H_p, \ x_G^*(\tau) = x_G(t)/H_p, \ B^* = B/H_p, \\ & r^* = D_p/D_s, \ R^* = H_p R/D_p, \ x^* = x/H_p. \end{aligned} \tag{19}$$

A. Summary of mathematical formulation.

1. Diffusion of solvent in polymer, $y^{*+}(\tau) < x^* < 1$. The differential equation (D.E.) can be written as

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x^*} \left[f_s(c) c \frac{\partial c}{\partial x^*} \right], \tag{20}$$

with the initial condition (I.C.)

$$c(x^*, \tau = 0) \equiv 1, \qquad y^{*+}(0) = 0 < x^* < 1 \tag{21}$$

and the boundary conditions (B.C.)

$$c = c_F, \quad x^* = y^{*+}(\tau), \quad \tau > 0; \quad \frac{\partial c}{\partial x^*} = 0, \quad x^* = 1, \quad \tau > 0. \tag{22}$$

2. Diffusion of dissolved polymer in the liquid, $y^{*-}(\tau) - B^* < x^* < y^{*-}(\tau)$. D.E.:

$$\frac{\partial c}{\partial \tau} = -\frac{dy^*}{d\tau} \frac{\partial c}{\partial x^*} + r^* \frac{\partial}{\partial x^*} \left[f_p(c) \frac{\partial c}{\partial x^*} \right], \tag{23}$$

I.C.:

$$c(x^*, \tau = 0) \equiv 0, \qquad -B^* < x^* < y^{*-}(0) = 0, \qquad (24)$$

B.C.:

$$c = 0, \qquad x^* = y^{*-}(\tau) - B^*, \qquad (25)$$

(*i*) source-limited analysis, if $0 < c < c_F$ at $x^* = y^{*-}(\tau)$, $0 < \tau < \tau_c$:

$$f_p(c)(\partial c/\partial x^*) = R^*, \qquad x^* = y^{*-}(\tau), \qquad (26)$$

(*ii*) flux-limited analysis, $\tau > \tau_c$:

$$c = c_F, \qquad x^* = y^{*-}(\tau). \qquad (27)$$

When $\tau = \tau_c$, both Eqs. (26) and (27) are satisfied.

3. Free boundary condition.

$$\frac{dy^*}{d\tau} = r^* f_p(c) \frac{\partial c}{\partial x^*}\bigg|_{x^* = y^{*-}(\tau)} - \frac{\partial c}{\partial x^*}\bigg|_{x^* = y^{*+}(\tau)}. \qquad (28)$$

4. Continuity conditions at the glass/gel transition, $x^* = x_G^*(\tau)$.

$$c\bigg|_{x^* = x_G^{*-}(\tau)} = c\bigg|_{x^* = x_G^{*+}(\tau)} = c_G,$$

$$\left[f_s(c) \frac{\partial c}{\partial x^*} \right]_{x^* = x_G^{*-}(\tau)} = \left[f_s(c) \frac{\partial c}{\partial x^*} \right]_{x^* = x_G^{*+}(\tau)}. \qquad (29)$$

B. Similarity variables.

The solution to the equations summarized above is singular at $\tau = 0$. The singularity can be built into the mathematical solution by the introduction of the similarity variable ξ and a new time scale η [4] defined by

$$\xi = x^* \tau^{-1/2}, \eta = \tau^{1/2}, \qquad (30)$$

and by letting

$$y^*(\tau) = \eta \zeta(\eta), x_G^*(\tau) = \eta Z_G(\eta). \qquad (31)$$

1. Diffusion of solvent in polymer, $\zeta^+(\eta) < \xi < \eta^{-1}$,
D.E.:

$$\frac{\partial}{\partial \xi}\left[f_s(c)c \frac{\partial c}{\partial \xi} \right] + \frac{1}{2} \xi \frac{\partial c}{\partial \xi} = \frac{1}{2} \eta \frac{\partial c}{\partial \eta}, \qquad (32)$$

B.C.:

$$c = c_F, \qquad \xi = \zeta^+(\eta),$$

$$\frac{\partial c}{\partial \xi} = 0, \qquad \xi = \eta^{-1},$$

$$(\text{or} \qquad c = 1, \qquad \xi \to \infty, \text{ when } \eta \to 0). \qquad (33)$$

2. Diffusion of dissolved polymer in liquid, $\zeta^-(\eta) - B^* \eta^{-1} < \xi < \zeta^-(\eta)$,
D.E.:

$$r^* \frac{\partial}{\partial \xi}\left[f_p(c) \frac{\partial c}{\partial \xi} \right] + \frac{1}{2}\{\xi - [\eta \zeta(\eta)]'\} \frac{\partial c}{\partial \xi} = \frac{1}{2}\eta \frac{\partial c}{\partial \eta}. \tag{34}$$

B.C.:

$$c = 0, \qquad \xi = \zeta^-(\eta) - B^* \eta^{-1}, \tag{35}$$

(i) source-limited analysis, if $0 < c < c_F$ at $\xi = \zeta^-(\eta)$, $0 < \eta < \eta_c$:

$$f_p(c)(\partial c/\partial \xi) = R^* \eta, \qquad \xi = \zeta^-(\eta), \tag{36}$$

(ii) flux-limited analysis, $\eta > \eta_c$:

$$c = c_F, \qquad \xi = \zeta^-(\eta). \tag{37}$$

When $\eta = \eta_c$, both Eqs. (36) and (37) are satisfied.

3. Free boundary condition.

$$[\eta \zeta(\eta)]' = 2r^* f_p(c) \frac{\partial c}{\partial \xi}\bigg|_{\xi = \zeta^-(\eta)} - 2\frac{\partial c}{\partial \xi}\bigg|_{\xi = \zeta^+(\eta)}. \tag{38}$$

4. Continuity conditions at the glass/gel interfaces, $\xi = Z_G(\eta)$.

$$c\bigg|_{\xi = Z_G^-(\eta)} = c\bigg|_{\xi = Z_G^+(\eta)} = c_G, \tag{39}$$

$$\left[f_s(c)\frac{\partial c}{\partial \xi} \right]_{\xi = Z_G^-(\eta)} = \left[f_s(c)\frac{\partial c}{\partial \xi} \right]_{\xi = Z_G^+(\eta)}.$$

4. Solution for small time. The solution for small time may be investigated by a power series expansion in η [4]. Accordingly, we derive the following:

1. Initial solution. Setting $\eta = 0$, Eqs. (32) through (39) become

$$\frac{d}{d\xi}\left[f_s(c^0)c^0 \frac{dc^0}{d\xi} \right] + \frac{1}{2}\xi \frac{dc^0}{d\xi} = 0, \qquad \zeta_0^+ < \xi < \infty,$$

$$c^0 = c_F, \qquad \xi = \zeta_0^+, \tag{40}$$

$$c^0 = 1, \qquad \xi \to \infty,$$

$$r^*\frac{d}{d\xi}\left[f_p(c^0) \frac{dc^0}{d\xi} \right] + \frac{1}{2}(\xi - \zeta_0) \frac{dc^0}{d\xi} = 0, \qquad -\infty < \xi < \zeta_0^-$$

$$c^0 = 0, \qquad \xi \to -\infty, \tag{41}$$

$$\frac{dc^0}{d\xi} = 0, \qquad \xi = \zeta_0^-,$$

$$\zeta_0 = 2r^* f_p(c^0) \frac{dc^0}{d\xi}\bigg|_{\xi = \zeta_0^-} - 2\frac{dc^0}{d\xi}\bigg|_{\xi = \zeta_{0+}}. \tag{42}$$

$$c^0\bigg|_{\xi = Z_{G0}^-} = c^0\bigg|_{\xi = Z_{G0}^+} = c_G,$$

$$f_s(c^0)\frac{dc^0}{d\xi}\bigg|_{\xi = Z_{G0}^-} = f_s(c^0)\frac{dc^0}{d\xi}\bigg|_{\xi = Z_{G0}^+},$$

where c^0 indicates the mathematical solution corresponding to the case $\eta = 0$, and $\zeta_0 = \zeta(\eta = 0)$, $Z_{G0} = Z_G(\eta = 0)$. Eq. (41) gives immediately

$$c^0 \equiv 0, \qquad -\infty < \xi < \zeta_0. \tag{44}$$

The solution for c^0, ζ_0, and Z_{G0} may be determined by a "shooting method" using a subroutine which solves, for an arbitrary $\bar{\zeta}$, the "initial value problem" in the space variable ξ of the ordinary differential equation

$$\frac{d}{d\xi}\left[f_s(\bar{c})\bar{c}\frac{d\bar{c}}{d\xi}\right] + \frac{1}{2}\,\xi\,\frac{d\bar{c}}{d\xi} = 0, \qquad \bar{\zeta} < \xi < \infty, \tag{45}$$

with one initial condition obtained from (40-2) and the other obtained by using (44) in (42):

$$\bar{c} = c_F, \qquad d\bar{c}/d\xi = -\tfrac{1}{2}\bar{\zeta}, \qquad \text{at } \xi = \bar{\zeta}. \tag{46}$$

Among all solutions $\bar{\zeta}$, $\bar{c}$, we look for ζ_0 such that $c^0(\infty) \to 1$. Since we anticipate a very sharp concentration gradient across the glass transition concentration in the polymer, this nonlinear initial value problem is integrated numerically with mesh size in ξ according to the square root of the diffusion coefficient factor $f_s(\bar{c})$.

Assuming that the above initial solutions c^0, ζ_0, and Z_{G0} are valid for small $\tau \to 0$, they can be interpreted in terms of the dimensionless space variables x^* and τ (or the physical variables x and t) by means of Eqs. (30), (18), and (19). Thus, the gel/liquid interface $y(t)$ is given, approximately for $t \to 0$, by

$$y(t) \cong H_p\zeta_0\eta = \zeta_0(D_s t)^{1/2}. \tag{47}$$

The glass/gel interface $x_G(t)$ may be computed approximately for $t \to 0$ according to

$$x_G(t) \cong H_p Z_{G0}\eta = Z_{G0}(D_s t)^{1/2}. \tag{48}$$

The concentration profile $c(x, t)$, approximated for $t \to 0$, may be computed from $c^0(\xi)$.

2. *Solution for small η.* For sufficiently small η, $0 < \eta \ll \eta_c$, assume that Eqs. (32) thru (39) may be linearized upon the solution c^0, ζ_0. Eq. (38) in its linearized difference form gives immediately

$$\zeta(\eta) = 2r^* f_p(c^0)\frac{dc^0}{d\xi}\bigg|_{\xi=\zeta_0^-} - 2\frac{dc^0}{d\xi}\bigg|_{\xi=\zeta_0^+} = \zeta_0. \tag{49}$$

To the first order in η, express $c(\xi, \eta) = c^0(\xi) + \eta c^1(\xi)$. The linearized problem in terms of $c^1(\xi)$ becomes:

(i) Diffusion of solvent in polymer.

D.E.:

$$\frac{d}{d\xi}\left[f_s(c^0)\,c^0\frac{dc^1}{d\xi}\right] + \frac{1}{2}\,\xi\,\frac{dc^1}{d\xi} = \frac{1}{2}\,c^1, \qquad \zeta_0^+ < \xi < \infty. \tag{50}$$

B.C.:

$$c^1 = 0,\ \xi = \zeta_0^+ \qquad dc^1/d\xi = 0,\ \xi \to \infty. \tag{51}$$

The solution is

$$c^1(\xi) \equiv 0, \qquad \zeta_0 < \xi < \infty. \tag{52}$$

(*ii*) Diffusion of dissolved polymer in liquid solution, (notice that $f_p(c^0) \equiv 1$).
D.E.:

$$r^* \frac{d^2 c^1}{d\xi^2} + \frac{1}{2} (\xi - \zeta_0) \frac{dc^1}{d\xi} = \frac{1}{2} c^1, \qquad \infty < \xi < \zeta_0^-, \tag{53}$$

B.C.:

$$dc^1/d\xi = R^*, \xi = \zeta_0^-, \qquad c^1 = 0, \xi \to -\infty. \tag{54}$$

The boundary-value problem of Eqs. (53), (54) may be solved numerically to yield $c^1(\xi)$, $-\infty < \xi < \zeta_0^-$.
Consequently, the solution for small η, $0 < \eta \ll \eta_c$ may be approximated by

$$\zeta(\eta) \cong \zeta_0$$

$$c(\xi, \eta) \cong c^0(\xi), \zeta_0^+ < \xi < \infty, \tag{55}$$

$$\cong \eta c^1(\xi), -\infty < \xi < \zeta_0^-$$

where $c^0(\xi)$, $\zeta_0^+ < \xi < \infty$ is obtained from the "initial value problem" given by the Eqs. (45) and (46), and $c^1(\xi)$ is the solution of the boundary value problem given by Eqs. (53) and (54).

5. Asymptotic behavior. It was found that the diffusion in the liquid solution establishes a "steady state" in very short time. Henceforth, the concentration in the liquid solution at the gel/liquid interface, denoted by c_p, remains constant. Also, the flux of the disassociated polymer in the liquid solution reaches the maximum diffusion capability in removing the disassociated polymer molecules from the gel/liquid interface, and it is given by the constant $D_p c_p / B$. Consequently, the free boundary condition, Eq. (28), becomes (assume $f_p(c) \cong 1$)

$$\frac{dy^*}{d\tau} = \frac{r^* c_p}{B^*} - \frac{\partial c}{\partial x^*}\bigg|_{x^* = y^{*+}(\tau)}. \tag{56}$$

Thus, one derives the following asymptotic behaviors:
1. While the glassy phase remains present, and $0 < x_G^*(\tau) \ll 1$, the concentration in the polymer may attain a constant profile that recedes with a constant front velocity U. In order to determine U, one considers the asymptotic behavior of the solution for the diffusion problem defined by Eqs. (20) and (22), for $y^{*+}(\tau) < x^* < \infty$, such that

$$\frac{dy^*}{d\tau} = u(\tau),$$

where $u(\tau) > 0$ and $u(\tau)$ approaches, asymptotically, to U.
Define the moving space coordinate X at $\tau > \tau^* \gg 0$, for some τ^*:

$$X = x^* - y^*(\tau) = x^* - \left\{ y^*(\tau^*) + \int_{\tau^*}^{\tau} u(\tau') \, d\tau' \right\}. \tag{57}$$

In terms of X and τ, Eqs. (20) and (22) become

$$\frac{\partial c}{\partial \tau} - u(\tau) \frac{\partial c}{\partial X} = \frac{\partial}{\partial X} \left[f_s(c) \, c \frac{\partial c}{\partial X} \right],$$

$$c = c_F, \quad \text{at } X = 0,$$
$$c = 1, \quad \text{as } X \to \infty. \tag{58}$$

At steady state, $\partial c/\partial \tau \to 0$ and $u(\tau) \to U$. The first integral of the steady state problem is given by

$$f_s(c)\, c \frac{\partial c}{\partial X} + Uc = U. \tag{59}$$

In particular, at $X = 0$, i.e. $x^* = y^*(\tau)$, $c = c_F$, $f_s(c_F) = 1$; hence

$$\left. \frac{\partial c}{\partial x^*} \right|_{x^* = y^*+(\tau)} = \left. \frac{\partial c}{\partial X} \right|_{X=0} = U \frac{1 - c_F}{c_F}. \tag{60}$$

Substitution of Eq. (60) and $dy^*/d\tau = U$ into Eq. (56), one obtains

$$U = c_F r^* c_p / B^*. \tag{61}$$

The concentration profile in the polymer may also be determined according to

$$\frac{\partial c}{\partial X} = U \frac{1 - c}{c f_s(c)}, X > 0. \tag{62}$$

2. Eventually, the glassy phase will disappear in the polymer, when $x_G^*(\tau) \to 1$. The concentration rapidly approaches c_F uniformly throughout the polymer, and the last term in Eq. (56) becomes negligible. Hence, $dy^*/d\tau \to r^* c_p / B^*$ asymptotically until complete dissolution, $y^* \to 1$.

6. Results for initial swelling. We have investigated three types of polymer dissolution. The concentration dependence factor $f_s(c)$ of the diffusion coefficient of the solvent in the polymer are given, respectively, by
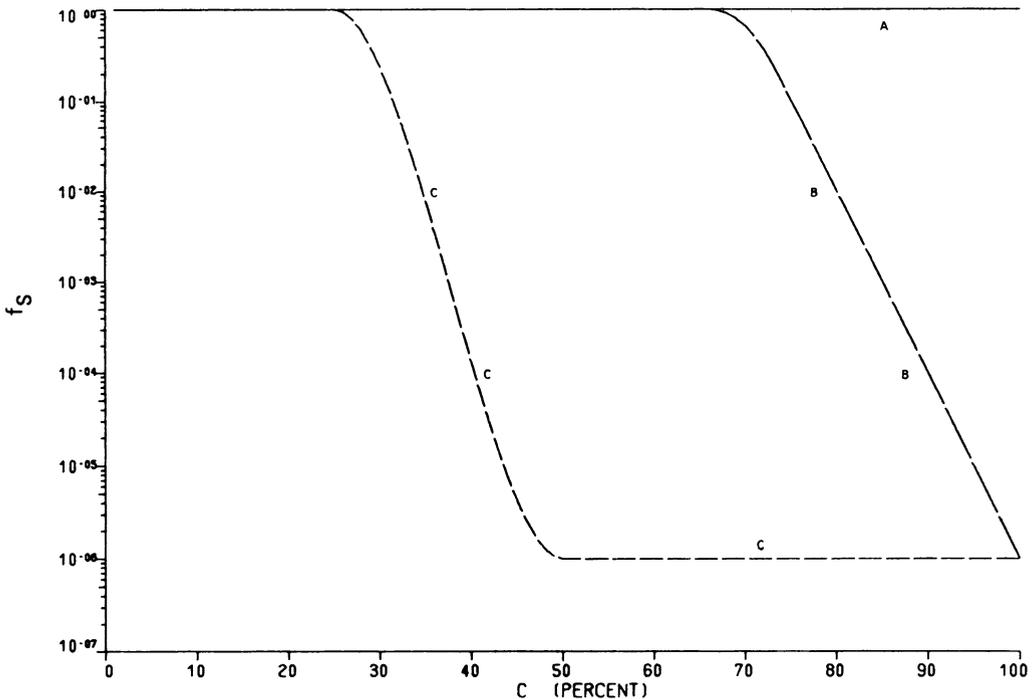
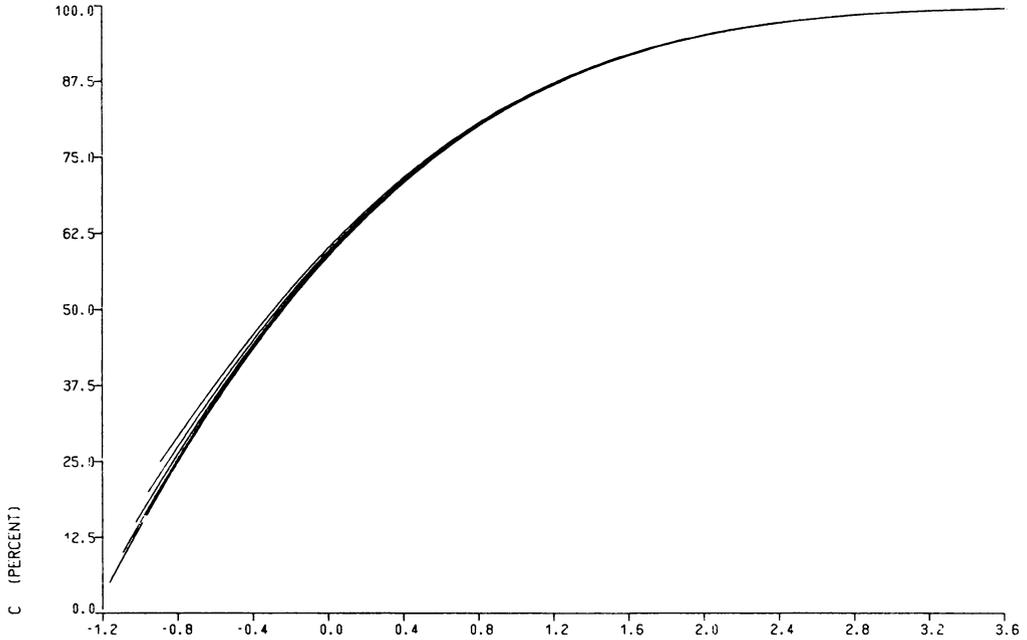FIG. 1. Diffusion coefficient factors for types A, B and C.

FIG. 2. Similarity solutions for type A polymer and CF = .05, (.05), .25.

A) $f_s(c) \equiv 1, 0 < c < 1$. This is dissolution of a rubbery polymer. No glassy phase exists. An example is that of the dissolution of polyisobutylene in mineral oil.

B) $f_s(c)$ may be approximated algebraically by

$$
\begin{aligned}
f_s(c) &= 1, 0 < c < 0.65, \\
&= 10 \exp(-10{,}000 \times (c - 0.65)^3 \times (0.85 - c)), 0.65 < c < 0.75, \\
&= 10 \exp(-20c + 14), 0.75 < c < 1.
\end{aligned} \tag{63}
$$

The glass transition concentration is taken to be $c_G = .75$. This type represents the dissolution of polystyrene in methyl ethyl ketone [7].

C) $f_s(c)$ may be approximated algebraically by

$$
\begin{aligned}
f_s(c) &= 1, 0 < c < 0.25, \\
&= 10 \exp(-96 \times (c - .25)^2 \times (5 - 8c)), 0.25 < c < 0.5, \\
&= 10^{-6}, 0.5 < c < 1.
\end{aligned} \tag{64}
$$

The glass transition concentration is taken to be $c_G = .35$. This type represents the dissolution of polystyrene in amylacetate [7].

The concentration dependence factors $f_s(c)$ of these three types are plotted in Fig. 1 and will be referred to, henceforth as types A, B, and C, respectively.

The practical range of the disassociation concentration c_F is $0 < c_F < .25$. The initial solutions $c^0(\xi)$ for $c_F = .05$, (.05), .25 are shown in Figs. 2, 3, 4 for the types A, B and C, respectively. The effect upon initial swelling due to these three types of polymer dissolution is shown in Fig. 5 for $c_F = .15$. The gel/liquid interface $y(t)$ and the glass/gel transition $x_G(t)$ are proportional to $(D_s t)^{1/2}$ as given by Eqs. (47) and (48), respectively, for small time t. Hence the thickness of the gel layer in the polymer increases, for small time t, according to
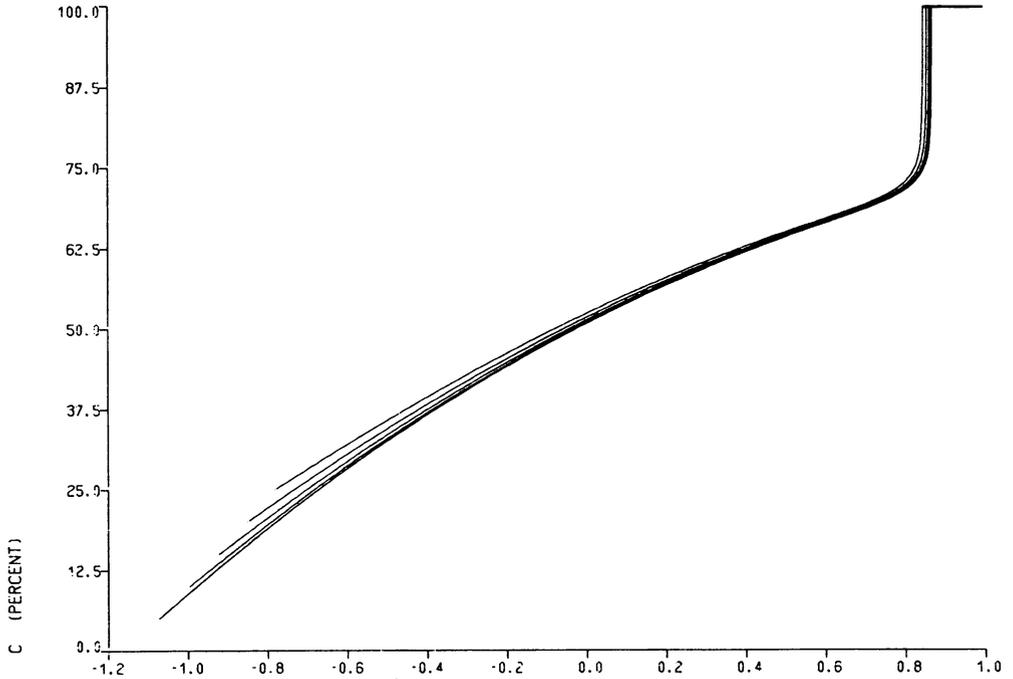
YIH-O TU

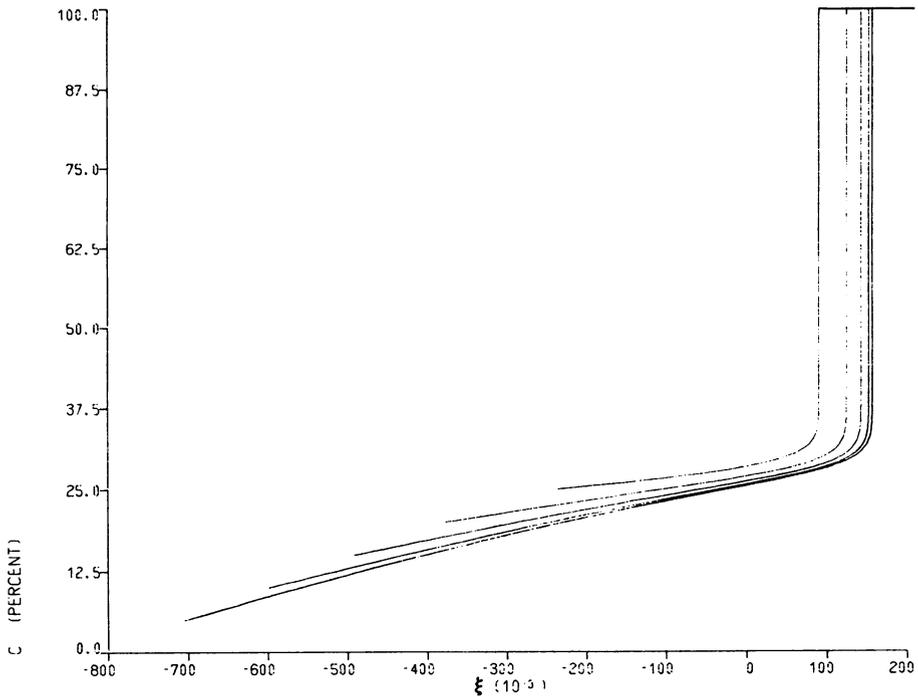FIG. 3. Similarity solutions for type *B* polymer and CF = .05, (.05), .25.

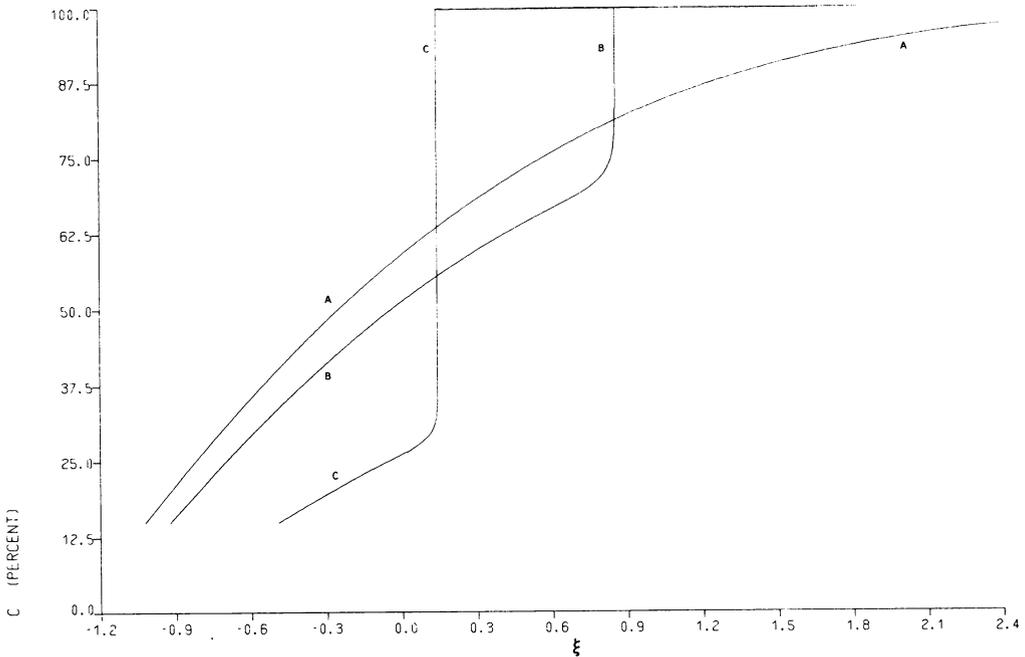FIG. 4. Similarity solutions for type *C* polymer and CF = .05, (.05), .25.

FIG. 5. Similarity solutions for polymer types A, B, C (CF = .15).

$$x_G(t) - y(t) = (Z_{G0} - \zeta_0)(D_s t)^{1/2}. \tag{65}$$

The values of Z_{G0} and ζ_0 are plotted in Fig. 6.

7. Numerical integration of the Stefan problem. The solution for small time derived in Sec. 4 is valid for $0 < \eta \ll \eta_c$. To continue the solution of the Stefan problem, Eqs. (20) thru (29) have to be integrated numerically. Using a technique suggested by Crank [5] and modified by Tadjbakhsh and Liniger [6], the method consists of the following steps:

(i) The moving gel/liquid interface $y^*(\tau)$ is extrapolated to the forward time level by means of an explicit forward difference expression of Eq. (28).

(ii) The differential equations (20) and (23) are first linearized upon the solution at τ and then replaced by the Crank-Nicholson difference operators. By this means, the concentration profiles of the forward time level can be determined algebraically.

(iii) Until the establishment of τ_c, as $\tau \leq \tau_c$ when $c \leq c_F$ at $x^* = y^{*-}(\tau)$, the analysis remains source-limited, and the boundary condition (26) is to be used. Thereafter, $\tau > \tau_c$, and the boundary condition (27) of the flux-limited analysis will be used.

For type A polymer dissolution, no glass transition exists, and no numerical complication was encountered in the calculation. Some results are presented in [3]. However, when the glass transition does exist, as in polymer dissolution of types B and C, we observe, from Figs. 3, 4 and 5, (a) there is a very sharp concentration gradient near the glass transition and (b) there is a very sharp inflection as $c \to 1$ in order to satisfy the condition $\partial c/\partial x^* = 0$ at $x^* = 1$ in Eq. (22). Consequently, very stringent conditions must be imposed on both the mesh size Δx^* and the time step size $\Delta \tau$ in the integration scheme. This in fact constitutes a very sharp boundary layer in which the exact concentration distribution is not of great interest, but for which the rate of motion is important. For this
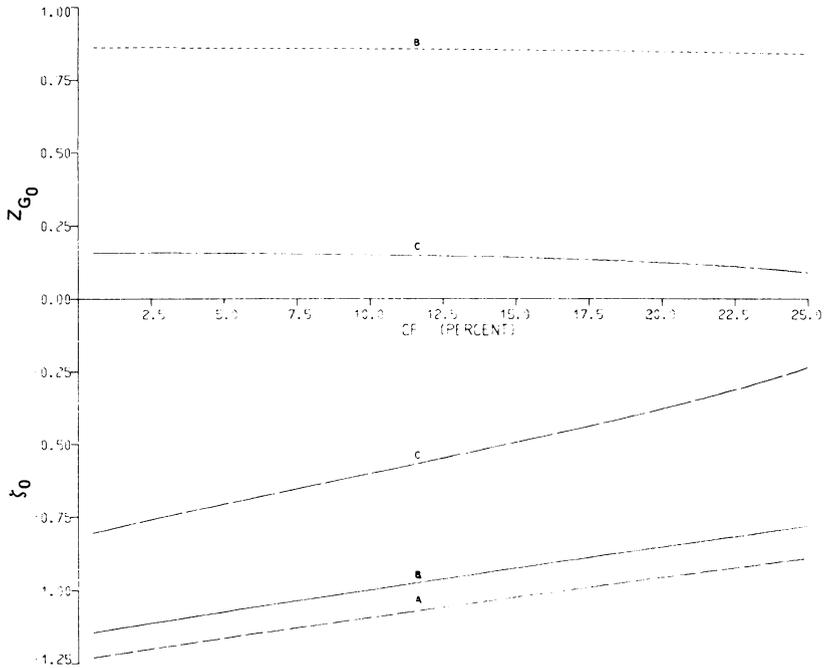
FIG. 6. Gel layers for polymer types A, B, C.

reason and because of the extreme difficulty of carrying out a difference solution, we have turned to a further approximation for the numerical solution.

In order to investigate the swelling and the dissolution of glassy polymer, it is assumed that the concentration profile in the glassy state of the polymer may continue to be approximated by $c^0(\xi)$ derived in Sec. 4. In the gel layer, the concentration is so determined that the concentration is continuous at the glass/gel transition, $x^* = x_G^*(\tau)$, satisfying the first continuity condition in Eqs. (29) throughout the duration of the existence of the glassy phase. Thereafter, the boundary condition $\partial c/\partial x^* = 0$ at $x^* = 1$ in Eq. (22) is again employed after the disappearance of the glassy phase. In view of the fact that the thickness of the gel layer, $x_G^*(\tau) - y^*(\tau)$, varies in τ, the mesh size in the gel layer is allowed to vary accordingly.

8. Results and discussion. Some examples of the numerical results are shown in Figs. 7a,b, 8a,b and 9 for polymer dissolution of the types A, B and C, respectively. Figs. 7a and 8a show the concentration profiles at ten successively selected time steps. Figs. 7b, 8b and 9 show the following quantities as functions of the time τ:

The gel/liquid interface $y^*(\tau)$, marked by YIF,

The glass/gel interface $x_G^*(\tau)$, marked by XGS,

The polymer concentration at the substrate $x^* = 1$, marked by CINF,

The polymer concentration in the liquid solution at the gel/liquid interface $y^*(\tau)$, marked by CPIF,

The rate at which the dissolved polymer is removed at the edge of the boundary layer in the liquid solution, marked by SINK.

The input data are:

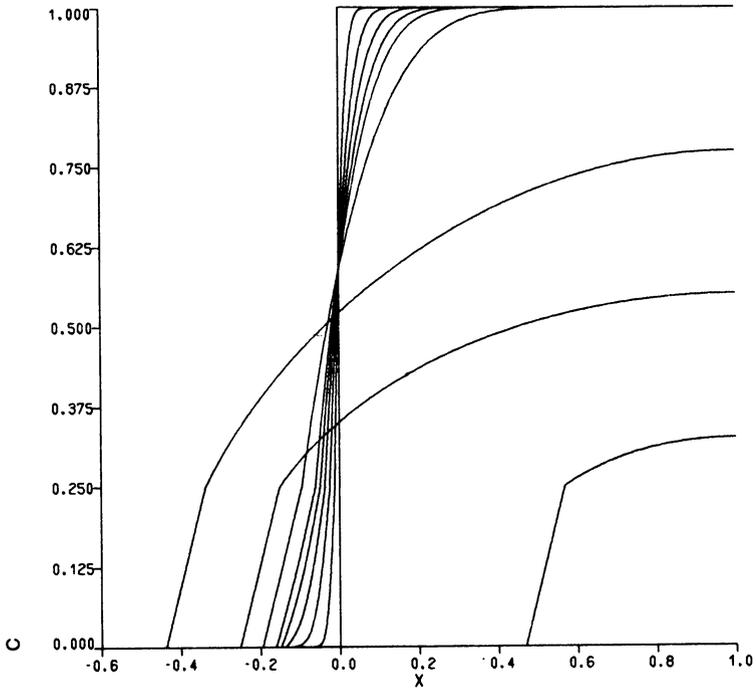Polymer original thickness, $H_p = 1$ cm,

FIG. 7a. Concentration profiles for type A polymer dissolution.

Boundary layer thickness, $B = .1$ cm,
Nominal diffusion coefficient of solvent in polymer, $D_s = 10^{-6}$ cm²/sec,
Nominal diffusion coefficient of dissolved polymer in solution, $D_p = 5 \times 10^{-7}$ cm²/sec,
Disassociation concentration, $c_F = .25$,
Disassociation rate, $R = .1$ cm/sec.
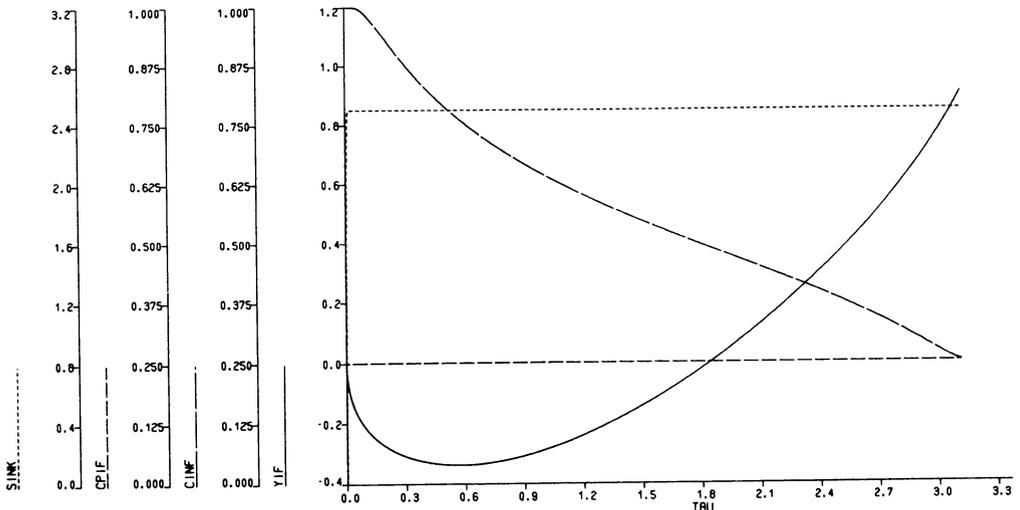By examining Figs. 7, 8 and 9, we observe the following:

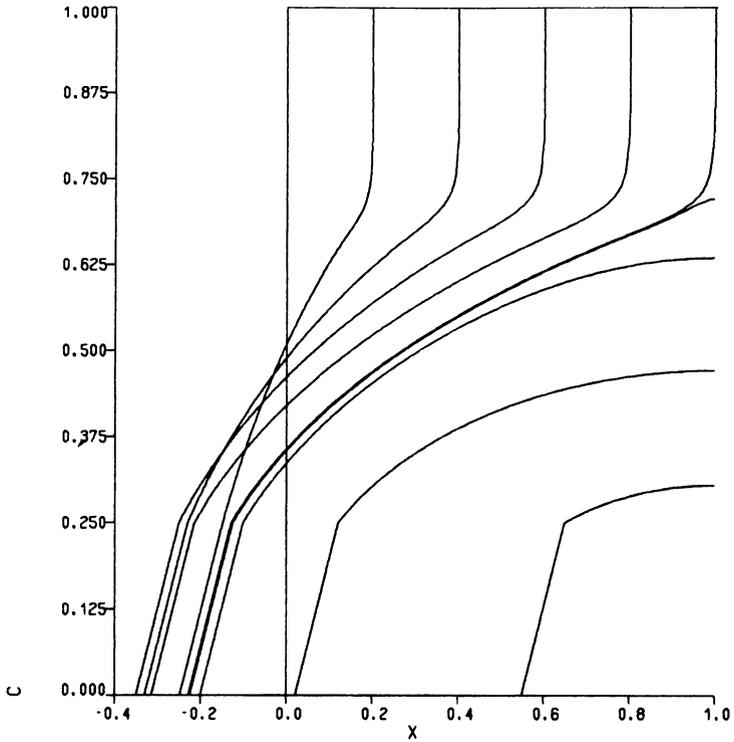FIG. 7b. Times series plots for type A polymer dissolution.

FIG. 8a. Concentration profiles for type *B* polymer dissolution.

1. For type *B* dissolution of glassy polymer, Fig. 8a exhibits the three distinctive regimes, (*i*) the liquid solution, $0 < c < c_F$, (*ii*) the gel layer, $c_F < c < c_G$, and (*iii*) the glassy phase, $c \to 1$, in the concentration profiles of the first five selected time steps, corresponding to XGS = .001, .2, .4, .6, .8 and $\tau < 1.4$ (see Fig. 8b).

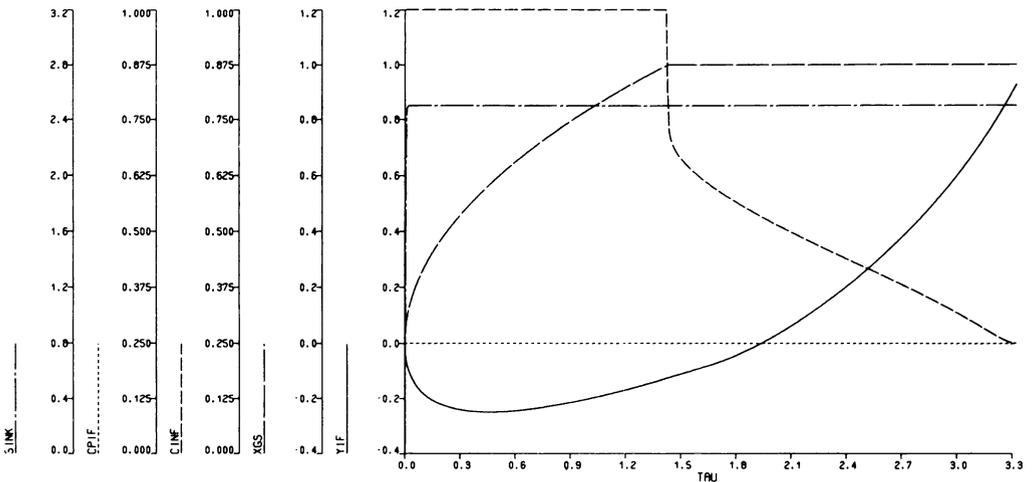2. The concentration profile in the liquid solution reaches a "steady state" near τ =

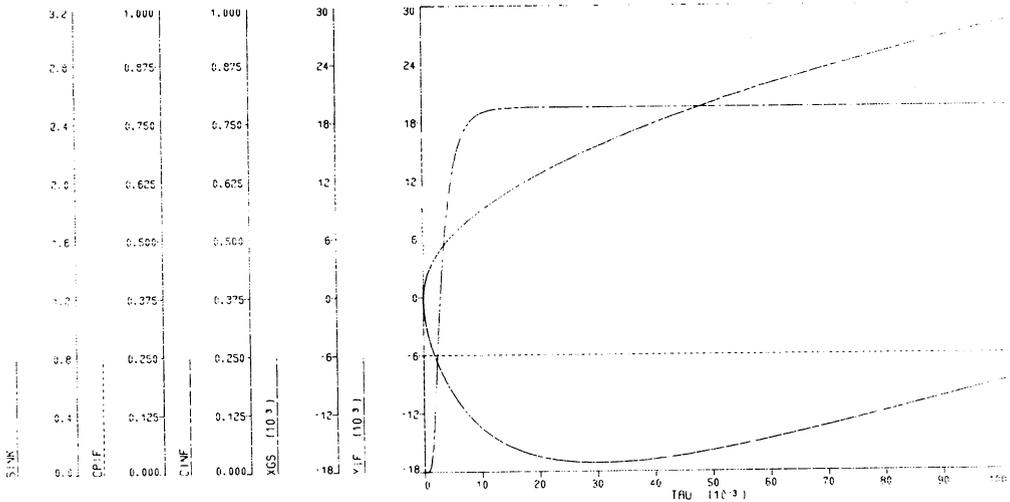FIG. 8b. Time series plots for type *B* polymer dissolution.

FIG. 9. Time series plots for type C polymer dissolution (small time).
$C_F = 0.25$

.015 when the curve SINK approaches the constant value $c_F/B^* = 2.5$ asymptotically (see Fig. 9). For $\tau \gg .015$, the concentration profiles follow the motion of the polymer/solution interface $y^*(\tau)$ without change in shape (see Figs 7a and 8a). Consequently, numerical integration of the concentration profile in the liquid solution is not needed for $\tau \gg .015$.

3. For the type C dissolution, there is very little swelling, $y_{min}^* \simeq -.017$, in Fig. 9 as compared to $y_{min}^* \simeq -.338$ in Fig. 7b of type A and to $y_{min}^* \simeq -.25$ in Fig. 8b of type B. The maximum gel layer thickness is about $(x_G^* - y^*)_{max} \simeq .045$, occuring in relatively short time, $\tau \simeq .1$. Thereafter, the dissolution is described by the following asymptotic behaviors: (i) the concentration in the polymer attains constant profile that recedes with constant front velocity $dy^*/d\tau = dx_G^*/d\tau = .3125$, given by Eq. (61), until the disappearance of the glassy phase in the polymer at about $\tau = 3.3$, and (ii), the dissolution continues at the rate approaching the final asymptotic velocity $dy^*/d\tau = 1.25$, until complete dissolution [8].

A more complete set of results and a description of the physical application will be found in [3]. Physical implications of the asymptotic behavior are discussed in [8].

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