# A Fluorescence Study on Dissolution Of Polymeric Glasses Prepared In Various Molecular Weights

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*Poly(methyl methacrylate) (PMMA) discs in various molecular weights, $M_w$, were prepared by free-radical polymerization of methyl methacrylate (MMA). Pyrene (P) was introduced during polymerization as a fluorescence probe to monitor the gelation and dissolution processes in chloroform vapor and solvent, respectively. In-situ steady state fluorescence (SSF) experiments were performed to monitor vapor uptake and chain desorption processes. Direct illumination of PMMA discs were performed to excite the P molecules embedded inside the PMMA glass. Variation in P intensity, I, was monitored during the swelling of the PMMA material exposed to chloroform vapor. It was observed that PMMA film swells like a crosslinked polymeric gel at early times by obeying the Li-Tanaka equation. Swelling time constants, $\tau_c$, of PMMA discs were measured and found to have a strong correlation with the molecular weight, of PMMA. In a separate experiment, when the PMMA discs were in chloroform, desorption of PMMA chains from glass discs was monitored by observing the change of pyrene fluorescence intensity. A diffusion model with a moving boundary was employed to quantify the fluorescence data observed from dissolving PMMA discs made at various molecular weights. It was observed that desorption coefficient, D, decreased by increasing $M_w$ by obeying the $D \approx M_w^{-1}$ law.*

## INTRODUCTION

Polymer dissolution in a solvent is an important phenomenon in a variety of industrial applications as well as academical understanding. Dissolution phenomenon plays an important role in microlithography where selectively irradiated regions of a photosensitive polymer are dissolved in proper solvents to obtain desired circuit patterns. In microlithography, it is important to design the polymer dissolution conditions in a way that will ensure the dissolution of the degraded/uncrosslinked portions of the pattern with minimal swelling of the unexposed/crosslinked portions. Polymer coatings are used to resist corrosion and contamination. A polymer film can be employed for separation in a variety of membrane applications. The semiconductor industry has an interest in controlling the dissolution rate of resist films. The dissolution of novalak resins in solvents is an important process in many semiconductor applications. Advantages of novalak resins are their nonswelling nature, aqueous-based developability, and etching resistance. In environmental applications, treatment of unsorted plastics for recycling and packaging has improved in the last decade. In control release applications of polymers, a solute is dispersed or molecularly dissolved in the polymer phase. Zeroth-order drug release systems have been designed by rendering the polymer dissolution process as the controlling step in the release phenomenon. In addition, polymer dissolution rate data have been used to determine glass transition temperature and other thermodynamic parameters associated with polymorphic changes. In all these applications, the rate of diffusion of solvents, swelling of polymer, and the mechanisms of dissolution processes are very important. Therefore, the diffusion of solvents in solid polymers has been the subject of numerous theoretical, as well as experimental, investigations in the past two decades. Since the dissolu-

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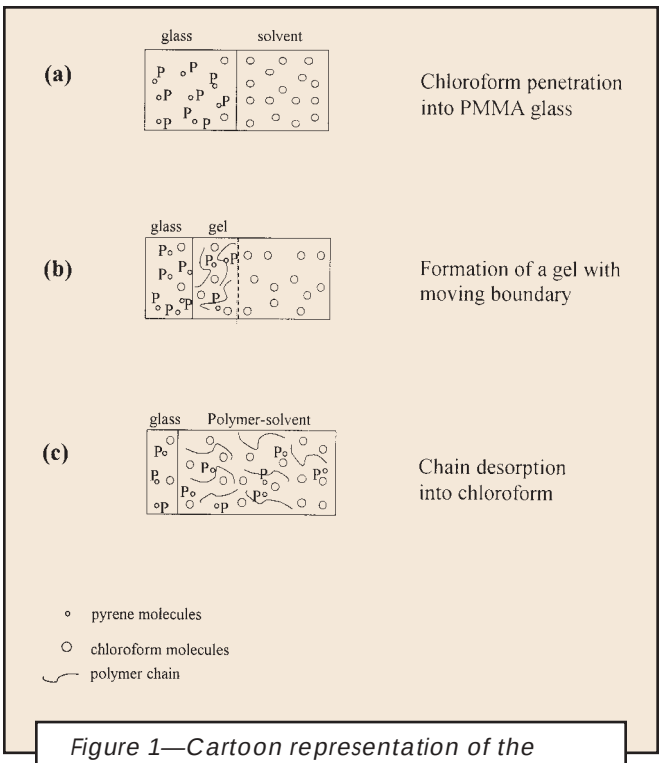


*Figure 1—Cartoon representation of the stages of polymer glass dissolution.*

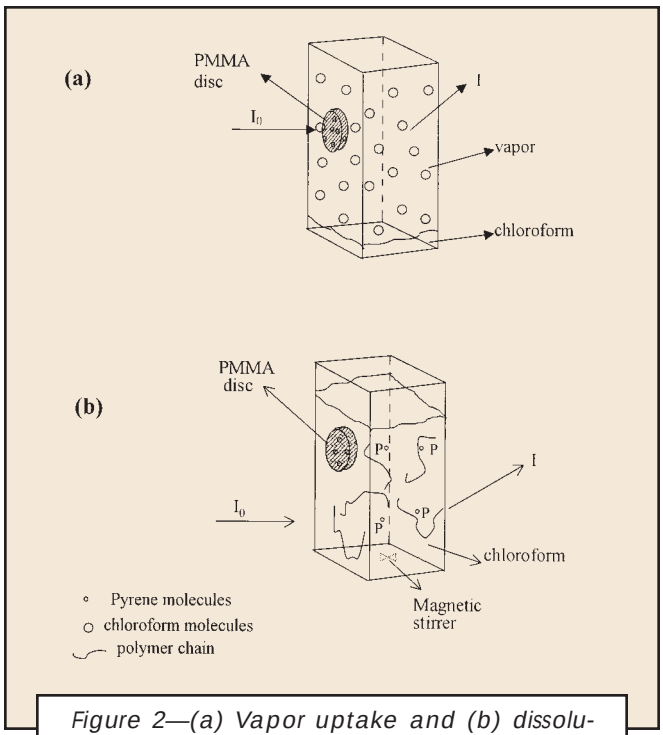


*Figure 2—(a) Vapor uptake and (b) dissolution cells in Perkin-Elmer Lambda 2S spectrophotometer.*

tion of polymer depends on both the extent of swelling as well as the diffusion rate of the solvent, these mechanisms have to be carefully investigated for the practical needs of industry.

Polymer dissolution process from bulk is very different from and more complicated than, small molecule dissolution. The dissolution of small molecules can be explained by simple diffusion laws[1] and a unique diffusion rate. However, polymeric glass dissolves mainly in three different stages: (a) solvent penetration, (b) polymer relaxation and formation of a gel with moving boundary and (c) diffusion of polymer chains into a solvent reservoir. A schematic representation of these three sequential steps for the dissolution of a polymeric glass is presented in *Figure* 1. In the first stage, the penetration distance of solvent molecules mainly depends on free volume, which in turn depends on the flexibility of the chains, backbone, and side groups, as well as the thermal history of the polymer. These first solvent molecules act as a plasticizer, and as a result these regions of the film start to swell. In the second stage, gel layer is created by the relaxing polymer chains. This moving transition layer is composed of both polymer chains and solvent molecules. If the solvent-polymer interractions are more dominant than polymer-polymer interractions, maximum swelling is obtained. This is the case when a good solvent is used during dissolution of a polymeric glass. Here, the advancing boundary is formed. In the last stage, chain disentanglement takes place, then chains separate from the gel and diffuse into the solvent, while the advancing boundary moves across the polymeric glass. The rate of dissolution can be represented by a velocity of solvent penetration, which determines the velocity of the gel front penetrating into the polymeric glass substance. The velocity of dissolution increases with stirrer frequency and decreases with the increase of the chain length due to an increasing entanglement of the polymer chains.

The penetration of solvent molecules into a glassy linear polymeric system does not proceed according to the Fickian diffusion model.[2] Penetration not described by the Fickian model is called anomalous diffusion, where the rate of transport is entirely controlled by polymer relaxation. On the other hand, in gel systems swelling is directly related to the viscoelastic properties. The gel elasticity and the friction between the network and solvent play an important role in the kinetics of gel swelling.[3-4] The elastic and swelling properties of permanent networks can be understood by considering two opposing effects, the osmotic pressure and the restraining force. Usually, the total free energy of a chemically crosslinked network can be separated into two terms: the bulk and the shear energies. The bulk energy of the system is related to the volume change, which is controlled by diffusion. The shear energy keeps the gel in shape by minimizing the nonisotropic deformation. Li and Tanaka[5] have developed a model where the shear modulus plays an important role that keeps gel in a shape due to the coupling of any changes in different directions. This model predicts that the geometry of the gel is an important factor, and that swelling is not just a pure diffusion process like the Fickian diffusion.

Historically, in-situ fluorescence quenching experiments in conjunction with laser interferometry were used to investigate dissolution of PMMA film in various solvents.[6,7] The real-time, nondestructive method for monitoring small molecule diffusion in polymer films

was developed.[8] This method is based on the detection of excited fluorescence molecules desorbing from a polymer film into a solution in which the film is placed. Steady state fluorescence (SSF) studies on dissolution of latex films and PMMA glasses using real-time monitoring of fluorescence intensity have been reported from our laboratory.[9-12] Recently, the fast transient fluorescence (FTRF) method was used to monitor dissolution of polymer glasses.[13,14] The effect of γ-irradiation on latex film dissolution was extensively studied using the SSF method where two different regimes of dissolution coefficients were attributed to two different molecular weight distributions caused by scission and branching of polymer chains when they were irradiated by γ-rays.[15] On the other hand, steady-state fluorescence measurements on the swelling of gels formed by the free radical crosslinking copolymerization (FCC) of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) in solution have been reported.[16] A pyrene (P) derivative was used as a fluorescence probe to monitor swelling, desorption, and drying in real-time during in-situ fluorescence experiments.[17] Recently, the FTRF technique was used for monitoring swelling of PMMA gels in solution.[18] Besides fluorescence, various other techniques have been used to study polymer dissolution, among which FTIR[19] and magnetic resonance[20] (MR) imaging are the most recent. Both techniques were elaborated to investigate entangled polymer dissolution in binary solvent mixtures. More conventional techniques were also applied recently for studying polymer dissolution. The most important ones are forced Rayleigh scattering,[21] potentiometric titration, isothermal titration calorimetry, and light scattering.[22]

In this work, two types of fluorescence experiments were designed to study and understand the mechanism of polymer dissolution processes. In order to do that, polymeric glasses formed from linear PMMA chains in various molecular weights were subjected to chloroform vapor to study swelling mechanism prior to dissolution. Our aim was to slow down the early stages (a and b) of polymer dissolution by exposing the polymeric glass to organic vapor to investigate the details of gel formation mechanism. In-situ SSF experiments were performed to observe the vapor uptake processes by the polymeric glass. Direct illumination of the disc-shaped glasses were performed to excite the pyrene molecules embedded inside the polymeric glasses prepared in various molecular weights of PMMA chains. Variation of P intensity against time was monitored during swelling of PMMA material. It was observed that at early times PMMA swells like a polymeric gel, which obeyed the Li-Tanaka model. Swelling time constants, $\tau_c$, were measured and were found to have a strong correlation with the molecular weight of PMMA. In the second type of experiment, the SSF technique was used to study the dissolution of PMMA glasses. Chloroform was used as a dissolution agent and in-situ SSF experiments were performed to monitor dissolution processes. Dissolution experiments were carried out by illuminating the chloroform reservoir and an increase in P intensity, I, was observed. Desorption coefficients, D, were measured and found to be inversely proportional to the molecular weight of polymer chains.

## THEORETICAL CONSIDERATIONS

### Kinetics of Swelling

The relative changes of diameter and thickness of disc-shaped gels are the same, indicating that the gel-swelling processes are not pure diffusional processes. In fact, the equality of the relative changes of diameter and thickness comes from the nonzero shear modulus, μ, which results. The change of total shear energy in response to any small change in shape that maintains a constant volume element within the gel should be zero. The high friction coefficient, *f*, between the network and the solvent overdamps the motion of the network, resulting in a diffusion-like relaxation. The equation of the motion of a network element during the swelling can be given by[5]

$$\frac{\partial \vec{u}}{\partial t} = D_c \vec{\nabla}^2 \vec{u} \qquad (1)$$

where $\vec{u}$ is the displacement vector measured from the final equilibrium location after the gel is fully swollen ($u=0$ at $t=\infty$). $D_c=(K+4\mu/3)/f$ is the collective diffusion coefficient. Here t denotes the time and K is the bulk modulus. Equation (1) has been used with some success

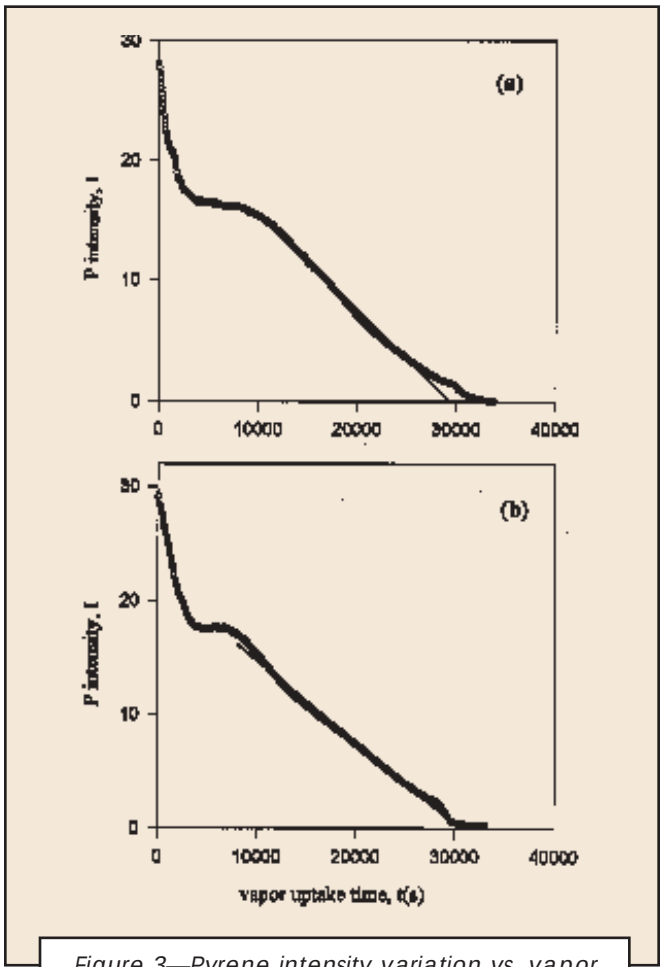


*Figure 3—Pyrene intensity variation vs. vapor uptake time during swelling of PMMA glass for (a) 6.4, (b) 10.6 × $10^5$ $gmol^{-1}$ molecular weight samples.*

to study the swelling of gels.[3] However, the studies did not properly treat the shear deformation that occurs within a gel during swelling and, hence, cannot explain, for example, the isotropic swelling of a cylindrical gel. This shortcoming was due to shear modulus of the network keeping the system in shape by minimizing the nonisotropic deformation. For a disc-shaped gel, any change in diameter is coupled to a change in thickness. The total energy of a gel can be separated into a bulk energy and a shear energy. The bulk energy is related to the volume change, which is controlled by diffusion. The shear energy, $F_{sh}$, on the other hand, can be minimized instantly by readjusting the shape of the gel.[5]

$$\partial F_{sh} = 0 \tag{2}$$

Each small diffusion process determined by equation (1) must couple to a small shear process given by equation (2) producing the following relation for a disc-shaped gel:

$$\frac{u_r(r,t)}{r} = \frac{u_z(a,t)}{a} \tag{3}$$

where r is the radius and a is the half thickness of the disc gel. Equation (3) indicates that the relative change in the shape of the gel is isotropic, i.e., the swelling rates of a disc in the axial (z) and radial (r) directions are the same.

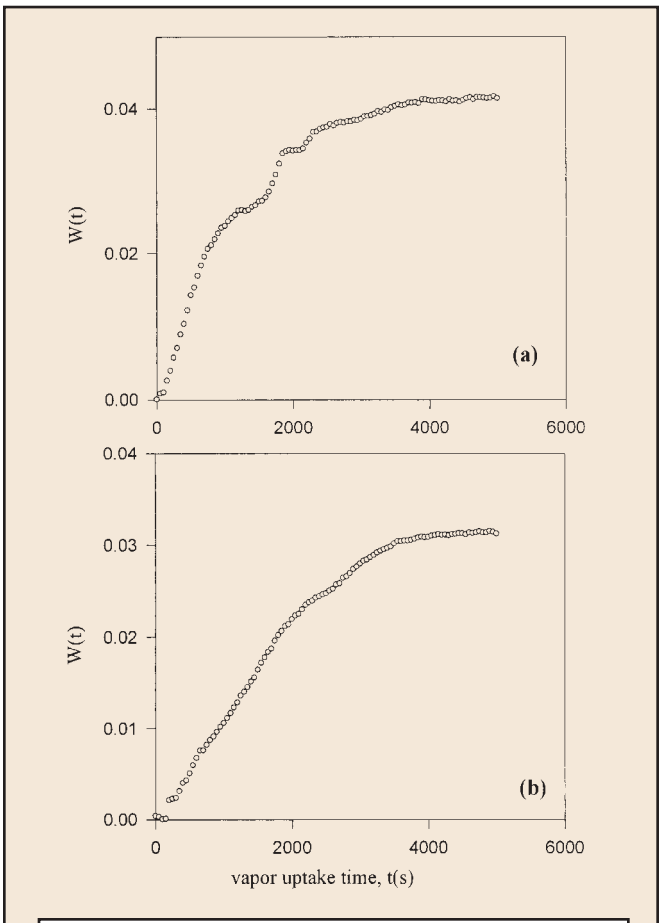


*Figure 4—Swelling curves of (a) 6.4 × 10⁵, (b) 10.6 × 10⁵ molecular weight PMMA samples.*

Simultaneous solution of equations (1) and (2) produces the following equations for the swelling of a gel disc in axial and radial directions:

$$u_z(z,t) = u_z(z,\infty)\sum_n B_n \exp(-t/\tau_n) \tag{4a}$$

$$u_r(r,t) = u_r(r,\infty)\sum_n B_n \exp(-t/\tau_n) \tag{4b}$$

where the axial and the radial displacements are expressed as series of components, each of them decaying exponentially with a time constant, $\tau_n$. The first terms of the expressions are dominant at large t, that is at the last stage of swelling. Equation (4) can also be written in terms of vapor and solvent uptakes W and $W_\infty$ at time t and at equilibrium, respectively, as follows:

$$\frac{W_\infty - W}{W_\infty} = \sum_{n=1}^{\infty} B_n \exp(-t/\tau_n) \tag{5}$$

In the limit of large t, or if $\tau_c$ is much larger than the rest of $\tau_n$, all higher terms ($n \geq 2$) in equation (5) can be omitted and the swelling kinetics are given by the following relation:

$$\left(1 - \frac{W}{W_\infty}\right) = B_1 \exp(-t/\tau_c) \tag{6}$$

It should be noted from equation (5) that $\Sigma B_n = 1$, therefore, $B_1$ should be less than 1. $B_1$ is related to the ratio of the shear modulus, μ, and longitudinal osmotic modulus, $M = (K + 4\mu/3)$. Hence, once the value of $B_1$ is obtained, one can determine the value of $R = \mu/M$. Here, we have to note that equation (6) can also be obtained by using the theoretical results[12] in the case of $R \rightarrow 3/4$ ($\mu/K \rightarrow \infty$), time constant $\tau_c \approx (3/4\text{-}R)^{-1}$ goes to infinity and all $B_n$s go to zero except $B_1$, which goes to unity. The dependence of $B_1$ on R for a disc can be found in the literature.[5] Time contant, $\tau_c$, is related to the collective diffusion coefficient $D_c$ at the surface of gel disc by

$$D_c = \frac{3a^2}{\tau_c \alpha_1^2} \tag{7}$$

where $\alpha_1$ is a function of R only and is given in the literature,[5] and a represents the half thickness of the gel in the final equilibrium state. Hence, $D_c$ can be calculated.

## Fluorescence Quenching

The theories of fluorescence quenching in glassy and viscous environments are well established.[23] A chromophore P in its ground state is converted to an electronically excited state P* by absorption of a photon $h\nu_{ex}$, i.e.,

$$P + h\nu_{ex} \rightarrow P^*$$

The excited state P* decays to P by producing a fluorescence with a life time $\tau_0$, through

$$P^* \rightarrow P + h\nu_{fl}$$

or the excited state P*, can be quenched by collision with quencher Q at a rate k, described by

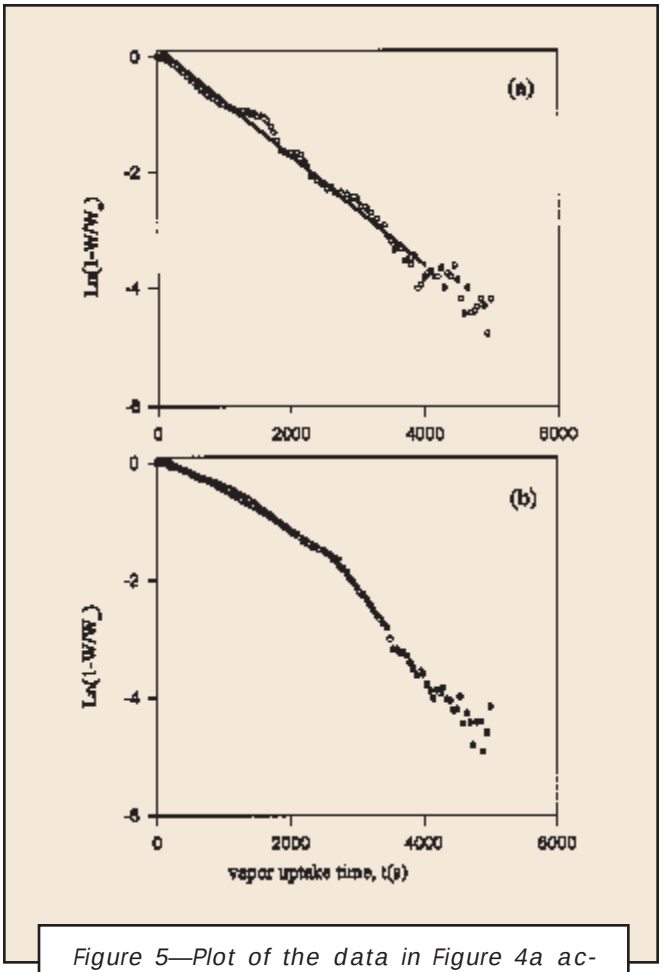


*Figure 5—Plot of the data in Figure 4a according to equation (14) for (a) 6.4 × 10^5, (b) 10.6 × 10^5 molecular weight PMMA samples.*

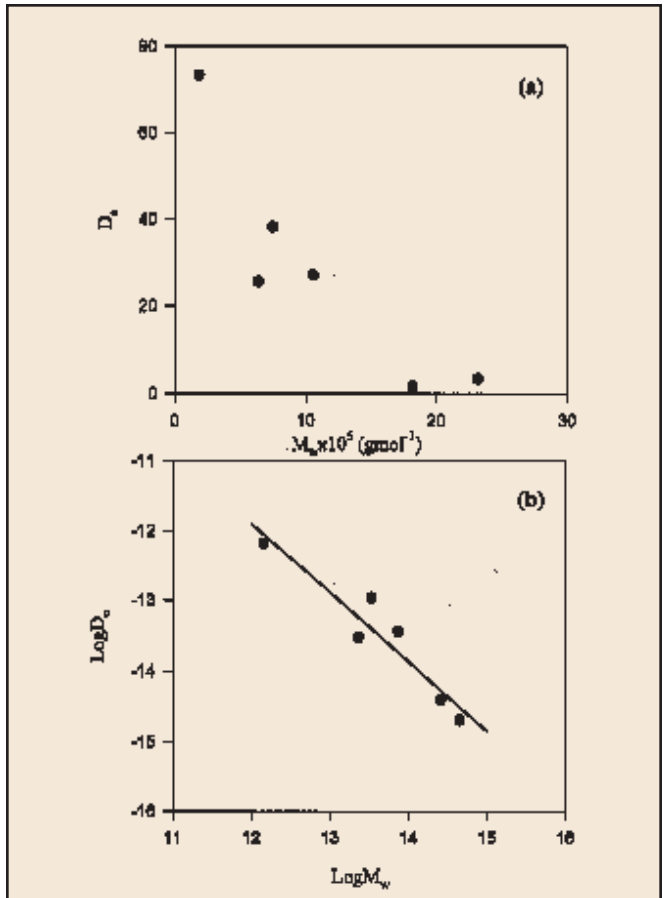


*Figure 6—(a) Plot of collective diffusion coefficient Dc vs. molecular weight $M_w$, (b) log-log plot of the data in (a). The slope of the linear relation produces the value of –0.98.*

$$P^* + Q \rightarrow P + Q$$

and even in the absence of excitation, P and Q are assumed capable of reacting to form a complex PQ with a rate $k_f$

$$P + Q \rightarrow PQ$$
$$\leftarrow$$

and PQ decays with a rate $k_b$.

The related rate equations governing the above processes are solved by neglecting diffusion and the following equation, which is known as the Stern-Volmer law in the absence of diffusion control, is obtained[19]:

$$\frac{I_0}{I} = 1 + (k\tau_0 + K)[Q] + k\tau_0 K[Q]^2 \quad (8)$$

Here, I and $I_0$ represent the intensities of chromophore with and without quencher and $K=k_f/k_b$.

Stern-Volmer law in the presence of diffusion at infinite concentration can be obtained by solving the many particle diffusion equation with reactive terms, for the probability densities of P* and Q and equation (8) are reproduced[23] with

$$k = \frac{4\pi N_A D_m pR}{1000}(M^{-1}s^{-1}) \quad (9)$$

where, $D_m=D_P+D_Q$ is the sum of the mutual diffusion coefficients of chromophore (P) and quencher (Q), respectively; $R=R_p+R_Q$ is the sum of their interaction radii; $N_A$ is the Avagadro's number; and p is a factor describing the reaction probability per collision. Here, $D_P$ and $D_Q$ are the mutual diffusion coefficients and $R_P$ and $R_Q$ are the radii of the P and Q molecules, respectively. At finite concentration, i.e., quenchers are present in sufficiently large concentrations (typically [Q]=0.1 M while $[P]=10^{-4}$ M) so that the complex formation can be neglected and equation (8) reduces to the form

$$\frac{I_0}{I} = 1 + k\tau_0[Q] \quad (10)$$

## EXPERIMENTAL

The monomers MMA (Merck) were freed from inhibitor by shaking with a 1.79 M aqueous KOH solution, washing with water, and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The initiator, 2,2'-azobisisobutyrronitrile (AIBN; Merck) was recrystallized twice from methanol and the solvent chloroform (Merck) was used as it was

**Table 1—Experimentally Measured Parameters of the Given PMMA Glasses**

| $M_w \times 10^5$ (g.mol$^{-1}$) | B1 | $\tau c \times 10^3$(s) | $Dc \times 10^{-5}$ (cm$^2$.s$^{-1}$) | $D \times 10^{-6}$ (cm$^2$.s$^{-1}$) |
|---|---|---|---|---|
| 23.0 | 1.0 | 20.1 | 3.2 | 4.4 |
| 18.0 | 0.95 | 3.5 | 1.5 | 5.0 |
| 10.5 | 0.91 | 6.1 | 26.9 | 11.0 |
| 7.5 | 1.0 | 0.9 | 38.1 | 12.0 |
| 6.5 | 1.0 | 1.8 | 25.5 | 14.0 |
| 2.0 | 1.0 | 0.4 | 73.3 | 26.6 |

received. The radical polymerization of MMA was performed in bulk in the presence of AIBN as an initiator. Six different amounts of AIBN were used to prepare six PMMA glasses in different molecular weights. AIBN and P ($4 \times 10^{-4}$ M) were dissolved in MMA and this solution was transformed into a round glass tube with a 10 mm internal diameter. Before polymerization, each solution was deoxygenated by bubbling nitrogen for 10 min. Radical polymerization of the MMA was performed at 65 ± 3°C. After polymerization was completed, the tubes were broken. Disc-shaped samples (approximately 0.2 cm) were cut for the vapor uptake and dissolution experiments. Molecular weights, $M_w$, listed in *Table* 1, were determined with size exclusion chromatography (Waters, model M-6000A) equipped with a refractive index detector using two polystyrene gel colons (500; 10,000 Å) at a flow rate of 1.0 ml/min in THF at 40°C and using polystyrene standards.

In-situ SSF experiments were performed using a Perkin-Elmer LS-50 spectrophotometer. All measurements were made at a 90° position and the slit widths were kept at 10 nm. Vapor uptake (swelling) experiments were performed in a 1 × 1 cm quartz cell, which was placed in the spectrofluorimeter. The fluorescence emission was monitored so that PMMA samples were illuminated by the excitation light. Disc-shaped PMMA glasses were placed at one side of a quartz cell with chloroform at the bottom and the sample was then illuminated with 345 nm excitation light. The pyrene fluorescence intensity, I, was monitored during the swelling of PMMA glass in chloroform vapor at 375 nm using the "time drive" mode of the spectrophotometer. Emission of P was recorded continuously at 375 nm as a function of time. The cell and the sample positions are presented in *Figure* 2a during swelling of PMMA glass in chloroform vapor.

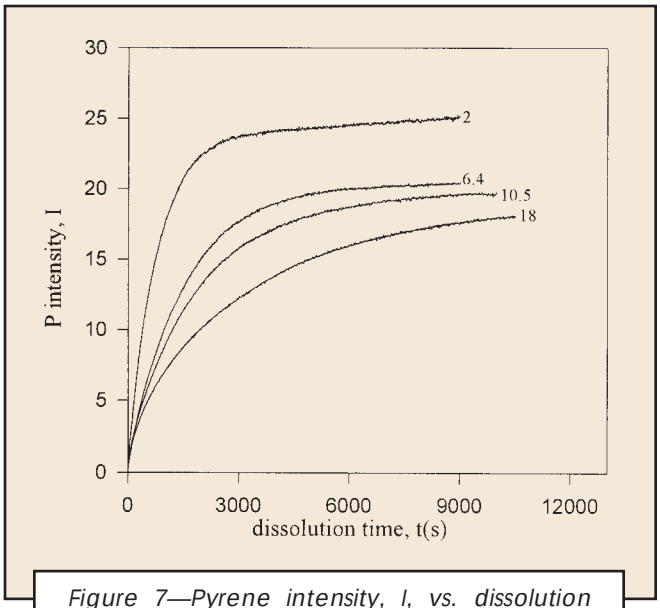


*Figure 7—Pyrene intensity, I, vs. dissolution time. Number on each curve indicates the molecular weight of PMMA samples, $M_w$, in gmol$^{-1}$. The cell was illuminated at 345 nm during dissolution.*

Dissolution experiments were performed in a 1 × 1 cm quartz cell, equipped with a magnetic stirrer that was placed in the LS-50 Perkin-Elmer spectrophotometer. Fluorescence emission was monitored at a 90° angle so that the film samples were not illuminated by the excitation light. Disc-shaped PMMA samples were attached at one side of a quartz cell filled with chloroform. The cell was then illuminated with 345 nm excitation light. The pyrene fluorescence intensity, I, was monitored during the dissolution process at 375 nm using the ''time drive'' mode of the spectrophotometer. Emission of P was recorded continuously at 375 nm as a function of time until there was no observable change in intensity. The dissolution cell and the sample position are presented in *Figure* 2b. The polymer-solvent mixture was stirred with a magnetic stirrer during the dissolution process to remove the gel layer.

## RESULTS AND DISCUSSION

The plot of P intensity, I, vs. vapor uptake time, t, for the PMMA disc with 6.4 and 10.6 × $10^5$ gmol$^{-1}$ molecular weights are presented in *Figure* 3a and b, respectively. It is seen that at early times of vapor uptake, I intensity drops exponentially and reaches a plateau at later times. Then, I intensity decreases linearly after a certain critical time, representing viscous flow. It is observed by the naked eye that at early times glassy discs swell until they start to flow.

### Swelling

Exponential decrease in I at early times most probably results from the quenching of excited pyrenes by the penetration of chloroform molecules into the swelling PMMA disc. In order to quantify the behavior of I at early times, equation (10) can be written as follows:

$$I = I_0(1 + k\tau_0[W])^{-1} \quad (11)$$

where $I_0$ and $\tau_0$ are the intensity and lifetime of P with no chloroform around, k is the quenching rate constant, and [W] is the concentration of chloroform vapor. For low quenching efficiency, where $\tau_0 k[W] << 1$, equation (11) becomes

$$I \approx I_0(1 - \tau_0 k[W]) \quad (12)$$

If equation (12) is integrated over the differential volume, dv, of the gel from its initial to final thicknesses, the following relation can be obtained for the vapor uptake as[24]

$$W = (1 - I/I_0)\frac{v}{k\tau_0} \quad (13)$$

Here, v represents the swollen volume of the PMMA disc, which can be measured experimentally. The quenching rate constant, k, and $\tau_0$ were obtained from separate measurements. The plots of the vapor uptake curves for the PMMA samples shown in *Figure* 3a and b are presented in *Figure* 4a and b, respectively, which are typical uptake curves of the Li-Tanaka model given in equation (6). The logarithmic form of the data in *Figure* 4 are fitted to the following relation produced from equation (6):

$$\mathrm{Ln}(1 - \frac{W}{W_\infty}) = \mathrm{Ln}B_1 - \frac{t}{\tau_c} \quad (14)$$

The fits are presented in *Figure* 5a and b for the disc samples with 6.4 and 10.6 × $10^5$ $gmol^{-1}$ molecular weights. The slope and the intercept of the curve in *Figure* 5a produce $\tau_c$ and $B_1$ values, respectively, which are listed in *Table* 1 together with the other findings. It is seen in *Table* 1 that as $M_w$ of the PMMA is increased, $\tau_c$ increases indicating slower penetration of chloroform molecules into the higher molecular weight PMMA glasses.

From $B_1$ values one can obtain $\alpha_1$ values,[5] and then from equation (7), $D_c$ values were produced and are plotted in *Figure* 6a against molecular weight of PMMA. The molecular weight dependence of $D_c$ in *Figure* 6a immediately predicts that linear, entangled PMMA chains form a network very similarly to the crosslinked gel, and during vapor uptake, PMMA discs behave similar to the swelling of crosslinked gel.[24] In other words, the effect of molecular weight in linear polymeric material is similar to the effect of a crosslinker agent in the crosslinked gel. In both cases, increasing either the $M_w$ or crosslinker content decreases the $D_c$ values. In a linear polymeric system, entanglement points behave similarly to the crosslinked points in the crosslinked gel, both of which possess equivalent swelling behaviors. Here, longer PMMA chains form a quite dense network where entanglement points move much slower than they move in low molecular weight PMMA discs.

In order to support these speculations, the relation between $D_c$ and $M_w$ has to be investigated. The slope of the $LogD_c$ vs. $LogM_w$ plot in *Figure* 6b gives 0.98 which offers us the following relation:

$$D_c \approx M_w^{-1} \quad (15)$$

Equation (15) can be satisfied when a polymer chain reptates in an entangled polymeric system.[25] Here one may conclude that in a swollen polymeric glass, the entangled network swells like a crosslinked network where chains can still reptate according to de Gennes' predictions.

## Dissolution

Pyrenes in polymer-solvent mixture in the fluorescence cell were excited at 345 nm during dissolution experiments and variation in P intensity, I was monitored with the "time drive" mode of the spectrophotometer. P intensities are plotted in *Figure* 7 as a function of dissolution time, t, for the PMMA discs for different molecular weight disc samples. It is seen that as dissolution time is increased, continuous increase in I is observed for all PMMA samples. Here, our aim is to interpret the increase in I which is proportional to the number of polymer chains desorbing from PMMA discs during dissolution. In *Figure* 7, it is seen that the rate of increase in I is varied depending on the molecular weight of PMMA chains.

Various mechanism and mathematical models were considered for the polymer dissolution.[26-30] Tu and Quano[26] proposed a model which included polymer diffusion in a liquid layer adjacent to the polymer and movement of the liquid-polymer boundary. The key parameter for this model was the polymer disassociation rate, defined as the rate at which polymer chains desorb from the gel interface. Lee and Peppas[27] extended this model for the situation of polymer dissolution rate where gel thickness was found to be proportional to $(time)^{1/2}$. Later Peppas et al. studied the dissolution of rubbery polymers in terms of disentanglement[28] and

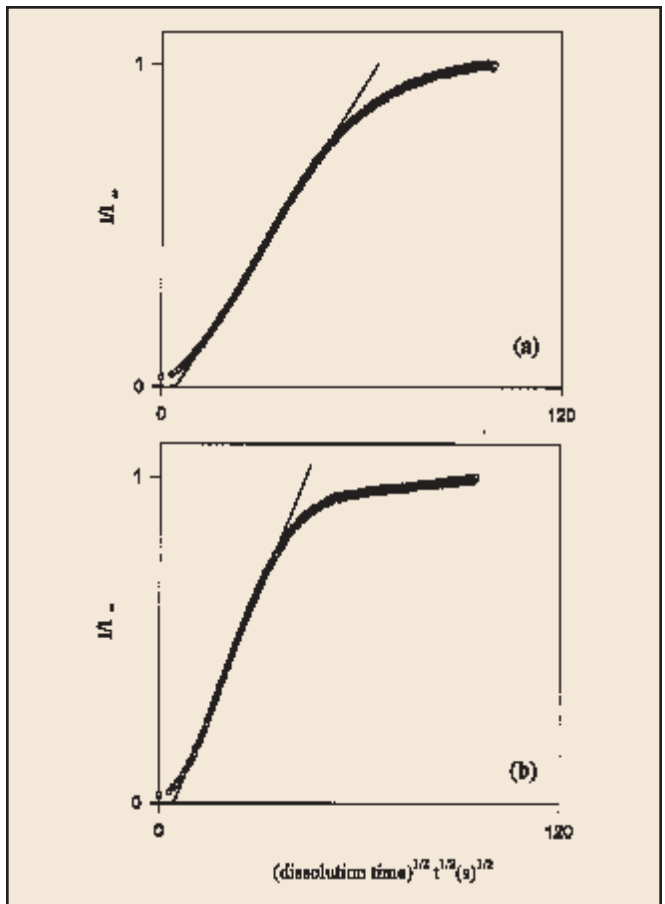


*Figure 8— Plots of I vs. $t^{1/2}$ for PMMA samples of molecular weight (a) 10.5, (b) 2.0 × $10^5$ $gmol^{-1}$, where t is the dissolution time. Data is fitted to equation (17) to produce desorption coefficients, D.*

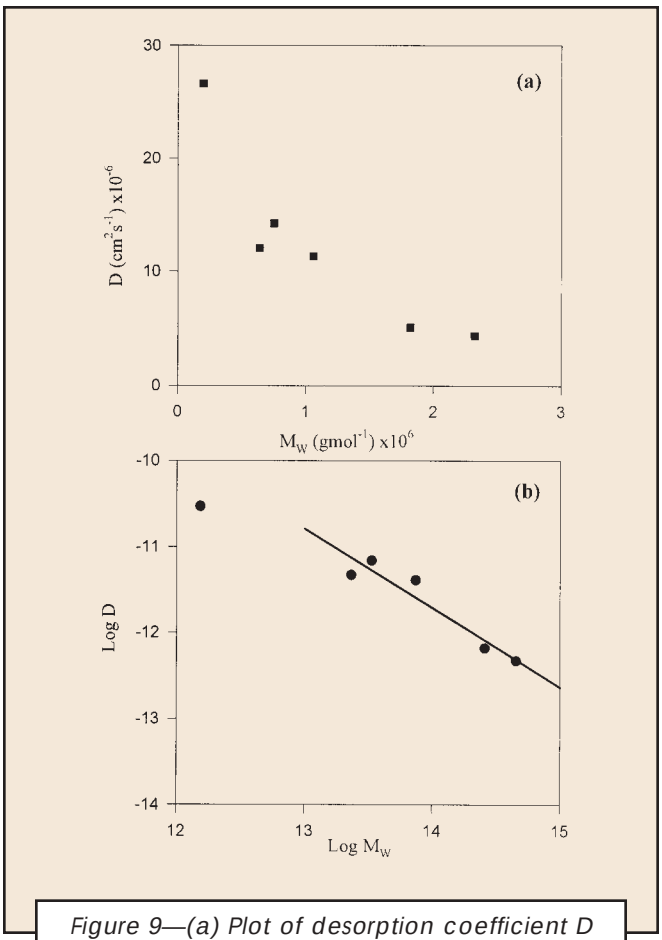


*Figure 9—(a) Plot of desorption coefficient D versus $M_W$. (b) Log-log plot of D vs. $M_w$. The slope of the linear relation produces the value of –0.92.*

reptation,[29] and showed that the dissolution phenomenon can be either disentanglement- or diffusion-controlled depending on the polymer molecular weight. A relaxation-controlled model was proposed by de Gennes and Brochard[30] where, after a swelling gel layer was formed, desorption of polymer from the swollen bulk was governed by the relaxation rate of the polymer stress. This rate was found to be of the same order of magnitude as the reptation time. The dependencies of the radius of gyration and the reptation time on polymer molecular weight and concentration were studied using a scaling law,[30] based on the reptation model. Vrentas[31] proposed a mathematical model for solvent dissolution of glassy polymers and calculated the dissolution curves, half-times, and pseudointerface positions at various times. The thermodynamics of dissolution of polymer glasses have been recently studied to interpret some experimental results obtained by calorimetric technique during vapor sorption.[32]

In this article, we considered a model in which diffusion occurs in two distinct regions separated by a moving interface.[1] The moving interface can be marked by a discontinuous change in concentration as in the absorption by a liquid of a single component from a mixture of gases or by a discontinuity in the gradient of concentration as in the progressive freezing of a liquid. The motion of the interface relative to the two regions it separates may be caused by disappearance of matter at the interface in one or both regions, which results in a bodily movement of the matter in one or both regions relative to the interface. Discontinuities have been observed in several practical systems; for instance, when two metals interdiffuse.[1] The sharp advancing boundary is well known in many polymer-solvent systems, which is considered a discontinuity for some purposes. When the diffusion coefficient is discontinuous at a concentration, c, that is, the diffusion coefficient is zero below c and constant and finite above c, then the total amount, $M_t$, of diffusing substance desorbed from unit area of a plane sheet of thickness, d, at time, t, is given by the following relation:

$$\frac{M_t}{M_\infty} = 2\left(\frac{D}{\pi d^2}\right)^{1/2} t^{1/2} \qquad (16)$$

where D is the constant desorption coefficient at concentration $c_1$. Here, $M_\infty = c_1 d$ is the equilibrium value of $M_t$. If one assumes that the diffusion coefficient of polymer chains in glass is negligible when compared to the desorbing coefficient, D, of polymer chains into solvent, then equation (16) can be written to employ our fluorescence data as follows:

$$\frac{I}{I_\infty} = 2\left(\frac{D}{\pi d^2}\right)^{1/2} t^{1/2} \qquad (17)$$

Here, it is assumed that $M_t$ is proportional to pyrene intensity, I, at time, t.

Plots of I versus $t^{1/2}$ are presented in *Figure* 8a and b for the PMMA discs with 10.6 and $2.0 \times 10^5$ gmol$^{-1}$ molecular weights, respectively. The desorption coefficient, D is obtained from the slope of the linear relation in *Figure* 8 using equation (17) and are listed in *Table* 1 together with the others. It is observed that D values have a strong correlation with the $M_w$ of PMMA samples. *Figure* 9a presents the relation between D and $M_w$ values, where D decreases as $M_w$ is increased, as expected. However, one would like to see the relation between D and $M_w$. The LogD-Log$M_w$ plot in *Figure* 9b presents the linear relation except for one point at low molecular weight. The slope of the linear relation in *Figure* 9b produces –0.92, which suggests the following relation:

$$D \approx M_w^{-1} \qquad (18)$$

between D and $M_w$ values. Equation (18) predicts that polymer chains reptate according to de Gennes' law[21] while they desorp from the glass disc. In other words, when the reptating polymer chain completely escapes from its tube, it immediately drops into the chloroform reservoir.

## CONCLUSION

This article introduces a new technique and model to elaborate on the dissolution mechanism in polymeric

glasses. In fact, even though the dissolution of polymer has been extensively studied for many years in various industrial applications, the mechanism of polymer dissolution is still not well understood. This work has been designed to create a bridge between mathematical modelling and industrial needs by investigating the dissolution process at the molecular level.

In summary, this work introduces the fluorescence technique to present the relation between molecular weight, $M_w$, with the $D_c$ and D during swelling and dissolution of polymeric glasses, respectively. It was observed that an entangled polymeric system behaved similar to a crosslinked polymeric network during swelling. The produced relations between $M_w$ with $D_c$ and D have shown that polymer chains reptate during swelling and dissolution processes, respectively. These results are consistent with the simulations of Peppas[28] et al., where it was demonstrated that the dissolution mechanism was disentanglement-controlled for high molecular weight polymers. Our results are also consistent with their approach by incorporating chain reptation and disentanglement into the mathematical model for the dissolution of glassy polymer.

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