# Small Molecule Desorption Prior to Dissolution of a Polymeric Glass

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**ABSTRACT:** Poly(methyl methacrylate) (PMMA) discs in various molecular weights ($M_w$) were prepared by free-radical polymerization. Pyrene (Py) was introduced during polymerization as a fluorescence probe. In situ steady state fluorescence experiments were performed to monitor desorption processes in chloroform solvent. When the PMMA discs were in chloroform, desorption of Py molecules were monitored by observing the change of Py fluorescence intensity $I_P$. To understand the mechanism of desorption, two different experiments were carried out in the meantime. In the first experiment, the weight of swelling and dissolving PMMA discs against dissolution time was monitored. The parallel experiment was conducted by measuring fluorescence intensity $I_P$ from the desorbing Py molecules. Then, a set of desorption experiments were performed by monitoring $I_P$ for various discs with different molecular weight of PMMA. A Fickian diffusion model was employed to quantify the fluorescence data produced from the swelling PMMA discs to measure desorption coefficients $D_d$. The measured $D_d$ values decrease as the molecular weight of PMMA is increased in the swelling glass. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 908–912, 2006

**Key words:** desorption; fluorescence; polymer glass; dissolution

## INTRODUCTION

Fluorescence dyes can be used to study local environments, basically with two types of experiments. When the dye is simply added to the system as a small molecule, the dye is referred to as probe, which is available commercially. As a consequence such experiments are easy to carry out, but often difficult to interpret because one has to know where the dye is located in the system. If one can prepare an experiment that allows the dye to be attached covalently to a specific component of a system such as polymer chain segment, such dyes are referred to as labels. The question can be raised that the presence of the dye perturb the system or perturb its own local environments in the system. Perturbations are most common where high dye concentration leads to aggregation, and in the the crystalline systems where the order in the system can be affected by the dye. Perturbations are much less likely when the fluorescent dye is incorporated into an amorphous fluid or glassy phase.

Because of its long excited singlet lifetime, pyrene (Py) chromophore[1] is an attractive choice for studying dynamics in polymers. Simple alkyl Py derivatives fluoresce intensely at wavelengths of 370–450 nm. Py has been successfully employed as the fluorescence probe in the study of micellar[2] and phospholipids dispersion.[3] These studies focus on the use of dynamics of quenching of Py monomer fluorescence and an excimer formation processes. The other application of the use of Py as a fluorescence probe is the study of the vibronic fine structure of its monomer fluorescence. The intensities of the various vibronic bands show a strong dependence on the solvent environment.[4] In the presence of polar solvents, there is an enhancement in the intensity of the 0–0 band, whereas there is little effect on other bands, thus the ratio of intensities of these bands has been used to study environmental change.

The mechanism of polymer film dissolution is much more complicated than small molecule dissolution. Small molecule dissolution can be explained by Fick's law of diffusion with a unique diffusion rate.[5] However, in polymeric systems, many anomalies or deviations from Fick's law of diffusion are observed,[6] particularly below the glass transition temperature of polymer. It has been well known that polymeric films dissolve mainly in three sequential steps: solvent penetration, polymer relaxation, and diffusion of polymer chains into the solvent reservoir.

Poly(methyl methacrylate) (PMMA) film dissolution was first studied using laser interferometry by varying molecular weight and solvent quality.[7] The interferometric technique was used to study dissolu-

tion of fluorescence-labeled PMMA films. By monitoring the intensity of fluorescence from the film along with the interferometric signal, the solvent penetration rate into the film and the dissolution were measured simultaneously.[8] A real-time, nondestructive method for monitoring small molecules diffusion in polymer films was developed.[9–11] This method is essentially based on the detection of excited fluorescence dyes diffusing out of a polymer film into a solution in which the film is placed. We have reported a steady state fluorescence (SSF) study on dissolution of both annealed hard latex films and PMMA discs, using real-time monitoring of fluorescence probes.[12–15] In these studies, effect of stirring, temperature, and solvent quality have been studied, and second and last steps of polymer dissolution were investigated. Fast transient technique was also used to study polymer dissolution where Py lifetimes were monitored during dissolution processes.[16]

The aim of this study is to present the behavior of the Py probes during swelling of polymeric glass prior to dissolution. Two parallel experiments were performed to distinguish the swelling and dissolution processes. Py molecules desorb from the polymeric glass during swelling.

In this work, SSF technique was used to study desorption of Py from of PMMA glasses in various molecular weights. Chloroform was used as a swelling agent, and in situ SSF experiments were performed to monitor desorption processes. Desorption experiments were carried out by illuminating the chloroform reservoir and increase in Py intensity $I_P$ was observed. Desorption coefficients ($D_d$) were measured and found to be inversely proportional on the molecular weight of polymer chains in PMMA glasses.

## EXPERIMENTAL

The monomer 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'-azobisisobutyronitrile (AIBN; Merck) was recrystallized twice from methanol and the solvent chloroform (Merck) was used as received. The radical polymerization of MMA was performed in bulk in the presence of AIBN as an initiator. Six different amount of AIBN were used to prepare six PMMA glasses in different molecular weights. AIBN and Py ($4 \times 10^{-4}M$) were dissolved in MMA and this solution was transformed into round glass tube of 10 mm internal diameter. Before polymerization, each solution was deoxygenated by bubbling nitrogen for 10 min. Radical polymerization of the MMA was performed at ($65 \pm 3$)°C. After polymerization was completed, the tubes were broken and disc-shaped samples (around 0.2 cm) were cut for the

**TABLE I**
**Experimentally Measured Parameters of the PMMA Discs and Desorption Coefficient $D_d$ of Pyrene**

| $M_w$ ($10^5$ g/mol) | Initial thickness $d_i$ (cm) | Final thickness $d_f$ (cm) | Diameter $R$ (cm) | $D_d$ ($10^{-10}$ m$^2$s$^{-1}$) |
|---|---|---|---|---|
| 23 | 0.20 | 0.35 | 0.81 | 1.2 |
| 18 | 0.21 | 0.33 | 0.81 | 1.5 |
| 11 | 0.23 | 0.27 | 0.80 | 2.5 |
| 8 | 0.23 | 0.26 | 0.80 | 3.3 |
| 6 | 0.21 | 0.26 | 0.82 | 2.3 |
| 2 | 0.23 | 0.24 | 0.80 | 4.6 |

swelling and dissolution experiments. Molecular weights ($M_w$) listed in Table I are determined with size exclusion chromatography (Waters, model M-6000A) equipped with refractive index detector using two polystyrene gel columns (50, 1000 nm) 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 90° position and the slit widths were kept at 10 nm. SSF experiments were performed in a $1 \times 1$ cm$^2$ quartz cell that was placed in the spectrofluorimeter. The fluorescence emission was monitored so that the excitation light can only illuminate the solvent reservoir. Disc-shaped PMMA glasses were placed at one side of a quartz cell filled up with chloroform, and solvent reservoir was then illuminated with 345 nm excitation light. The Py fluorescence intensity, $I_P$, was monitored during the desorption of Py from PMMA glass in chloroform at 375 nm using the "time drive" mode of the spectrophotometer. Emission of Py was recorded continuously at 375 nm as a function of time. The cell and the sample positions are presented in Figure 1(a,b) during swelling and dissolution of PMMA glass in chloroform vapor. Here, it has to be mentioned that desorption of Py molecules take place during swelling of PMMA glass.

## RESULTS AND DISCUSSION

Two separate experiments were designed; in the first experiment, swelling and dissolving polymer discs were weighed at each time step. In the meantime, Py intensity from the solvent reservoir was monitored to detect the small molecule (Py) desorption from the disc. Figure 2(a,b) present the disc weights ($W_t$) and Py intensity ($I_P$) versus swelling and dissolution time ($t$), respectively. It is seen that $W_t$ first increases and then decrease by increasing swelling and dissolution time, $t$. However, Py intensity ($I_P$) increases continuously by increasing $t$ and then saturates. These behaviors can be explained as follows: at early times, PMMA disc
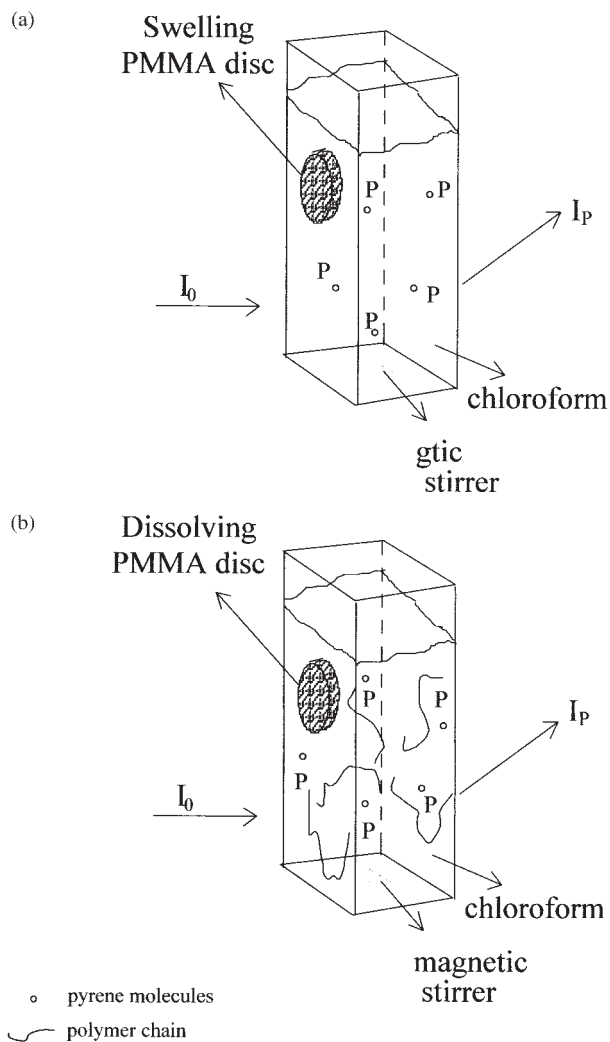
(a)



(b)



**Figure 1** Fluorescence cell and sample position during (a) swelling of PMMA glass (desorption of Py molecules also take place) and (b) dissolving of PMMA glass.

swells by absorbing chloroform molecules into polymer disc. In the meantime, Py molecules are washed out by chloroform from the PMMA disc and as a result, $I_P$ increase by increasing desorption (swelling) time. (Here in fact swelling time corresponds to the desorption time $t_d$). As $I_P$ saturates, PMMA disc starts to dissolve and $W_t$ values decrease. Here, all these process can be summarized as follows. Small molecules (Py) desorbed before dissolution process started from the swelling polymeric glass. With this knowledge, small molecule desorption was investigated from various discs formed by different molecular weights of PMMA.

## Desorption from swelling PMMA glass

Py intensities ($I_P$) are plotted in Figure 3 as a function of desorption time ($t_d$) for the PMMA discs at different molecular weights $M_w$. It is seen that as desorption

time is increased continuous increase in $I_P$ is observed for all PMMA samples. $I_P$ is proportional to the amount of Py desorbing from PMMA discs during swelling. In Figure 3, it is seen that the rate of increase in $I_P$ depends on molecular weight.

They are various mechanism and mathematical models for diffusion in polymers. Tu and Quano[17] proposed a model, which includes polymer diffusion in a liquid layer adjacent to the polymer and moving 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. Later Astarita and Sarti[18] proposed a model, which takes glassy to swollen transition kinetics explicitly into account. Lee and Peppas[19] extended Tu and Quano's model for the situation of polymer dissolution rate where gel thickness was found to be proportional to (time)$^{1/2}$. A relaxation controlled model was proposed by Brochard and de Gennes[20] where, after a swelling gel layer was formed, desorption of polymer from the swollen bulk was
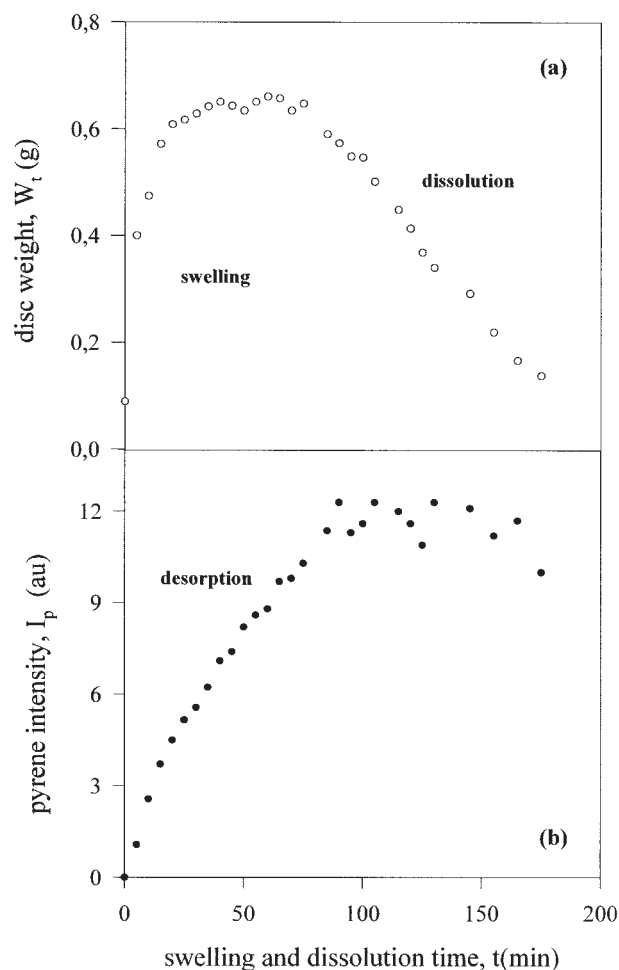


**Figure 2** Variation of (a) weight of PMMA glass during swelling and dissolution and (b) Py intensity ($I_P$) during desorption (swelling).

governed by the relaxation rate of the polymer stress. This rate was found to be of the same order of magnitude as the repration time. The dependencies of the radius of gyration and the repration time on polymer molecular weight and concentration were studied, using a scaling law,[21] based on the repration model.

In this work, we found it appropriate to use the simple model called Case I diffusion kinetics for the small molecule (Py) desorption from the polymeric glass, which is described below.

A solution to Fick's 2nd Law of diffusion in one dimension for a constant diffusion coefficient ($D$) and fixed boundary conditions, for sorption and desorption in and out of a thin slab is obtained and given by the following relation[5]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2 D\pi^2 t}{d^2}\right) \quad (1)$$

Here, $M_t$ represents the amount of materials absorbed or desorbed at time $t$, $M_\infty$ is the equilibrium amount of material, and $d$ is the thickness of slab. Equation (1) presents the model for Case I diffusion, i.e., generally known as Fickian diffusion.

The desorption curves, in Figure 3 can be quantified by fitting the data to eq. (1). Figure 4(a–c) present the plot of the following relation for glass samples in various molecular weights, respectively.

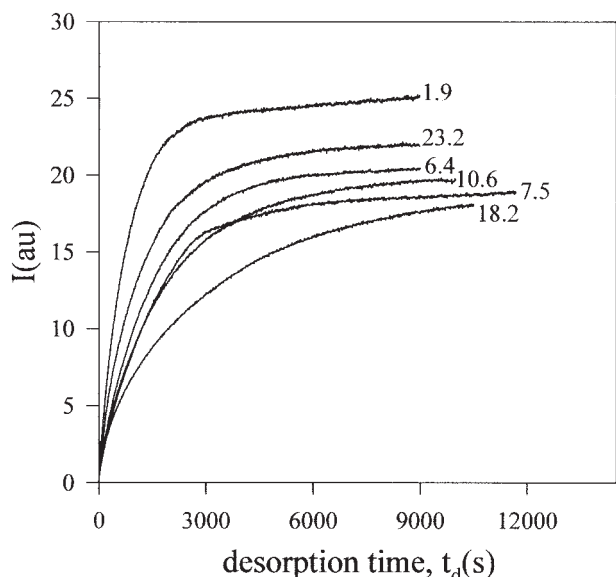$$\ln\left(1 - \frac{I_p}{I_{p\infty}}\right) = B - At \quad (2)$$

**Figure 3** Py intensity variation versus desorption time, $t_d$, during swelling of PMMA glass at various molecular weights. Numbers on each curve present $M_w$ in g/mol ($10^5$).
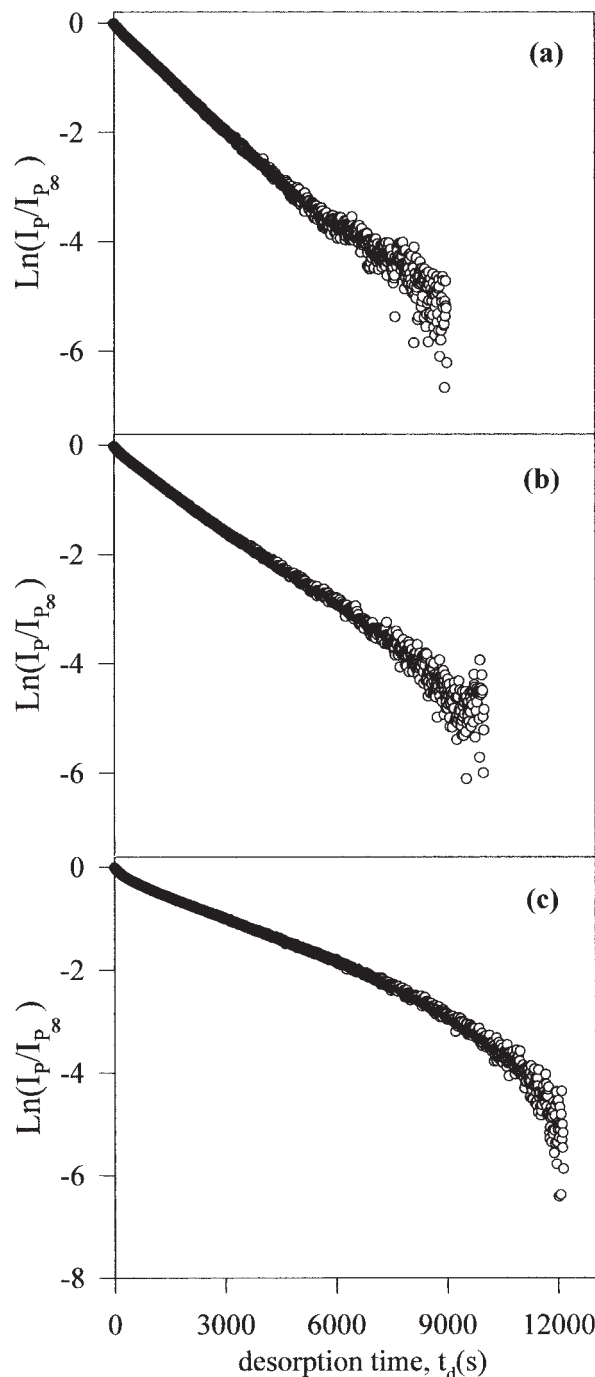
**Figure 4** Plots of desorption curves for Py from PMMA for various molecular weights of (a) $6 \times 10^5$, (b) $11 \times 10^5$, and (c) $23 \times 10^5$ g/mol.

This is the logarithmic form of eq. (1) for $n = 0$ with $A = Dd\pi2/d2$ and $B = \ln(8/\pi2)$ parameters. Here, it is assumed that $IP$ is proportional to the amount of Pys desorbing from the discs and $IP\infty$ presents its value at the equilibrium condition. $Dd$ is the desorption coefficient for Py molecules. In Figure 4, all dissolution curves are digitized for numerical treatment. Deviations from the linearity in Figure 4(a–c) at long times
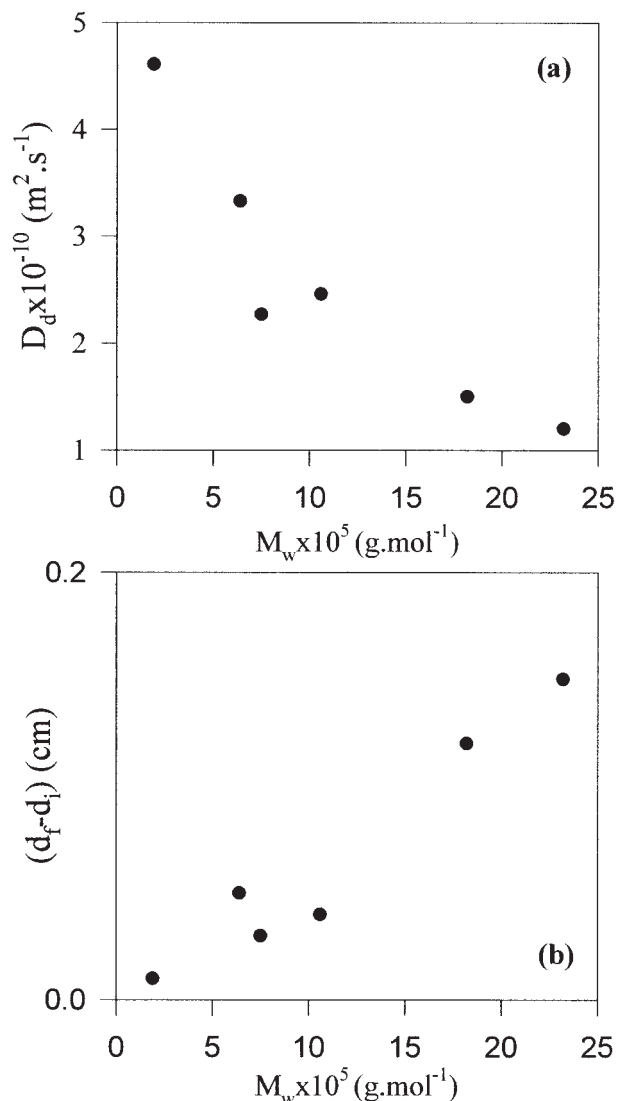
**Figure 5** Plots of (a) desorption coefficient ($D_d$) and (b) difference between final and initial thickness of PMMA discs versus molecular weight, $M_w$.

present equilibration of the dissolution process. Linear regions of the curves at intermediate times in Figure 4(a–c) follow the Fickian diffusion model. When the linear portions of the curves in Figure 4(a–c) are compared to computations using eq. (2), Py desorption coefficients ($Dd$) are obtained and are listed in Table I. When one compares the observed $Dd \approx 10-10$ m2/s$-1$ values with the selfdiffusion coefficient of desorbing polymer chains from PMMA latex films,[15,22] ($\approx 10-14$ to $10-15$ m2/s) 5–4 orders of magnitude difference can be seen, which is expected because small molecules such as Py desorp much faster than the polymer molecules.

$Dd$ values versus $Mw$ are plotted in Figure 5(a)

where it is seen that as $Mw$ increased, desorption of small molecules from the swelling PMMA glass slows down. This desorption behavior can be explained by the swelling capacity of PMMA glass. The differences of final and initial thicknesses versus $Mw$ are plotted in Figure 5(b) where one can see the swelling capability of PMMA glass in various molecular weights. It is seen that as $Mw$ increased, PMMA glass swelled more, indicating that the distance between the entanglement points are crucial for the swelling capacity of the polymeric glass. Combining the results in Figure 5(a,b), one may conclude that higher molecular weight glass swells more and in the same time solvent molecules enter into the swelling glass more slowly. As a result, small molecule (Py) desorption from the glass is much slower for the high molecular weight PMMA glasses.

In conclusion, this work suggests that one has to be careful to use fluorescence probes to monitor polymer dissolution. In other words, this work has shown that small molecules desorption and chain dissolution are not one-to-one processes. The previous one happened earlier than the later one as a result one can not monitor the polymer dissolution by using free probes.

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