# Fast Transient Fluorescence Technique (FTRT) for Studying Dissolution of Polymer Glasses

# Ö. PEKCAN, Ş. UĞUR

Istanbul Technical University, Department of Physics, 80626, Maslak, Istanbul, Turkey

Received 3 June 1998; accepted 31 December 1998

ABSTRACT: The fast transient fluorescence technique (FTRT) was used for studying the swelling and dissolution of a glassy polymer formed by free-radical polymerization of methyl methacrylate (MMA). Anthracene (An) was introduced during polymerization as a fluorescence probe to monitor swelling and dissolution. Swelling and dissolution processes of disc-shaped poly(methyl methacrylate) (PMMA) glasses in a chloroform–heptane mixture were monitored by measuring the fluorescence lifetimes of An from its decay traces. A method is developed for low quenching efficiencies for measuring lifetimes,  $\tau$ , of An, and it was observed that  $\tau$  values decreased as the dissolution process proceeded. Desorption, D, and mutual diffusion,  $D_m$ , coefficients of An molecules were measured during dissolution of PMMA and found to be around  $5.4 \times 10^{-6}$  (cm<sup>2</sup>/s) and  $2.2 \times 10^{-5}$  (cm<sup>2</sup>/s), respectively. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 948–957, 1999

Key words: fluorescence; lifetime; dissolution; polymer diffusion

# **INTRODUCTION**

When an organic dye absorbs light, it becomes electronically excited; then, fluorescence occurs from the lowest-excited singlet state and decays over a timescale typically of nanoseconds.<sup>1,2</sup> In addition to unimolecular decay pathways for deexcitation of excited states, there are a variety of bimolecular interactions which can lead to deactivation. These are referred to collectively as quenching processes, which enhance the rate of decay of an excited-state intensity, I, as follows:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

where A is the preexponential factor and  $\tau$  is the lifetime which characterizes the timescale of the

excited-state decay. It is defined here in Eq. (1) in terms of the measured decay intensity. For dilute solutions of dye molecules in isotropic media, exponential decays are common. In more complex systems, deviations are often observed. Under these conditions, one sometimes describes the decay in terms of the mean decay time  $\langle \tau \rangle$ .

Fluorescence dyes can be used to study local environments with two types of experiments: When the dye is simply added to the system as a small molecule, the dye is referred to as a probe. Such probes are 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 which allows the dye to be attached covalently to a specific component of a system such as a polymer-chain segment, such dyes are referred to as labels. The question can be raised: Does the presence of the dye perturb the system or perturb its own local environment in the system? Perturbations are most common in systems where high dye concen-

Correspondence to: Ö. Pekcan.

Journal of Applied Polymer Science, Vol. 74, 948–957 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/040948-10



**Figure 1** Cartoon representation of polymer glass dissolution. d is the thickness of the glass and L is the position of the advancing solvent swollen gel front.

tration leads to aggregation and in crystalline systems where the order of the system is affected by the dye. Perturbations are much less likely when the fluorescent dye is incorporated into an amorphous fluid or glassy phase.

For about two decades, the transient fluorescence (TRF) technique for measuring fluorescence decay has been routinely applied to study many polymeric systems using dyes both as a probe and/or as labels.<sup>3–7</sup> TRF spectroscopy using a direct energy transfer (DET) and quenching method has been used to characterize internal morphologies of composite polymeric materials.<sup>8,9</sup> DET is simply quenching and is used to describe any bimolecular process which decreases the emission decay rate. There are many such mechanisms: The most common ones are electron transfer, exciplex and excimer formation, nonemissive self-quenching, and heavy atom effects.<sup>1,2</sup> The most important feature of these quenching mechanisms involves interactions between groups over different interaction distances. A single-photon counting (SPC) technique which produces decay curves and measures lifetimes in conjunction with DET was used to study the diffusion of small dye molecules within the interphase domain of anthracene and/or phenantrene-labeled poly(methyl methacrylate) (PMMA) particles.<sup>10</sup> Mean lifetimes of fluorescing donor dye molecules were measured during diffusion. A Fickian model<sup>11</sup> for diffusion was employed to produce diffusion coefficients which were found to be around  $10^{-19}$  and  $10^{-16}$  cm<sup>2</sup> s<sup>-1</sup> at room temperature and at temperatures above the glass transition.

The mechanism of polymer dissolution is much different from and is more complicated than that governing the dissolution of small molecules, because simple diffusion laws no longer apply.<sup>11</sup> The

dissolution of small molecules is usually governed by a single diffusion step; however, at least three different steps have to be considered in the case of polymer dissolution: (a) solvent diffusion, (b) polymer relaxation, and (c) polymer desorption (see Fig. 1). When a glassy polymer is exposed to an organic solvent, the solvent molecules start to diffuse into the glass, which is presented in Figure 1(a). The penetration distance depends mainly on the free volume, which, in turn, depends upon the flexibility of the chain, backbone, and side groups as well as on the thermal history of the polymer. First, solvent molecules act as a plasticizer of the polymer, and as a result, this region of the glass starts to swell. In step (b), the polymer chain begins to relax, creating a swollen gel layer which is composed of both polymer chains and solvent molecules. If the solvent-polymer interactions are more favorable than are the polymer-polymer interactions, maximum swelling is obtained. These polymer chains eventually separate from the bulk and diffuse freely into the solvent. This last step, (c), characterizes the onset of the dissolution process which involves the disentanglement of each individual chain from the swollen gel layer, resulting in diffusion of polymer chains into the pure solvent.

Solvent penetration in polymers has been studied by various techniques. The most traditional ones are the weight measurements and monitoring the redistribution of isotopic tracers in the polymer.<sup>12</sup> The electron spin resonance (ESR) technique is used to investigate nonsolvent penetration into PMMA latex particles.<sup>13</sup> The ESR method based on the scavenging of radicals produced by high-energy  $\gamma$ -irradiation of PMMA by oxygen was used for the measurement of the diffusion coefficient in PMMA.<sup>14</sup> Penetration of naphthalene molecules into PMMA latex particles stabilized by polyisobutylene (PIB) was studied by a time-resolved fluorescence technique below the  $T_g$ .<sup>15</sup> Fluorescence quenching and depolarization methods have been used for penetration and dissolution studies in solid polymers.<sup>16–18</sup> An *in situ* fluorescence quenching experiment in conjunction with laser interferometry was used to investigate the dissolution of PMMA film in various solvents.<sup>19</sup> A real-time nondestructive method for monitoring small molecule diffusion in polymer films was developed,<sup>20,21</sup> which is, basically, based on the detection of excited fluorescence molecules desorbing from a polymer film into a solution in which the film is placed.<sup>22,23</sup> Recently, we reported an *in situ* steady-state fluorescence (SSF) method on the dissolution of latex film and polymer glasses using real-time monitoring of fluorescence probes<sup>24–27</sup> desorbing from these materials.

In this work, the strobe technique, which is called fast transient fluorescence (FTRF) was used to study the dissolution of PMMA glasses prepared by free-radical polymerization. The major advantage of the strobe technique over other lifetime instruments is the time duration of a single experiment which takes only seconds. (Single-lifetime measurements in a single-photon counting instrument takes hours.) In this work, this advantage of the strobe technique is used to make at least 20–30 lifetime experiments during the dissolution of a polymer glass over a time period of 5 h. A chloroform-heptane mixture was used as a dissolution agent and in situ FTRF experiments were performed to observe the dissolution processes. Dissolution experiments were carried out by illuminating the PMMA glass, and fluorescence decay traces were observed using a Strobe Master System (SMS).

# THEORETICAL CONSIDERATION

Various mechanisms and mathematical models have been considered for polymer dissolution: Tu and Quano<sup>28</sup> 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. Lee and Peppas<sup>29</sup> extended this model for films to the situations of the polymer dissolution rate where the gel thickness was found to be proportional to  $(time)^{1/2}$ . A relaxation-controlled model was proposed by Brochard and de Gennes,<sup>30</sup> 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 the polymer molecular weight and concentration were studied using a scaling law<sup>31</sup> based on the reptation model.

In this article, we employed a simpler model developed by Enscore et al.<sup>32</sup> to interpret the results of polymer swelling and dissolution experiments. This model includes Case I and Case II diffusion kinetics.

#### **Case I or Fickian Diffusion**

The solution of a unidirectional diffusion equation for a set of boundary conditions was cited by Cranck.<sup>11</sup> For a constant diffusion coefficient, D, and fixed boundary conditions, the sorption and desorption transport in and out of a thin slab is given by the following relation:

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

Here,  $M_t$  represents the amount of materials absorbed or desorbed at time t,  $M_{\infty}$  is the equilibrium amount of the material, and d is the thickness of the slab.

#### **Case II Diffusion**

The Case II transport mechanism is characterized by the following steps: As the solvent molecules enter into the polymer film, a sharp advancing boundary forms and separates the glassy part of the film from the swollen gel [see Fig. 1(b)]. This boundary moves into the film at a constant velocity. The swollen gel behind the advancing front is always at a uniform state of swelling. Now, consider a cross section of a film with thickness *d*, undergoing Case II diffusion as in Figure 1, where *L* is the position of the advancing sorption front,  $C_0$  is the equilibrium penetrant concentration, and  $k_0$  (mg/cm<sup>2</sup> min) is defined as the Case II relaxation constant. The kinetic expression for the sorption in the film slab of an area *A* is given by

$$\frac{dM_t}{dt} = k_0 A \tag{3}$$

The amount of penetrant,  $M_t$ , absorbed in time t will be

$$M_t = C_0 A(d - L) \tag{4}$$

After eq. (4) is substituted into eq. (3), the following relation is obtained:

$$\frac{dL}{dt} = -\frac{k_0}{C_0} \tag{5}$$

It can be seen that the relaxation front, positioned at L, moves toward the origin with a constant velocity,  $k_0/C_0$ . The algebraic relation for L, as a function of time t, is described by eq. (6):

$$L = d - \frac{k_0}{C_0}t \tag{6}$$

Since  $M_t = k_0 A t$  and  $M_{\infty} = C_0 A d$ , the following relation is obtained:

$$\frac{M_t}{M_{\infty}} = \frac{k_0}{C_0 d} t \tag{7}$$

#### **Fluorescence Quenching**

Emission of fluorescence is the radiative transition of an electronically excited molecule from its singlet excited state to its ground state.<sup>1,2</sup> Fluorescence quenching normally refers to any bimolecular process between the excited singlet state of a fluorescent molecule and a second species that enhances the decay rate of the excited state. One can schematically represent the process as

$$F^* \xrightarrow{k_j, k_{\mathrm{nr}}} F$$
 (8)

$$F^* \xrightarrow{k_q[Q]} F \tag{9}$$

where F and  $F^*$  represent the fluorescent molecule, and its excited form, Q, is the quencher, and  $k_f$ ,  $k_{\rm nr}$ , and  $k_q$  represent the fluorescence, nonradiative, and quenching rate constants, respectively. Many types of processes lead to quenching. Kinetically, the quenching process can be divided into two main categories: dynamic and static. In dynamic quenching, diffusion to form an encounter pair during the excited-state lifetime of the fluorescent molecule leads to quenching. In static quenching, diffusion does not occur (which is not of our interest). Dynamic quenching is most likely to occur in a fluid solution, where the dye or quencher are free to move. If the quenching rate can be characterized in terms of a single-rate coefficient  $(k_q)$  and the unquenched decay rate of F, in terms of a unique lifetime,  $\tau_0$ , then the quenching kinetics will follow the Stern-Volmer equation as follows:

$$\tau^{-1} = \tau_0^{-1} + k_a[Q] \tag{10}$$

where [Q] represents the quencher concentration. The fluorescence quenching process used in this article involves monomer "internal quenching" induced by solvent viscosity changes.

### **EXPERIMENTAL**

The monomers MMA (Merck, Germany) were freed from the inhibitor by shaking with a 10% 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 solvents chloroform and heptane (Merck) were used as they were.

The radical polymerization of MMA was performed in bulk in the presence of AIBN as an initiator. AIBN (0.26 wt %) and An ( $4 \times 10^{-4} M$ ) were dissolved in MMA and this solution was placed into a round glass tube of 15-mm internal diameter. Before polymerization, the solution was deoxygenated by bubbling nitrogen for 10 min and then radical polymerization of MMA was performed at a temperature of 65 ± 3°C. After polymerization was completed, the tube was broken and disc-shaped thin films (around 0.4 cm) were cut for the swelling and dissolution experiments.

*In situ* fluorescence decay experiments were performed using Photon Technology International's (PTI) Strobe Master System (SMS). In the strobe, or pulse-sampling technique,<sup>2,33</sup> the sample is excited with a pulsed light source. The name comes about because the photo multiplier tube (PMT) is gated or strobed by a voltage pulse that is synchronized with the pulsed light source. The intensity of the fluorescence emission is measured in a very narrow time window on each pulse and saved in a computer. The time window is moved after each pulse. The strobe has the effect of turning the PMT and measuring the emission intensity over a very short time window. When the data have been sampled over the appropriate range of time, a decay curve of the fluorescence intensity versus time can be constructed. Because the strobe technique is intensity-dependent, the strobe instrument is much faster than is SPC and even faster than a phase fluorimetry instrument. A strobe instrument is much simpler to use than is SPC and the data are easier to interpret than is a phase system. Because of these advantages, SMS is used to monitor the dissolution of PMMA glasses which takes place in a time period of a few hours.

All dissolution measurements were made at a 90° position and slit widths were kept at 5 nm. Dissolution experiments were performed in a round quartz cell which was placed in the SMS and fluorescence decay was collected over three decades of decay. Disc-shaped samples were placed in a quartz cell filled with a chloroform (90%)–heptane (10%) mixture and the samples were then illuminated with a 356-nm excitation light and anthracene fluorescence emission was detected at 400 nm. The uniqueness of the fit of the data to the model was determined by  $\chi^2$  ( $\chi^2 < 1.20$ ), the distribution of weighted residuals, and the autocorrelation of the residuals. All measurements were made at room temperature.

# **RESULTS AND DISCUSSION**

Dissolution experiments were performed using a chloroform-heptane mixture as a dissolution agent. Figure 2 presents the fluorescence decay profiles of An at various dissolution steps. It is observed that as the dissolution time is increased excited anthracenes decay faster, indicating that quenching of excited anthracenes occurs. Here, the role of the solvent is to add the quasi-continuum of states needed to satisfy energy-resonance conditions, that is, the solvent acts as an energy sink for rapid vibrational relaxation which occurs after the rate-limiting transition from the initial state. Birks et al. studied the influence of solvent



**Figure 2** Fluorescence decay profiles of excited An, at various dissolution steps. Number at each curve presents the dissolution times in 1 min. The sharp peaked curve is the lamp profile.

viscosity on the fluorescence characteristics of pyrene solutions in various solvents and observed that the rate of monomer internal quenching is affected by the solvent quality.<sup>34</sup> We previously reported a viscosity effect on low-frequency intramolecular vibrational energies of excited naphthalene in swollen PMMA latex particles.<sup>35</sup>

Recently, it was shown that excited pyrene molecules are quenched in a chloroform-heptane mixture due to the low viscous environment of heptane during film dissolution.<sup>26</sup> It was considered that collosional quenching of pyrenes occurs in a low viscous heptane  $(3.8 \times 10^{-4} \text{ Pa s})$  environment, in which pyrenes are quenched much easier than is possible in chloroform which has relatively high viscosity  $(5.8 \times 10^{-4} \text{ Pa s})$ . However, one must be careful in preparing a chloroform-heptane mixture because a high heptane content results in zero desorption coefficients,<sup>26</sup> due to that a bad solubility and low heptane content cause very fast dissolution, which can be difficult to control.

To probe the dissolution processes during solvent penetration, the fluorescence decay curves were measured and were fitted to eq. (1). A typical decay curve and its fit to eq. (1) is shown in Figure 3. A and  $\tau$  values were produced at each dissolution step using linear least-square analysis. To quantify these observations, the integrated area under the fluorescence decay curve is used at each step of the dissolution process:



**Figure 3** Fit of the decay curve of An to eq. (1) for the dissolution at 110 min.

$$\langle I \rangle = \int I \, dt = A\tau \tag{11}$$

The  $\langle I \rangle$  values are plotted versus the dissolution time,  $t_d$ , in Figure 4 for the dissolving PMMA glass. It is seen that at the beginning the  $\langle I \rangle$ values do not change much, then suddenly decrease around 100 min as the dissolution time,  $t_d$ , is increased. This behavior indicates that the quenching of An molecules takes place during solvent diffusion. At the beginning, before solvent penetration starts, the An intensity is called  $\langle I_0 \rangle$ ; after solvent diffusion starts, some An molecules are quenched and the intensity decreases to  $\langle I \rangle$  at time  $t_d$ . At the end of dissolution at the equilibrium state, An intensity reaches  $\langle I_{\infty} \rangle$ . The relation between the solvent sorption,  $M_{t_d}$ , and intensity is now given by the following relation:

$$\frac{M_{t_d}}{M_{\infty}} = \frac{\langle I_0 \rangle - \langle I \rangle}{\langle I_0 \rangle - \langle I_{\infty} \rangle} \tag{12}$$

Since 
$$\langle I_0 \rangle \gg \langle I_\infty \rangle$$
, eq. (12) becomes

$$\frac{M_{t_d}}{M_{\infty}} = 1 - \frac{\langle I \rangle}{\langle I_0 \rangle} \tag{13}$$

This relation predicts that as  $M_{t_d}$  increases,  $\langle I \rangle$  is decreased. Equation (13) is quite similar to the equation used to monitor oxygen uptake by PMMA spheres.<sup>36,37</sup> Combining eq. (13) with eq. (7) and assuming that number of quenched An molecules are proportional to  $\langle I \rangle / \langle I_0 \rangle$ , the following relation can be obtained at early times:

$$\frac{\langle I \rangle}{\langle I_0 \rangle} = 1 - \frac{k_0}{C_0 d} t_d \tag{14}$$

At early times, the data in Figure 4 are plotted in Figure 5 according to eq. (14), where a linear relation is obtained. The linear regression of curve in Figure 5 provides us with a  $k_0$  value of  $7.9 \times 10^{-1}$  (mg/cm<sup>2</sup> min). At long times, combining eq. (13) with eq. (2), the following relation is obtained:

$$\operatorname{Ln}\left(\frac{\langle I\rangle}{\langle I_0\rangle}\right) = \operatorname{Ln} B_1 - At_d \tag{15}$$

where  $B_1 = 8/\pi^2$  and  $A = D\pi^2/d^2$ . The data above 100 min in Figure 4 are plotted in Figure 6 according to eq. (15), where the linear regression of the curve produced a *D* value of  $5.3 \times 10^{-6}$  (cm<sup>2</sup>/s).



**Figure 4** Plot of the integrated area under the fluorescence decay profiles versus dissolution time,  $t_d$ .



**Figure 5** Fit of the data in Figure 4 to eq. (14) at early times. The slope of the linear relation produced a  $k_0$  value.

The area, I, under the decay curves is also measured using the proper software of PTI and are plotted versus the dissolution time in Figure 7. Similar to previous observations, the I intensity did not change much at early times; however, it decreased drastically at longer times by indi-



**Figure 6** Fit of the data in Figure 4 to eq. (15) at longer times. The slope of the linear relation produced a D value.



**Figure 7** Plot of the intensity, *I*, versus dissolution time,  $t_d$ .

cating that the dissolution process has started. Now, eqs. (14) and (15) become

$$\frac{I}{I_0} = 1 - \frac{k_0}{C_0 d} t_d$$
(16)

and

$$\operatorname{Ln}\left(\frac{I}{I_0}\right) = \operatorname{Ln} B_1 - At_d \tag{17}$$

Data in Figure 7 were fitted to eqs. (16) and (17) at early and longer times. Results are presented in Figures 8 and 9, respectively, where  $k_0 = 6.2 \times 10^{-1}$  (mg/cm<sup>2</sup> min) and  $D = 5.7 \times 10^{-6}$  (cm<sup>2</sup>/s) values are produced from the slopes of the linear relations.

 $\tau$  values obtained during dissolution of PMMA glass are plotted versus  $t_d$  in Figure 10. To quantify these results, a Stern–Volmer type of quenching mechanism is proposed for the fluorescence decay of An in a glass sample during the dissolution process, where eq. (10) can be employed. For low quenching efficiency,  $\tau_0 k_q [M_{t_d}] \ll 1$ , eq. (10) becomes

$$\tau \approx \tau_0 (1 - \tau_0 k_q [M_{t_d}]) \tag{18}$$

where  $[M_{t_d}]$  is the quencher (heptane) concentration at time  $t_d$ . Here, using a 10% heptane con-



**Figure 8** Fit of the data in Figure 7 to eq. (16) at early times. The slope of the linear relation produced a  $k_0$  value.

tent in the solvent mixture, a low quenching environment for the excited An molecules is satisfied, which also caused slower and controllable dissolution. The relation between the lifetime of An and  $M_{t_d}$  in dissolving glass can be obtained approximately using the volume integration of eq. (18), and the following relation is obtained:

$$\frac{\tau}{\tau_0} = 1 - C \, \frac{M_{i_d}}{M_\infty} \tag{19}$$

where  $C = \tau_0 k_q M_{\infty} / v$ . Here, v is the volume of the glass. The solvent sorption is calculated over the differential volume as



**Figure 9** Fit of the data in Figure 7 to eq. (17) at longer times. The slope of the linear relation produced a D value.



**Figure 10** Plot of lifetimes,  $\tau$ , of An versus dissolution time,  $t_d$ .

$$M_{t_d} = \int_0^{d_x} [M_{t_d}] \, dv$$
 (20)

where dv is the differential volume in the glass and the integration is taken from 0 to d.

At early times, eq. (19) can be written as

$$\frac{\tau}{\tau_0} = 1 - k_q \tau_0 \frac{k_0}{d} t_d \tag{21}$$

where eq. (7) is used. Data in Figure 10 were fitted to eq. (21) at early times and are presented in Figure 11, where the  $k_q$  values were obtained and found to be 1.0 and  $1.3 \times 10^7 (M^{-1} \text{ s}^{-1})$  by using the previously obtained  $k_0$  values from Table I where  $\tau_0$  was taken as 6.45 ns. At longer times, by combining eq. (19) with eq. (2), the following relation is produced:

$$\frac{\tau}{\tau_0} = 1 - C + B_2 \exp(-At_d) \tag{22}$$

Here,  $B_2 = CB_1$ . Data in Figure 10 at longer times were fitted to eq. (22), which produced a Dvalue as  $5.2 \times 10^{-6}$  (cm<sup>2</sup>/s), where the  $B_1$  values used were obtained from the fit of the data in Figures 6 and 9 at long times. Fit of the data in Figure 10 is presented in Figure 12.



**Figure 11** Fit of the data in Figure 10 to eq. (21) at early times. The slope of the linear relation produces a  $k_q$  value.

The measured parameters, using three different methods, are listed in Table I. The order of magnitude of the  $D(10^{-6} \text{ cm}^2/\text{s})$  values are consistent with our previous observation in a chloroform-heptane mixture,<sup>26</sup> where a steady-state fluorescence technique was employed.

The quenching rate constant,  $k_q$ , which is found to be  $1.15 \times 10^7 (M^{-1} \text{ s}^{-1})$ , is given in the Smoluchowski model,<sup>1</sup> where the magnitude of  $k_q$ is related to the diffusion coefficient of the interacting species:

$$k_q = \frac{4\pi N D_m R}{1000} \tag{23}$$

Here,  $D_m$  is the mutual diffusion coefficient; N, Avagadro's number; and R, the sum of the interaction radii.  $D_m$  was calculated from eq. (23) using experimentally measured  $k_q$  values and found to be  $2.2 \times 10^{-5}$  (cm<sup>2</sup>/s), on average, where R is

	$k_0 \;({ m mg/cm^2min})  imes 10^{-1}$	$D~({ m cm^{2/\!s}})  onumber \  imes 10^{-6}$
$\langle I \rangle / \langle I_0 \rangle$	7.9	5.3
I/I <sub>0</sub>	6.2	5.7
$\tau / \tau_0$	—	5.2

Table I  $k_0$  and D Values

1.2 1.00.8  $\tau/\tau_0$ 0.6 0.4 0.2 100 140 20 40 60 80 120 0 dissolution time t<sub>d</sub> (min)

**Figure 12** Fit of the data in Figure 10 to eq. (22) at longer times. The slope of the linear relation produced a D value.

taken as 7.15 å. The observed  $D_m$  is typical for a small molecule, diffusing in a liquid environment,<sup>3,4</sup> and is an order of magnitude larger than is the averaged desorption coefficient, D (5.4  $\times$  10<sup>-6</sup> cm<sup>2</sup>/s). This result is expected, because desorption of An together with polymer chains from a swollen gel is always slower than the Brownian motion of An in a liquid environment.

In summary, this article introduces a novel method which uses the FTRF technique to measure the D and  $D_m$  coefficients during dissolution of a polymeric material in a good solvent. Here, one has to notice that since we measured lifetimes no environmental corrections to the data, which are quite problematic when one uses fluorescence intensity data from steady-state spectrometers, are needed.

# REFERENCES

- Birks, J. B. Photophysics of Aromatic Molecules; Wiley-Interscience: New York, 1971.
- 2. Lakowicz, J. R. Principles of Fluorescence Spectroscopy; Plenum: New York, 1983.
- Pekcan, O.; Winnik, M. A.; Croucher, M. D. Macromolecules 1983, 16, 699.
- 4. Pekcan, O.; Winnik, M. A.; Croucher, M. D. J Polym Sci Polym Lett 1983, 21, 1011.

- Pekcan, Ö.; Winnik, M. A.; Croucher, M. D. Phys Rev Lett 1988, 61, 641.
- Pekcan, Ö.; Egan, L. S.; Winnik, M. A.; Croucher, M. D. Macromolecules 1990, 23, 2210.
- 7. Pekcan, Ö. Chem Phys Lett 1992, 20, 198.
- Winnik, M. A. In Polymer Surfaces and Interfaces; Feast, J.; Munro, H., Eds.; Wiley: London, 1983, Chapter 1.
- Winnik, M. A.; Pekcan, Ö.; Chen, L.; Croucher, M. D. Macromolecules 1988, 21, 55.
- 10. Pekcan, O. J Polym Sci 1996, 59, 521.
- Crank, J. Mathematics of Diffusion, 2nd ed.; Clarendon: Oxford, 1975.
- 12. Crank, J.; Park, G. S. Diffusion in Polymers; Academic: London, 1968.
- 13. Veksli, Z.; Willer, W. G. J Polym Sci 1976, 54, 299.
- Kaptan, Y.; Pekcan, Ö.; Güven, O. J Appl Polym Sci 1989, 37, 2537.
- 15. Pekcan, Ö. J Appl Polym Sci 1993, 49, 151.
- Guillet, J. E. In Photophysical and Photochemical Tools in Polymer Science; Winnik, M. A., Ed.; Reidel: Dordrecht, 1986.
- 17. Nivaggioli, T.; Wang, F.; Winnik, M. A. J Phys Chem 1992, 96, 7462.
- Pascal, D.; Duhamel, J.; Wang, Y.; Winnik, M. A.; Napper, D. H.; Gilbert, R. Polymer 1993, 34, 1134.
- Limm, W.; Dimnik, G. D.; Stanton, D.; Winnik, M. A.; Smith, B. A. J Appl Polym Sci 1988, 35, 2099.
- 20. Lu, L.; Weiss, R. G. Macromolecules 1994, 27, 219.

- Kronganz, V. V.; Mooney, W. F.; Palmer, J. W.; Patricia, J. J. J Appl Polym Sci 1995, 56, 1077.
- Kronganz, V. V.; Yohannan, R. M. Polymer 1990, 31, 1130.
- He, Z.; Hammond, G. S.; Weiss, R. G. Macromolecules 1992, 25, 501.
- Pekcan, Ö.; Canpolat, M.; Kaya, D. J Appl Polym Sci 1996, 60, 2105.
- 25. Pekcan, Ö.; Uğur, Ş. Polymer 1997, 38, 5579.
- 26. Pekcan, Ö.; Uğur, Ş.; Yilmaz, Y. Polymer 1997, 38, 2183.
- 27. Pekcan, Ö.; Uğur, Ş. J Appl Polym Sci, in press.
- Tu, Y. O.; Quano, A. C. IBM J Res Dev 1977, 21, 131.
- 29. Lee, P. I.; Peppas, A. J Control Release 1987, 6, 207.
- Brochardt, F.; de Gennes, P. G. Physco Chem Hydrodyn 1983, 4, 313.
- Papanu, J. S.; Soane, D. S.; Bell, A. T. J Appl Polym Sci 1989, 38, 859.
- Enscore, D. J.; Hopfenbergard, H. B.; Stannett, V. T. Polymer 1977, 18, 793.
- Ware, W. R.; James, D. R.; Siemiarczuk, A. Rev Sci Instrum 1992, 63, 1710.
- Birks, J. B.; Lumb, M. D.; Munro, I. H. Proc R Soc Ser A 1964, 227, 289.
- 35. Pekcan, Ö. J Appl Polym Sci 1995, 57, 125.
- Kaptan, Y.; Pekcan, Ö.; Güven, O. J Appl Polym Sci 1992, 44, 1595.
- Kaptan, Y.; Pekcan, Ö.; Güven, O. J Appl Polym Sci 1989, 37, 2537.