

Pyrene lifetimes for monitoring polymer dissolution: a fast transient fluorescence study

Ş. Uğur, Ö. Pekcan*

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

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Abstract

Fast transient fluorescence technique (FTRT) was used to measure pyrene (Py) lifetimes during dissolution of glassy polymer, which is formed by free radical polymerization of methyl methacrylate (MMA), and Py was introduced during polymerization as a fluorescence probe to monitor swelling and dissolution. The dissolution process of poly(methyl methacrylate) (PMMA) glass was performed in chloroform (80%)–heptane (20%) mixture. Fluorescence lifetimes of Py from its decay traces were used to monitor the dissolution process. A model was derived for low quenching efficiencies for measuring mean lifetimes, $\langle\tau\rangle$, of Py and it was observed that $\langle\tau\rangle$ values decreased as the dissolution process proceeded. Desorption, D and mutual diffusion, D_m coefficients of Py molecules were measured during dissolution of PMMA and found to be around 1.19×10^{-6} and $1.23 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Fluorescence dyes can be used to study the local environment, 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 a 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 perform an experiment that allows the dye to be attached covalently to a specific component of a system such as a polymer chain segment, these dyes are referred to as labels. In this context a question can be raised, whether the presence of the dye perturbs the system or perturbs its own local environment in the system. Perturbations are most common in cases where high dye concentrations lead to aggregation, and to 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.

As a result of its long excited singlet lifetime, Py chromophore [1] is an attractive choice for studying the dynamics in polymers. Simple alkyl Py derivatives fluoresce intensely at wavelengths of 370–450 nm. Py has been

successfully employed as a fluorescence probe in the study of micellar [2] and phospholipid dispersion [3]. These studies focus on the use of the dynamics of quenching of Py monomer fluorescence and an excimer formation process. 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 was used to study the environmental change.

For about two decades, the transient fluorescence (TRF) technique for measuring the fluorescence decay has been routinely applied to study many polymeric systems using dyes both as a probe and/or as labels [5–9]. TRF spectroscopy with direct energy transfer (DET) and quenching method has been used to characterize the internal morphologies of composite polymeric materials [10,11]. Quenching besides DET is the general word used to describe any bimolecular process, which decreases the emission decay rate. The most important feature of these quenching mechanisms involves interaction 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

* Corresponding author. Tel.: +90-0212-285-3213; fax: +90-0212-285-6386.

small dye molecules within the interphase domain of anthracene and/or phenanthrene labeled poly(methyl methacrylate) (PMMA) particles [12]. The mean lifetimes of donor dye molecules that exhibit fluorescence were measured during diffusion. A Fickian model [13] for diffusion was employed to produce diffusion coefficients, which were found to be around 10^{-19} and 10^{-16} $\text{cm}^2 \text{s}^{-1}$, at room and above glass transition temperatures.

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: solvent diffusion, polymer relaxation, and polymer desorption. The penetration distance depends mainly on free volume, which in turn depends upon the flexibility of the chain, backbone and side groups, as well as the thermal history of the polymer. Firstly, the solvent molecule acts as a plasticizer of the polymer and as a result, this region of the glass starts to swell, then the polymer chain begins to relax, creating a swollen gel layer, which is composed of both the polymer chains and the solvent molecules. If the solvent–polymer interactions are more favorable than 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 characterizes the onset of the dissolution process, which involves the disentanglement of each individual chain from the swollen gel layer, resulting in the diffusion of polymer chains into the solvent reservoir.

Fluorescence quenching and depolarization methods have been used for penetration and dissolution studies in solid polymers [14–16]. In situ fluorescence quenching experiment, in conjunction with laser interferometry, was used to investigate the dissolution of PMMA film in various solvents [17]. The real-time non-destructive method for monitoring small molecule diffusion in polymer films was developed [18,19], which is based on the detection of excited fluorescence molecules desorbing from a polymer film into a solution in which the film is placed [20,21]. Recently, we have reported in situ steady state fluorescence (SSF) method on the dissolution of latex film and polymer glasses using real-time monitoring of fluorescence probes [22–25], desorbing from these materials.

In this work, Py lifetimes were measured using the strobe technique, which is named as FTRF. The major advantage of strobe technique over other lifetime instruments is the time duration of a single experiment, which takes only few seconds. However, single lifetime measurement in single photon counting instrument takes hours. In this work, this advantage of strobe technique is used to make at least 40–50 lifetime experiments during the dissolution of polymer glass (which took at least 8 h). Chloroform (80%)–heptane (20%) 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 the Strobe Master System (SMS).

2. Fluorescence quenching

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



where F and F^* represent the fluorescent molecule, and its excited form, Q is the quencher. k_f , k_{nr} and k_q represent the fluorescence, non-radiative and quenching rate constants, respectively. Many types of processes lead to quenching. Kinetically, quenching process can be divided into two main categories: dynamic and static. In the dynamic quenching, diffusion to form an encounter pair during the excited state lifetime of the dye leads to quenching. Whereas in the static quenching, diffusion does not occur (which is not of interest to us). Dynamic quenching is most likely to occur in 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, τ_0 , then the quenching kinetics will follow the Stern–Volmer equation as follows

$$\tau^{-1} = \tau_0^{-1} + k_q[Q], \quad (3)$$

where $[Q]$ represents the quencher concentration.

3. Experimental

The monomers MMA (Merck) 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, AIBN (Merck) was recrystallized twice from methanol and solvents, chloroform and heptane (Merck) were used as is. The radical polymerization of MMA was performed in bulk in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. AIBN (0.26 wt.%) and Py (4×10^{-4} M) were dissolved in MMA and this solution was placed in 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 $65 \pm 3^\circ\text{C}$ temperature. After polymerization was completed, the tube was broken and disc shape thin films (around 0.5 cm) were cut for the swelling and dissolution experiments.

In situ fluorescence decay experiments were performed using Photon Technology International's (PTI) SMS. In the

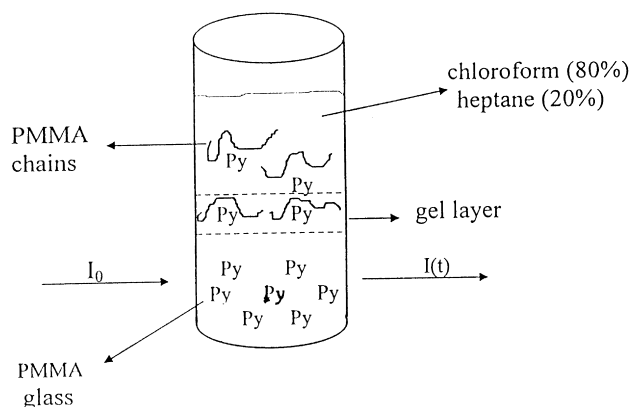


Fig. 1. The position and illumination of PMMA disc in the quartz cell of the SMS instrument. $I(t)$ is the emitted light at time t , and $I_0 = A_1 + A_2$ is the excited light at time, $t = 0$.

strobe, or pulse sampling technique [26] the sample was excited with a pulsed light source. The name is derived from the fact that the PMT is gated or strobed by a voltage pulse that is synchronized with the pulsed light source. The intensity of 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 off the PMT and measuring the emission intensity over a very short time window. When the data were sampled over the appropriate range of time, a decay curve of fluorescence intensity versus time can be constructed. As the strobe technique is intensity-dependent, strobe instrument is much faster than SPC, and even faster than phase instrument. Strobe instrument is much simpler to use than SPC and the data is easier to interpret than the phase system. As a result of these advantages SMS is used to monitor the dissolution of PMMA glasses, which take about few hours.

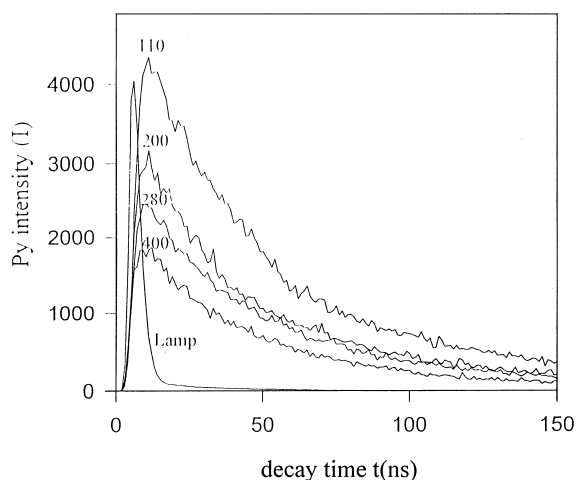


Fig. 2. Fluorescence decay profiles of excited Py, at various dissolution steps. Number at each curve present the dissolution times in minute. The sharp peaked curve is the lamp profile.

All the dissolution measurements were made at 90° position and slit widths were kept at 20 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 shape of samples were placed in a quartz cell filled with chloroform (80%)–heptane (20%) mixture and samples were then illuminated with 345 nm excitation light and Py fluorescence emission was detected at 395 nm. The position and illumination of the PMMA disc is shown in Fig. 1. The uniqueness of the fit of the data to the model is determined by χ^2 ($\chi^2 < 1.20$), the distribution of weighted residuals, and the autocorrelation of the residuals. All the measurement were made at room temperature.

4. Results and discussion

Dissolution experiments were performed using a chloroform–heptane mixture as dissolution agent. Fig. 2 shows the fluorescence decay profiles of Py at various dissolution steps. It is observed that as the dissolution time is increased, excited Py decay faster, thereby indicating that the quenching of excited Py increase. Here the role of the solvent is to add the quasi-continuum of states needed to satisfy the energy resonance conditions, i.e. the solvent acts as an energy sink for rapid vibrational relaxation, which occurs after the rate limiting transition from the initial state. Briks et al. studied the influence of solvent viscosity on the fluorescence characteristics of Py solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality [27]. We reported the viscosity effect on low frequency intramolecular vibrational energies of excited naphthalene in swollen PMMA latex particles [28].

In order to probe the dissolution processes during solvent penetration, the fluorescence decay curves were measured and fitted to the sum of two exponential:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right), \quad (4)$$

where t represents the decay time, τ_1 and τ_2 are the long and short components of Py lifetimes, and A_1 and A_2 are the corresponding amplitudes of the decay curves. A typical decay curve and its fit to Eq. (4) is shown in Fig. 3. A_i and τ_i values were produced at each dissolution step using the non-linear least squares analysis. It was observed that the τ_1 values do not change, but τ_2 values decrease, and A_1 and A_2 values scattered randomly as dissolution time, t_d , is increased.

4.1. Area under decay curve

In order to quantify these observations, the integrated area under the fluorescence decay curve is calculated at each step

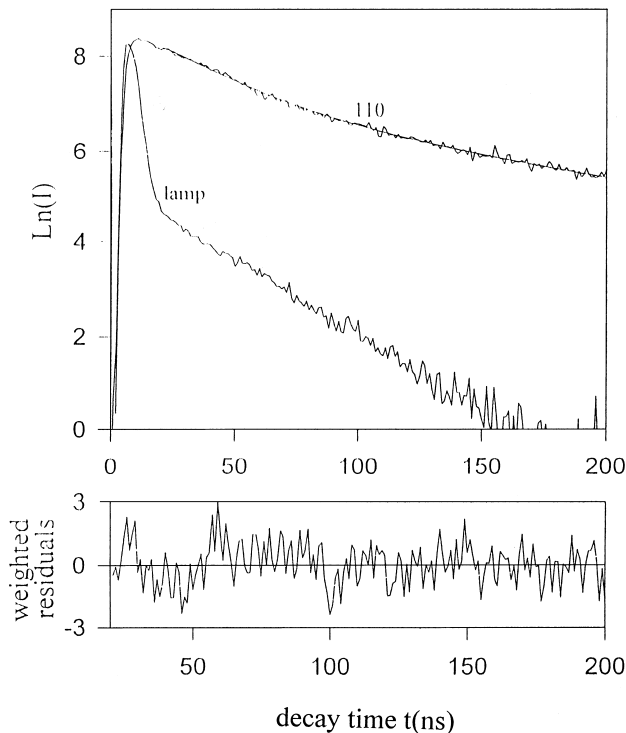


Fig. 3. The fit of the decay curve of Py to Eq. (4), for the dissolution at 110 min.

of the dissolution process using the following relation

$$\langle I \rangle = \int I dt = A_1 \tau_1 + A_2 \tau_2. \quad (5)$$

It is observed that $\langle I \rangle$ values decreased as the dissolution time, t_d , is increased. This behavior indicates that the quenching of Py molecules takes place during solvent diffusion. At the beginning, before solvent penetration start Py

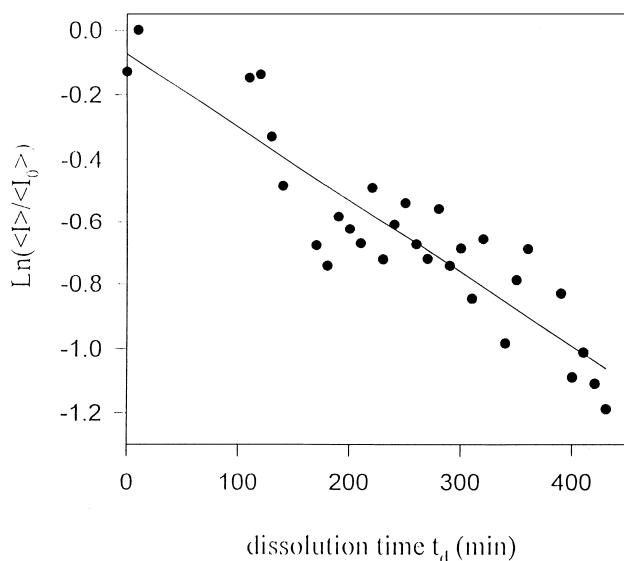


Fig. 4. The fit of the logarithmic plot of $\langle I \rangle$ data to Eq. (9). The slope of the linear relation produced the D value.

intensity is called $\langle I_0 \rangle$, after solvent diffusion starts some Py molecules are quenched and intensity decreases to $\langle I \rangle$ at time t_d . At the end of dissolution, at equilibrium state, Py intensity reaches $\langle I_\infty \rangle$. The relation between the solvent sorption, M_{t_d} , and Py intensity is now given by the following relation

$$\frac{M_{t_d}}{M_\infty} = \frac{\langle I_0 \rangle - \langle I \rangle}{\langle I_0 \rangle - \langle I_\infty \rangle} \quad (6)$$

as $\langle I_0 \rangle > \langle I_\infty \rangle$, Eq. (6) becomes

$$\frac{M_{t_d}}{M_\infty} = 1 - \frac{\langle I \rangle}{\langle I_0 \rangle}. \quad (7)$$

This relation predicts that as M_{t_d} increases, $\langle I \rangle$ is decreased. Eq. (7) is quite similar to the equation used to monitor the oxygen uptake by PMMA spheres [29,30]. 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 [13]

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

Here, M_t represents the amount of materials absorbed or desorbed at time t , M_∞ is the equilibrium amount of material, and d is the thickness of the slab. Combining Eq. (8) with Eq. (7) and assuming that the number of unquenched Py molecules are proportional to $\langle I \rangle / \langle I_0 \rangle$, the following relation can be written as

$$\ln\left(\frac{\langle I \rangle}{\langle I_0 \rangle}\right) = \ln B_1 - A t_d, \quad (9)$$

where $B_1 = 8/\pi^2$ and $A = D\pi^2/d^2$. Normalized $\langle I \rangle$ data are plotted in Fig. 4 according to Eq. (9), where linear regression of the curve produced B_1 and D values as 0.93 and $0.97 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. Here one has to note the agreement between the theoretical and observed B_1 values.

4.2. Mean lifetimes

Mean lifetimes of Py were calculated from the relation

$$\langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}. \quad (10)$$

Using τ_i and A_i values for dissolving the PMMA glass, $\langle \tau \rangle$ values are measured and are observed to decrease exponentially as t_d is increased. In order to quantify these results, Stern–Volmer type of quenching mechanism is proposed for the fluorescence decay of Py in glass sample during dissolution process, where Eq. (3) can be employed. For low quenching efficiency, $\tau_0 k_q [M_{t_d}] < 1$, Eq. (3) becomes

$$\tau \approx \tau_0 (1 - \tau_0 k_q [M_{t_d}]). \quad (11)$$

Here $[M_{t_d}]$ is the quencher (solvent) concentration at time t_d . The relation between the lifetime of Py and $[M_{t_d}]$ in dissolving glass can be obtained approximately using the

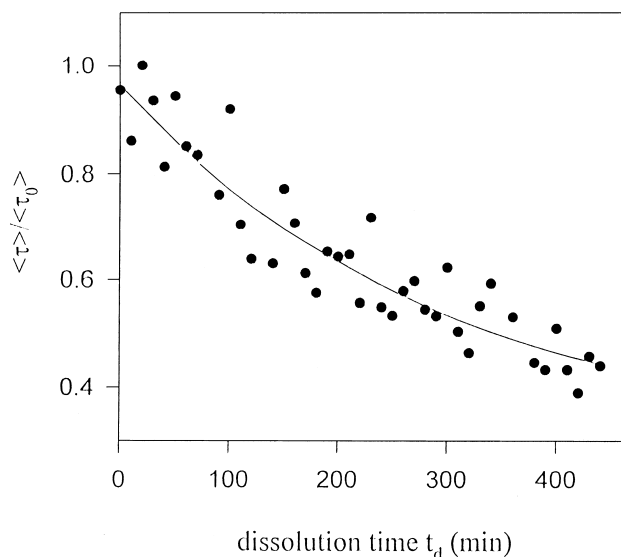


Fig. 5. The fit of the normalized $\langle \tau \rangle$ data to Eq. (14). The fit of the data to Eq. (14) produced the D value.

volume integration of Eq. (11) and the following relation is obtained

$$\frac{\langle \tau \rangle}{\langle \tau_0 \rangle} = 1 - C \frac{M_{t_d}}{M_\infty}, \quad (12)$$

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

$$M_{t_d} = \int_0^d [M_{t_d}] dv, \quad (13)$$

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

Combining Eqs. (12) and (8), the following relation is determined

$$\frac{\langle \tau \rangle}{\langle \tau_0 \rangle} = 1 - C + B_2 \exp(-At_d). \quad (14)$$

Here $B_2 = CB_1$. Normalized $\langle \tau \rangle$ data are fitted to Eq. (14) in Fig. 5, which produced the D value as $1.41 \times 10^{-6} \text{ cm}^2/\text{s}$. The quenching rate constant, k_q , is also obtained from this fit and found to be $6.66 \times 10^5 \text{ m}^{-1} \text{ s}^{-1}$ where B_1 value is used from previous measurement. These observed values of D ($10^{-6} \text{ cm}^2/\text{s}$) are consistent with our previous observations [24].

The quenching rate constant, k_q , is given by the Smoluchowski model [1], as in Eq. (15) where the magnitude of k_q is related to the diffusion coefficient of the interacting species as

$$k_q = \frac{4\pi ND_m R}{1000}, \quad (15)$$

where D_m is the mutual diffusion coefficient, N the Avogadro number, and R the sum of the interaction radii. D_m was

calculated from Eq. (15), using the experimentally measured value of k_q , and found to be $1.23 \times 10^{-6} \text{ cm}^2/\text{s}$, where R is taken as 7.15 \AA . The observed D_m is typical of a small molecule, diffusing in a liquid environment [5,6], and is slightly larger than the average desorption coefficient, D ($1.19 \times 10^{-6} \text{ cm}^2/\text{s}$). This result is as expected, because desorption of Py together with polymer chains from a swollen gel is always slower than the Brownian motion of Py in a liquid environment.

In summary, this paper introduced a novel method, which uses the FTRF technique to measure D and D_m coefficients during dissolution of polymeric material in a good solvent. Here, one has to note that, as we measured the lifetime, no environmental corrections are needed to elaborate the data which are quite problematic when one uses fluorescence intensity data from steady state measurements.

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