

# Solvent Effect on Fluorescence Lifetimes at Swollen Glassy–Rubber Interphase Domains in Blendlike Particles

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## SYNOPSIS

Fluorescence of naphthalene (N) labeled to poly(methyl methacrylate) (PMMA) particles sterically stabilized by polyisobutylene (PIB) was studied by transient fluorescence method in iso-octane, hexadecane, and in powder form. When samples of dispersions are annealed above 60°C, their room temperature lifetimes increase, and when powder samples are so annealed, lifetimes decrease. Self-quenching effects among N\*/N pairs were eliminated to isolate unimolecular lifetimes. Low-frequency intramolecular vibrations are found responsible for the temperature dependence of nonradiative transition of excited N molecules. Corresponding activation energies are measured and found to be between 2300 and 1100 cal/mol. Solvent effects on these activation energies are discussed. © 1995 John Wiley & Sons, Inc.

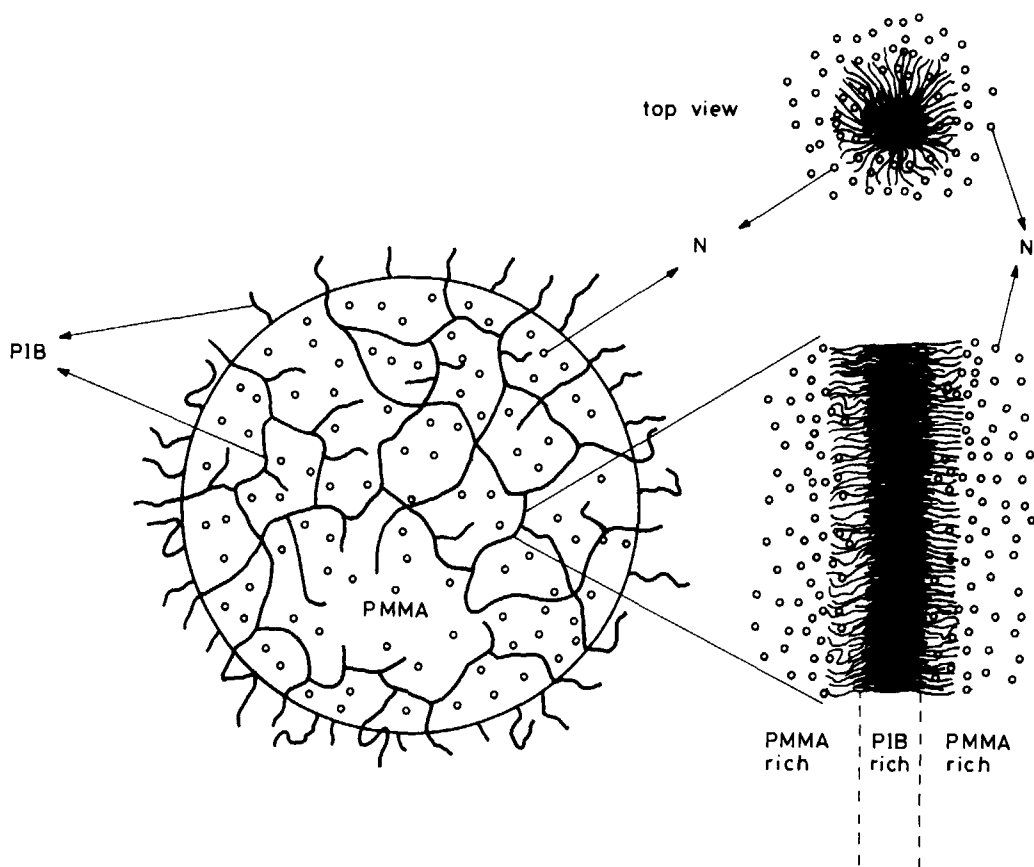
## INTRODUCTION

The fluorescence decay method has been used to study the internal morphology of blendlike poly(methyl methacrylate) (PMMA) particles.<sup>1–5</sup> These particles are spherical and usually prepared by dispersion polymerization of methyl methacrylate (MMA) in cyclohexane in the presence of butyl rubber.<sup>6</sup> The major component in this type of particle, PMMA homopolymer of broad molecular weight distribution, is present at about 95–97% by weight. During the reaction, grafting occurs between the butyl rubber and the growing PMMA chains. Most of the graft copolymer is buried in the particle interior, where it forms an interconnected network<sup>2–4</sup> of polyisobutylene (PIB). Some graft copolymer forms a monolayer on the particle surface, which serves as the steric stabilizer. Thus, these particles have an interpenetrating networklike global morphology. This global feature of the morphology has been of interest and studied carefully.<sup>2–4</sup>

The nature of the interface between the PIB and PMMA phases, where they mix and form an interphase domain, was studied using transport experiments<sup>7</sup> involving fluorescence quenching and

energy transfer within PMMA–PIB particle dispersion in aliphatic hydrocarbon liquid with a fluorescence dye. It was observed that the distribution of PIB phase in PMMA showed a Gaussian type distribution.<sup>7</sup> In Figure 1, cartoon representation of the interphase structure in PMMA–PIB particle is depicted for illustration, where PMMA phase is exclusively labeled with naphthalene N. Solvent penetration into nonaqueous dispersions (NAD) of PMMA–PIB particles were examined by ESR Spectroscopy, and the interconnected nature of the particle was found to be responsible for the penetration of solvent molecules into glassy PMMA phase and/or PIB–PMMA interphase domains.<sup>8</sup> The measured diffusion coefficients in various solvents were found inversely proportional to the apparent viscosity of the environment inside the interphase domain, and maximum diffused amount of solvent molecules in to the particle was found inversely proportional to polymer–solvent interaction through the solubility parameters.<sup>8</sup>

It has been known that the fluorescence decay of aromatic molecules are effected by both radiative and nonradiative processes.<sup>9</sup> If the possibility of perturbation due to oxygen is excluded, the radiative probabilities are found to be relatively independent of environment and even of molecular species. Environmental effects on nonradiative transitions, which are primarily intramolecular in



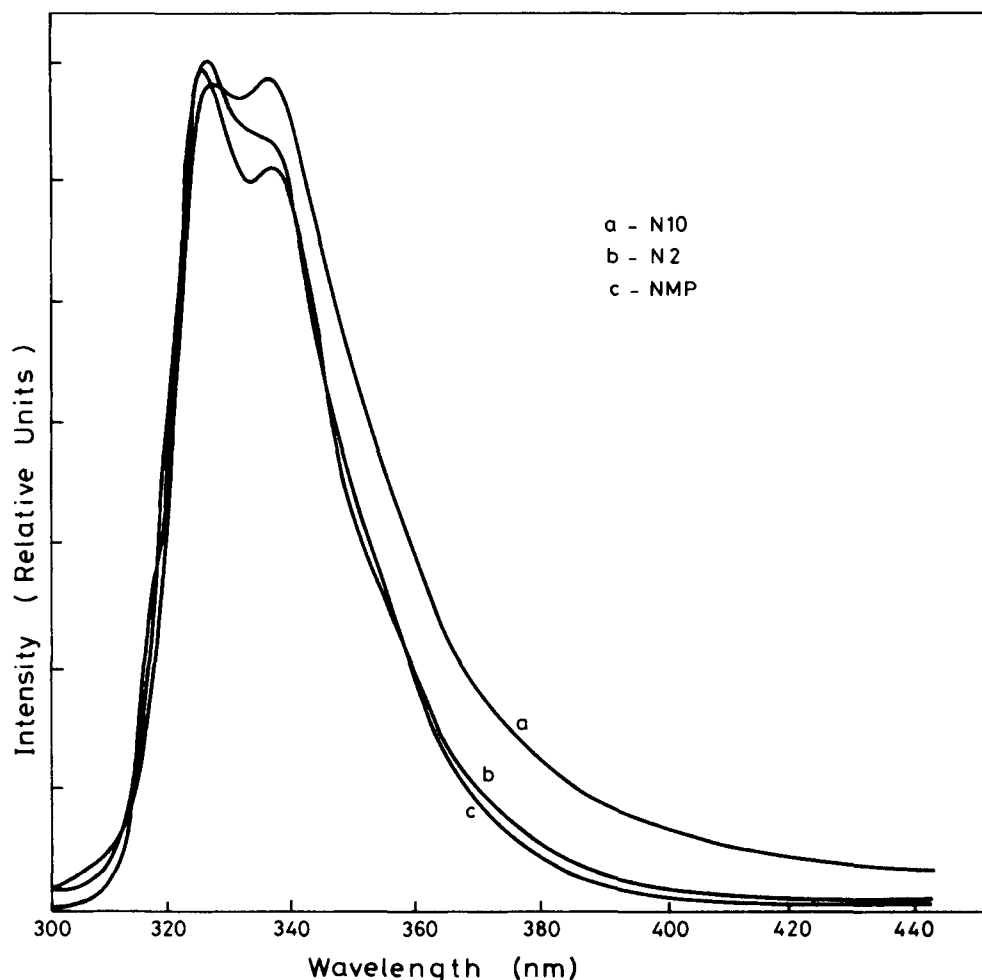
**Figure 1** Cartoon representation of naphthalene-labeled PMMA-PIB particle with the magnified part of the interphase domain.

nature, are believed to arise from a break down of the Bohr-Oppenheimer approximation.<sup>10</sup> The role of the solvent in such a picture is to add the quasicontinuum of states needed to satisfy energy resonance conditions. The solvent acts as an energy sink for rapid vibrational relaxation, which occurs after the rate-limiting transition from the initial state. The effects of the environment on such transitions are expected to be larger above room temperature.<sup>11</sup> As the temperature of a liquid solution is varied, the environment about the molecule changes and much of the change in absorption spectra, fluorescence yields, and fluorescence lifetimes in solution can be related to the changes in solvent viscosity. A matrix that changes little with temperature will enable one to study molecular properties themselves without changing environmental influence. PMMA has been used such a matrix in many studies.<sup>12</sup>

The fluorescence lifetimes of almost all aromatic molecules studied, show a decrease as the temperature is raised.<sup>9</sup> Because, in most cases the radiative lifetime remains constant, the decrease in fluores-

cence lifetime corresponds to an increased rate for radiationless loss of energy. This increase can be either in the intersystem crossing from excited singlet ( $S_1$ ) to triplet ( $T_1$ ) or in the direct transition from  $S_1$  to ground singlet ( $S_0$ ). The activation energies for these processes were found to be 250 to 500  $\text{cm}^{-1}$ .<sup>9</sup>

In this article, solvent effects on activation energies of unimolecular processes of naphthalene (N) in PMMA-PIB particles were studied. We presented the observations on the fluorescence decay of N groups covalently attached to PMMA chains of NAD of PMMA-PIB particles. Two types of labeled materials, one with monomer mol ratio of approximately 13 : 100 : 2 for IB : MMA : N, is referred to a N2, the other, of approximately 13 : 100 : 10, as N10, were examined. Their fluorescence decay profiles were measured when these particles are in hexadecane, isoactane, and in powder form. Successive lifetime measurements were carried out during annealing, above and at room temperature. Corrections on lifetimes to isolate the bimolecular reactions at interphase domains were made to obtain the unimo-



**Figure 2** Fluorescence spectra of dispersions of N10 and N2 compared with NMP in iso-octane at room temperature.

lecular lifetimes of N groups. Activation energies were measured when PMMA particles are in powder form in hexadecane and in isoactane dispersions. Powder particles were used as a reference environment for the unchanged matrix. 1-Naphthyl(methyl) pivalate (NMP) was used as a reference fluorescence dye molecule to compare the lifetimes with N-labeled PMMA particles.

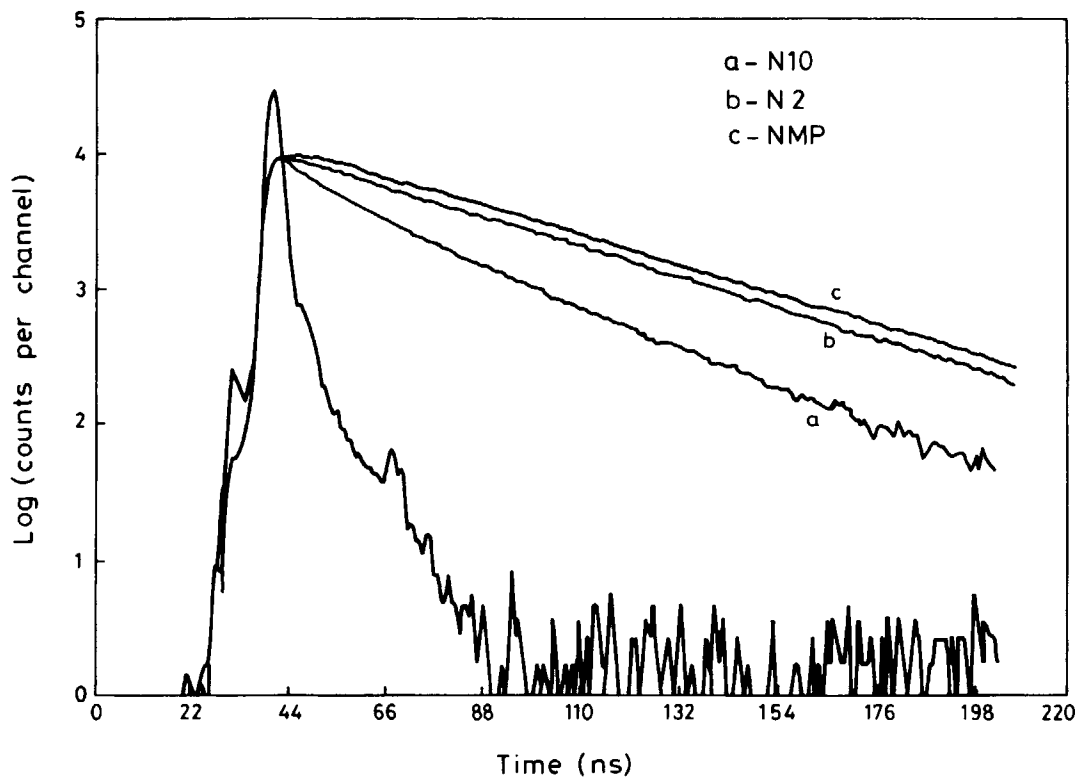
## EXPERIMENTAL

The polymer particles were prepared in a two-step process.<sup>6</sup> Polyisobutylene of nominal molecular weight 10,000 was added to a cyclohexane solution of MMA containing azobisisobutyronitrile (AIBN) as a free-radical initiator. The solution was refluxed for several hours to induce polymerization of the methyl methacrylate. The growing PMMA chains were added across double bounds present in the

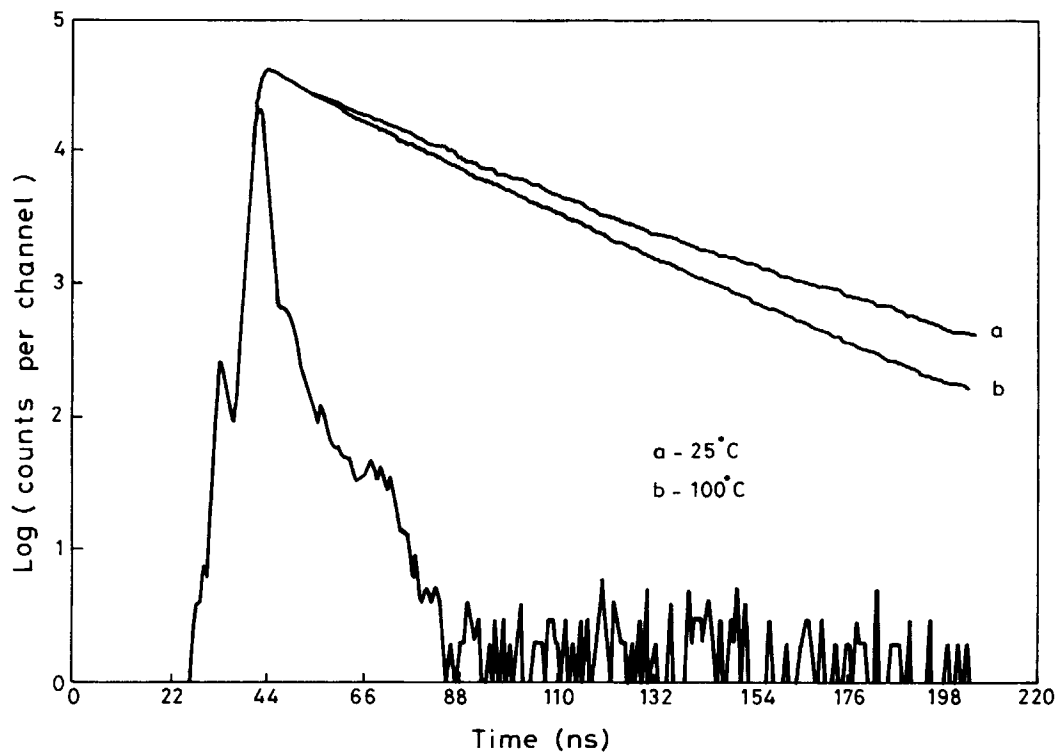
polyisobutylene to give a graft copolymer soluble in cyclohexane.

Polymerization was terminated before the copolymer became insoluble in the cyclohexane solvent. This material, the dispersant, was collected and purified by precipitation with methanol. The dispersant was then added to a second reaction vessel containing MMA and AIBN in cyclohexane. This solution was refluxed overnight.

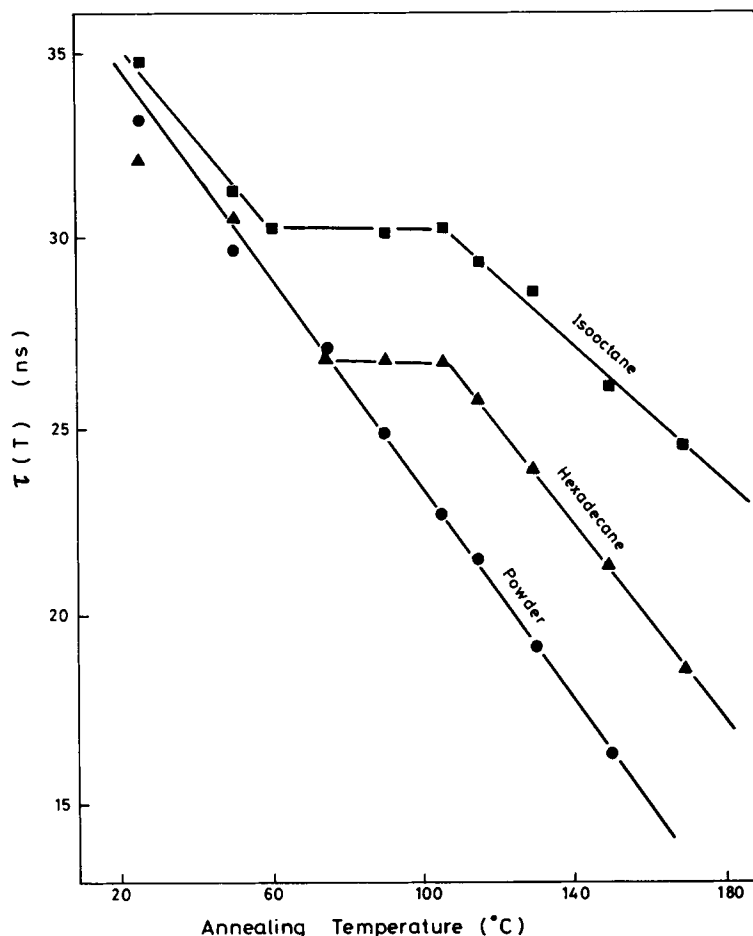
It became increasingly turbid as the reaction progressed. The particles were separated from solvent and unreacted monomers were excluded by repeated cycles of centrifugation, decanting the supernatant liquid, and redispersing the particles in fresh solvent. Dispersion in cyclohexane could be freeze dried and stored as a powder. The powders could be redispersed by subjecting their suspensions in alkane solvents to a few seconds exposure to an ultrasonic cleaning bath. Scanning and transmission electron microscopy studies in-



**Figure 3** Fluorescence decay profiles of dispersions of N10, N2, and NMP in iso-octane at room temperature.



**Figure 4** Fluorescence decay curves of N10 dispersions in iso-octane (a) at room temperature; (b) at 100°C temperature.



**Figure 5** Plots of  $\tau(T)$  lifetimes vs. annealing temperature for samples of N10 in iso-octane, hexadecane, and powder sample. (Measurements were made at given temperatures.)

indicated that the particle diameters ranged from 1 to 3  $\mu\text{m}$ .

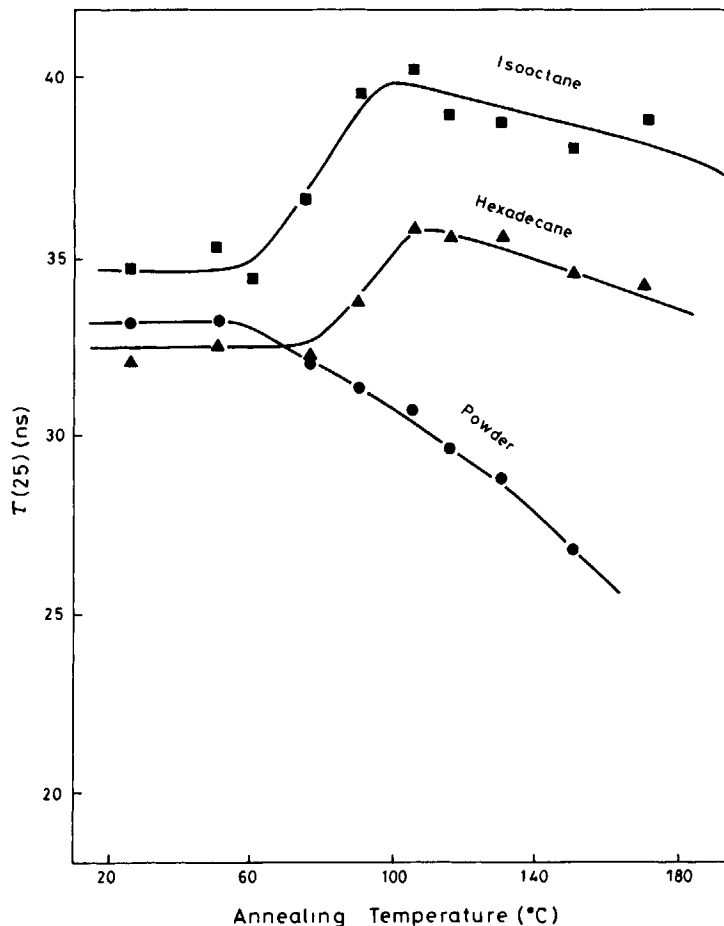
These particles formed transparent solutions in ethyl acetate and in deuteriochloroform. NMR spectra of these latter solutions permitted the composition of the polymers to be determined. Operationally, the PMMA phase in the particle is labeled by incorporating a comonomer containing a N group in the MMA polymerization step of particle preparation. The comonomer, 1-naphthylmethyl methacrylate, has a reactivity ratio somewhat less than unity for copolymerization with MMA. Hence, if MMA is in excess, the tendency will be against block of N groups. The assumption of a statistical distribution of N groups within PMMA chains is reasonable.

Dispersions in iso-octane and hexadecane solvents (ca. 3–5 mg/mL) were prepared by sonicating the mixture for 1 or 2 min in a ultrasonic cleaning bath. These samples in 12 mm o.d. quartz tubes fitted with a graded seal were degassed by several freeze-pump-thaw cycles and sealed under vacuum. Powder

samples were placed in 3 mm i.d. quartz tubes and sealed under vacuum.

Fluorescence decay profiles were measured by the time-correlated single photon counting technique,<sup>13</sup> exciting the samples at 280 nm and observing the emission through an interference filter at 337 nm. The samples were turbid to opaque. Although the excitation and emission optics were at 90° to one another, samples often had to be positioned so that one measured essentially front-face fluorescence. Fluorescence decays for these samples were nonexponential but could be fitted to a sum of two exponential terms. The fits were reasonable ( $\chi^2 < 1.3$ ). Data analysis allowed for a small correction because of scattered light (the scatter parameter varied between 0.1 to 0.5).

During the experiments, the samples were heated to the annealing temperature and kept there for 2–3 h and fluorescence decay were measured at that temperature. Each sample was allowed to cool to room temperature, and the fluorescence decay pro-



**Figure 6** Plots of  $\tau(25)$  lifetimes vs. annealing temperature for samples of N10 in iso-octane, hexadecane, and a powder sample. (Measurements were made at room temperature after annealing of the samples.)

files  $I(t)$  were remeasured. The samples were then reheated to the next higher annealing temperature and the processes were repeated.

## RESULTS AND DISCUSSION

The fluorescence spectra of N2 and N10 are shown in Figure 2. Even though the mean local concentration of N groups in N10 is quite high (ca.  $0.9M$ ), relatively little excimer emission is seen.

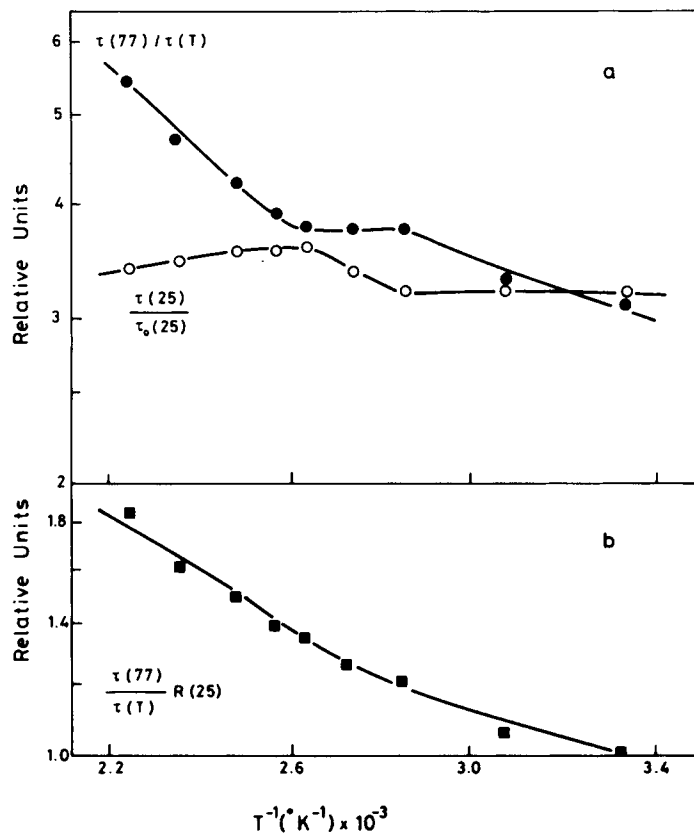
Normally, the absence of excimer emission from a chromophores such as naphthalene implies that these groups do not interact. Fluorescence decay measurements, described below, indicate that substantial quenching occurs in these samples. In amorphous solids, where motion is restricted or prevented, deactivation can occur from  $N^*/N$  pairs where the geometry leading to excimer emission cannot be achieved. This process is referred to as "self-quenching" or "con-

centration quenching." These are phenomenological terms and refer to any process of the form  $[N^* + N \rightarrow 2N]$ . Not much is known about the detailed mechanism of the deactivation process for naphthalene self-quenching. One could speculate that the interacting species are excimers whose decay, for example, by intersystem crossing to the triplet state, is much faster than their fluorescence.

A fluorescence decay trace of N10 is compared with N2 and NMP in iso-octane in Figure 3. Although nonexponential in form, it can be fit to a sum of two exponential terms

$$I(t) = A_s e^{-t/\tau_s} + A_l e^{-t/\tau_l}$$

We refer to the long-component lifetime as  $\tau_l$ , with a prefactor  $A_l$ , and the short-component lifetime as  $\tau_s$ , with a prefactor  $A_s$ . In some samples, a very short additional component was detected in  $I(t)$  and was attributed to light scattering.



**Figure 7** Plots of (a)  $\tau(77)/\tau(T)$  and  $R(25) = \tau(25)/\tau_0(25)$ , and (b) the product of ratios

$$\frac{\tau(77)}{\tau(T)} R(25)$$

vs.  $T^{-1}$  ( $^{\circ}\text{K}$ ) for the dispersion of N10 in hexadecane. Ratios and their products are given in relative units for comparison.

For us, the most significant observation is that the decay components, particularly  $\tau_l$ , are much shorter than that of an isolated N group in a PMMA matrix. For example, in a particle sample containing 0.03 mol % N, we measured a fluorescence decay time of 54 ns.<sup>14</sup> For N2, typical values of  $\tau_l$  are 43 ns; and for N10, 33 ns.

In other words, the higher local concentration of N leads to a faster decay of fluorescence.

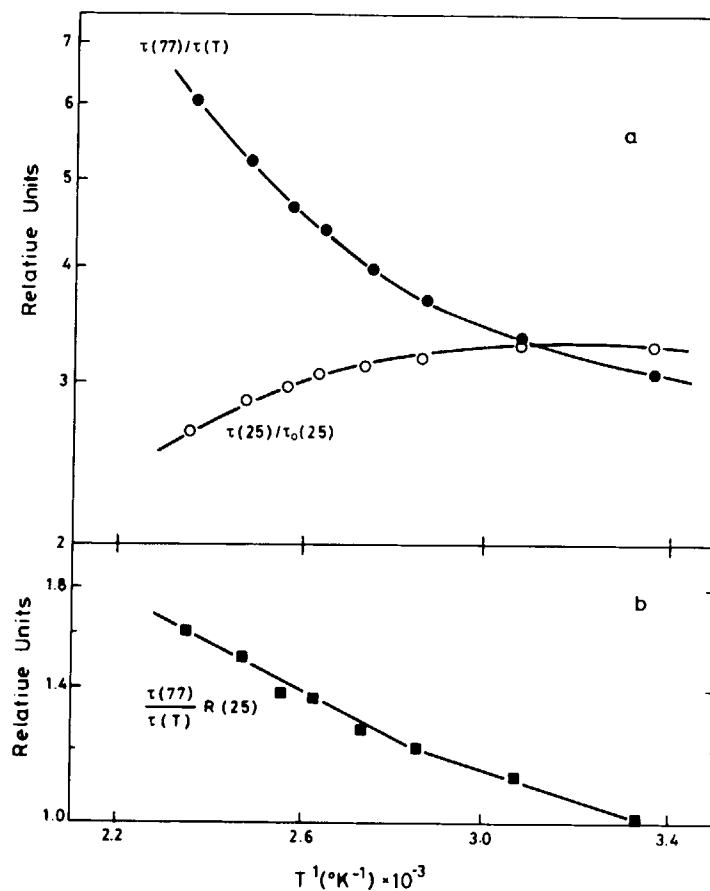
In order to help us understand these results, we measured the fluorescence lifetimes of the model compound, NMP at low concentrations in several solvents at 22 $^{\circ}\text{C}$ . In iso-octane we found that  $\tau = 46$  ns and in an polyisobutylene matrix  $\tau = 43$  ns. These values are shorter than that of the naphthylmethyl chromophore in a PMMA matrix. One explanation for the shorter lifetimes of the N groups in N2 and N10 compared to that of PMMA film is that in the former a significant fraction of the chromophores

are located in the interphase region of the particle. Isolated N chromophores exposed to PIB, iso-octane, or hexadecane should have a shorter lifetime than those located in a pure PMMA environment.

In all fluorescence decay experiments, because  $\tau_l$  and  $\tau_s$  lifetimes displayed similar behaviors against annealing temperature, from now on we will use only  $\tau_l$  lifetimes for the interpretation of the results.  $\tau(T)$  and  $\tau(25)$  will be referred to  $\tau_l$  lifetimes, measured at given annealing temperature and at room temperature after cooling down the samples, respectively.

### A-Annealing Effects

Fluorescence decay profiles,  $I(t)$  of N10 in iso-octane at room temperature and at 100 $^{\circ}\text{C}$  is presented in Figure 4. At 100 $^{\circ}\text{C}$ , faster decay in N10 fluorescence is observed compared to N10 decay at room temperature. As the temperature was raised  $\tau(T)$ , lifetimes



**Figure 8** Plots of same parameters of Figure 7 for N10 powder sample.

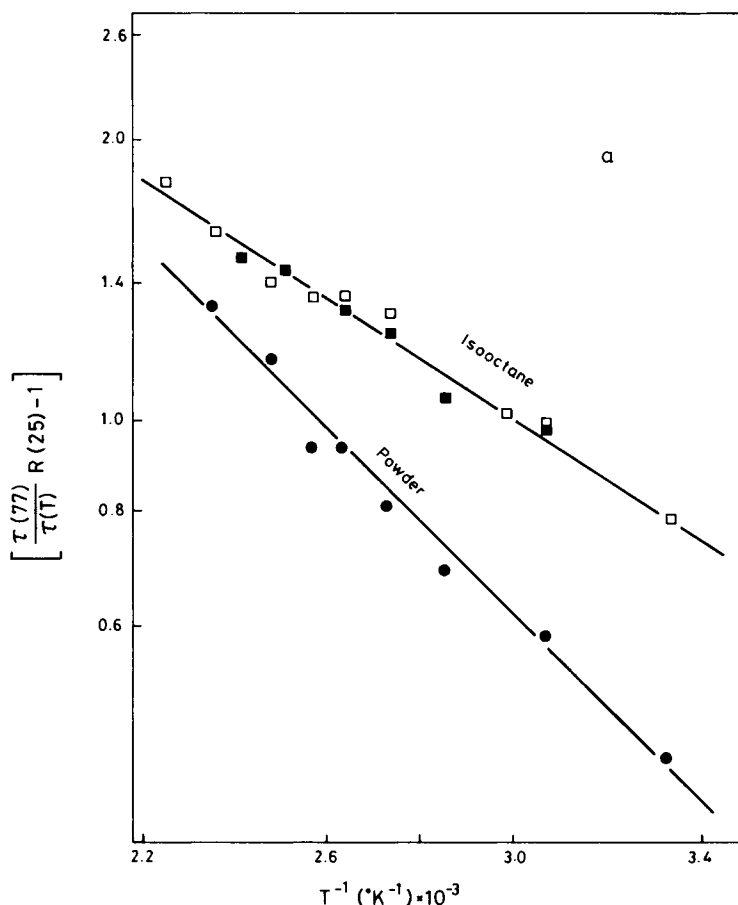
of N10 in iso-octane and in hexadecane decreased, presenting a short plateau in between 60 to 115°C. However, for powder samples,  $\tau(T)$  lifetimes displayed continuous decrease as the temperature was raised. Fluorescence lifetimes,  $\tau(T)$  of N10 are plotted vs. annealing temperature for the two types of dispersions and powder samples in Figure 5.

In Figure 6, fluorescence lifetimes,  $\tau(25)$ , measured at room temperature, are presented vs. annealing temperature. It is seen that  $\tau(25)$  values of the N10 dispersions are not effected by annealing the samples up to 60°C; however, they increased when the samples were heated successively to higher temperatures. Above 105°C  $\tau(25)$  values slightly decreased by increasing the temperature. Annealing the powder sample of N10 above 60°C leads only to a decrease in  $\tau(25)$ , which is substantial, from 33 to 26 ns. Our interpretation of this result is that the annealing process leads to an increase in self-quenching between  $\text{N}^*/\text{N}$  pairs. This might occur through a contraction of the phase containing the N groups or a migration of N groups into the interphase domain where their local concentration would

increase. If one were presume that all the N groups were located specifically in the PMMA rich domains, the effects of annealing here would have to be interpreted in terms of contraction within that phase. The volume changes necessary to cause a decrease in  $\tau(25)$  from 33 to 26 ns would be manifold larger than one could anticipate from the known thermal expansion coefficient of PMMA.

Annealing dispersions of N10 in iso-octane and hexadecane leads to an increase  $\tau(25)$ . The extent of the increase goes up with temperature when the annealing temperature is in the range 60–105°C but becomes less pronounced when the dispersions are heated to higher temperatures. The increase of  $\tau(25)$  could be due to the movement of N groups into the PMMA phase where the intrinsic lifetime of the chromophore is longer. We think this is unlikely. If the N groups were preferentially soluble in PMMA rather than PIB, this process would be most prominent in the powder samples where the volume fraction of interphase is smallest. Most probably, iso-octane and hexadecane swell the interphase domain. Heating should promote the extent of swelling. Upon





**Figure 9** Plots of eq. (4) for dispersion of N10. (a) In iso-octane (two different samples); (b) in hexadecane. (In both figures, plots are compared with powder N10.)

cooling to room temperature, PMMA is once again below its glass transition temperature ( $T_g$ ) and solvents are trapped within the interphase domain. As in the case of the powder samples, annealing probably leads to a net movement of N groups to the interphase. Because of swelling by solvent penetration, there must be a net dilution of N groups and a decrease of self-quenching.

High temperature lifetimes  $\tau(T)$  of N10 in iso-octane were found to be much longer than in hexadecane. Similar behaviors were observed for room temperature lifetimes  $\tau(25)$  of N10 dispersions. These results can be explained with the solvent viscosities which are 0.5 (cp) for iso-octane and 3.45 (cp) for hexadecane.<sup>15</sup> These qualities of solvents may effect the both lifetimes [ $\tau(T)$  and  $\tau(25)$ ] in the swollen interphase domains.

### B-Solvent Effects on Activation Energies

The temperature dependence of  $\tau(T)$  lifetimes can be quantified by combining the models developed by

Lin-Bersohn<sup>16</sup> and Inokuti-Hirayama.<sup>18</sup> A complete theoretical derivation relating to the temperature dependence of radiationless transition for unimolecular decay was given by Lin and Bersohn,<sup>16</sup> where vibrational relaxation time was assumed to be much shorter than the electronic relaxation time. Resonance interaction among the solute molecules in the solvent was assumed to be very small, and electronic relaxation occurs through energy transfer from electronic levels to vibrational levels. They have derived the equation as follows:

$$\left( \frac{\tau(77)}{\tau(T)} - 1 \right) = A e^{-\Delta E/kT} \quad (1)$$

where,  $\tau(77)$  and  $\tau(T)$  are the unimolecular lifetimes at 77 K, and at higher temperatures, respectively.  $A$  and  $\Delta E$  are related to the vibrational levels. Kropp and Dawson<sup>9</sup> have observed that temperature dependence of fluorescence lifetimes of many aromatic hydrocarbons doped in PMMA matrix obey the eq. (1). They have also shown that in most cases the

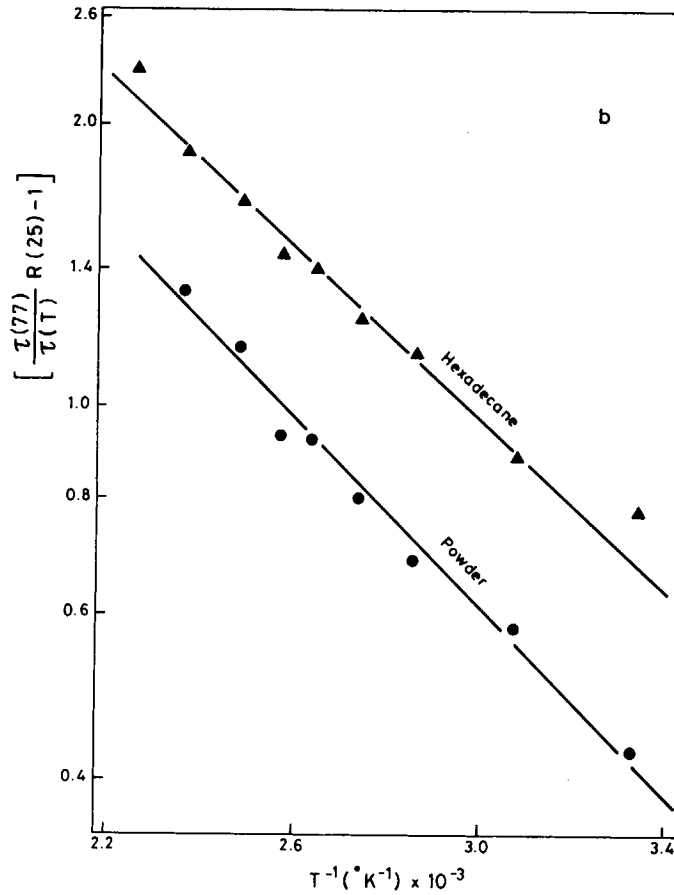


Figure 9 (Continued from the previous page)

radiative lifetime of fluorescence emission is temperature independent.

In our observations, the shorter fluorescence lifetimes at high temperatures may correspond to an increased rate for radiationless loss of energy. Since eq. (1) can only be used for the unimolecular processes, in our purpose we have to eliminate the bimolecular processes from our measured fluorescence lifetimes. In other words, self-quenching processes due to the concentration has to be removed from measured  $\tau(T)$  lifetimes.

Self-quenching in rigid media is normally interpreted in terms of active sphere model first presented by Perrin,<sup>17</sup> which was then modified by Inokuti and Hirayama,<sup>18</sup> to account for observations made by Ermolaev<sup>19</sup> that the triplet lifetime of a chromophore in a rigid matrix varies with its concentration. Based upon this model, it was shown that the phosphorescence intensity should decay as

$$I(t) = I_o \exp(-t/\tau_o - [N]/[N_o]) \quad (2)$$

Here,  $\tau_o$  is the unimolecular lifetime and  $[N_o]$  is called the critical transfer concentration, defined by  $[N_o] = 3/(4\pi R_o^3)$ , where  $R_o$  is the critical transfer radius. According to eq. (2), increasing  $N$  concentration,  $[N]$ , the decay rates increase due to self-quenching between  $N$  molecules. In our case, eq. (2) can be used to eliminate the bimolecular processes from fluorescence lifetimes. In order to do that decay time,  $\tau(25)$  can be written to depend upon  $[N]$  according to following equation:<sup>20</sup>

$$\frac{\tau(25)}{\tau_o(25)} = 1 - \frac{[N]}{[N_o]} \quad (3)$$

Here,  $[N]$  represents the local concentration of  $N$  groups in labeled particles. In NMP systems with  $10^{-5}$  m concentration, the  $\tau(25)/\tau_o(25)$  ratio must be always taken in unity, which means all processes are unimolecular in nature. Then the fluorescence lifetime of NMP is taken as unimolecular lifetime ( $\tau_o(25) = 46$  ns). However, in N10 dispersions, due to the swelling, local  $[N]$  concentration changes and

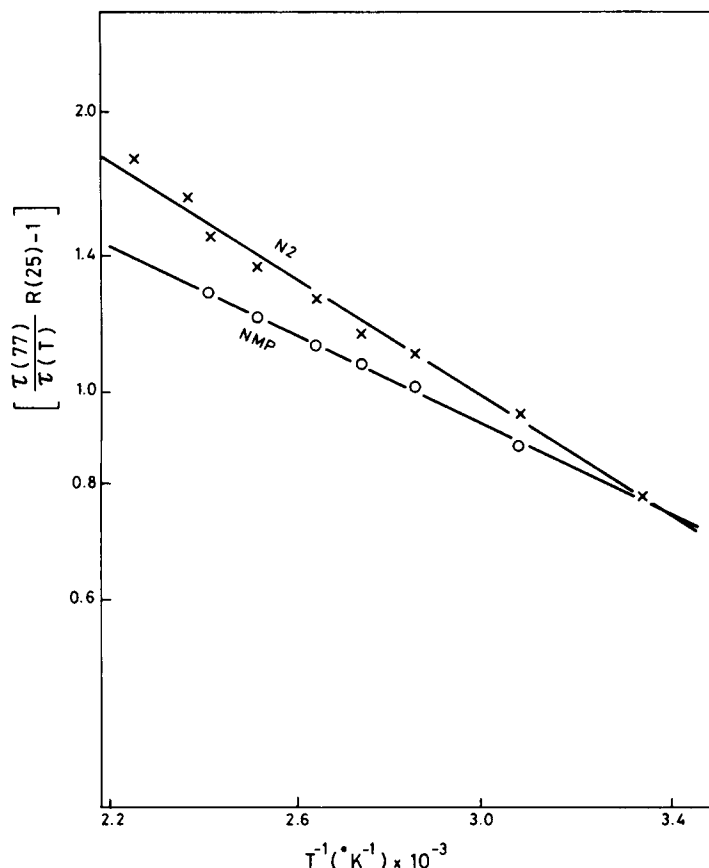


Figure 10 Plot of eq. (4) for dispersion of N2 and NMP in iso-octane.

$\tau(25)$  lifetime varies at each annealing step, as a result  $R(25) = \tau(25)/\tau_o(25)$  ratio changes. In Figure 7(a),  $\tau(77)/\tau(T)$  ratios are compared with the  $R(25)$  for N10 in hexadecane as a function of  $T^{-1}$  ( $^{\circ}\text{K}^{-1}$ ) in semilog scale.  $\tau(77) = 82$  ns was used, and ratios were taken in relative units to compare them in the same scale. In Figure 7(b), the product of the ratios are plotted vs.  $T^{-1}$  ( $^{\circ}\text{K}^{-1}$ ), where continuous behavior is observed. The discontinuities in ratios due to swelling and self-quenching in Figure 7(a) compensate each other after multiplication and smooth decrease is observed vs.  $T^{-1}$  ( $^{\circ}\text{K}^{-1}$ ) in Figure 7(b). Similar features were observed in dispersions of N10 and N2 in iso-octane.  $\tau(77)/\tau(T)$  and  $R(25)$  ratios presented continuous decrease and increase

vs.  $T^{-1}$  ( $^{\circ}\text{K}^{-1}$ ) for N10 powder, respectively. These ratios and their products are plotted against  $T^{-1}$  ( $^{\circ}\text{K}^{-1}$ ) in Figure 8(a) and 8(b), respectively. Compensation between environmental changes and self-quenching is again seen in Figure 8(b). A smooth decrease in the product of ratios in Figures 7(b) and 8(b) may suggest that  $R(25)$  ratio can be used as a parameter to isolate the unimolecular processes from the fluorescence lifetimes. In this purpose, eq. (1) can be modified and written in the following form:

$$\left( \frac{\tau(77)}{\tau(T)} R(25) - 1 \right) = Ae^{-\Delta E/kt} \quad (4)$$

Table I

	N10		N2	NMP	
Environment	Powder	Hexadecane	Iso-octane	Iso-octane	Iso-octane
$\Delta E$ (cal/mol)	2262	2045	1438	1413	1080

In Figure 9(a) and 9(b), log plots of eq. (4) for dispersions of N10 in iso-octane and in hexadecane are compared with N10 powder sample. In both cases, plots showed straight lines in the semi-log scale. In Figure 10, plots of eq. (4) for N2 and NMP in iso-octane are presented where, in the latter case,  $R(25) = 1$  was taken.

These results all indicate that modification of eq. (1) by using the self-quenching ratio [eq. (3)] eliminated the bimolecular processes from the fluorescence lifetimes. Activation energies, now belong to unimolecular lifetimes, can be obtained from the plots of eq. (4). The measured  $\Delta E$  values are listed in Table I for N10, N2, and NMP in various environments.

Activation energies in Table I suggest that the low-frequency intramolecular vibrations are responsible for the temperature dependence of non-radiative transitions of the excited molecule.<sup>21</sup> From above results, one may conclude that these activation energies are effected by the environment around the excited molecule. For example  $\Delta E$  for N10 in hexadecane is found much larger than in iso-octane, and  $\Delta E$  for powder N10 is found larger than both of them. On the other hand,  $\Delta E$  is observed smallest for NMP in iso-octane. Our observed,  $\Delta E = 2262$  cal/mol value for N10 powder, in which naphthalenes are covalently attached to PMMA chains, is much larger than Siegel's  $\Delta E = 1380$  cal/mol value,<sup>21</sup> where N molecules are free in the PMMA matrix. Larger  $\Delta E$  in PMMA particles may be attributed to the effects of segmental constraints of Polymer chain on excited N molecule. Such constraints are usually effect on the nuclear conformations of the excited molecule.<sup>21</sup>

As the matrix constraints on N molecules decrease due to swelling of interphase domains by alkene solvents, activation energies decrease. Because iso-octane has smaller viscosity than hexadecane, matrix constraints of an N can be expected much less than in the former one; as a result,  $\Delta E$  values in iso-octane were found to be smaller in N10 and N2 dispersions. The role of solvent in such systems is to add the quasicontinuum of states needed to satisfy energy resonance conditions, then solvent acts as an energy sink for rapid vibrational relaxation that occurs after the rate-limiting transition from the initial state.<sup>10,11</sup>

I would like to thank to Professor M. A. Winnik for providing me with his facilities and his stimulating ideas.

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Received July 11, 1994

Accepted December 2, 1994