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FLUORESCENCE IN STRUCTURED MEDIA: A LOOK AT POLYMER COLLOIDS*

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Abstract - Non-aqueous dispersions of PMMA containing naphthalene and anthracene groups of fluorescence probes, and sterically stabilised by P1B have been studied by fluorescence spectroscopy. The results presented, are inconsistent with a core-shell structure for the particles and as a consequence a new model, based upon a phase-separated microphase structure for the particles is proposed.

INTRODUCTION

Polymer colloids are polymer particles, ranging in size from tens of Angstroms to tens of microns, dispersed in a liquid medium (Ref. 1). They comprise a broad spectrum of materials, with industrial applications primarily in the coatings field (inks, waxes, paints, toners). Some of these materials are quite complex, containing several different incompatible polymers (Ref. 2). Others are seemingly quite simple, such as the monodisperse polystyrene latexes, which one considers to be homogeneous isotropic plastic spheres. These systems have been studied extensively by electron microscopy. Nonetheless, very little is known of their morphology, particularly in multicomponent particles. Even less is known about the details of the particle formation process.

Our interest in these systems was kindled through discussions with colleagues at the Xerox Research Centre of Canada. I had been touting the great potential of fluorescence probe techniques in polymer science, drawing analogies to their applications to biopolymers (Ref. 3). Several people at Xerox, particularly M.D. Croucher suggested that a study of alkane dispersion of polymer particles might be useful. Such materials can serve as high technology coloured inks in liquid development electrostatic imaging systems. Croucher and I began our collaboration some three years ago with the aid of a special grant from NSERC Canada.

Non-aqueous dispersions (Ref. 2) are stabilized against flocculation by a surface covering of a polymer which is very soluble in the medium (the "continuous phase"). The soluble polymer is anchored to the particle. Its chains protrude into the solvent. Since these chains are in a good solvent, they form swollen coils which resist interpenetration by coils of the polymer on a second particle. This resistance to the interpenetration of surface-bound polymer coils inhibits the close approach of two particles. This stabilization mechanism is called "steric stabilization."

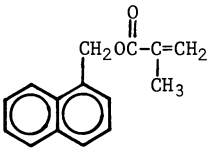
The polymer particle itself is normally insoluble in the medium. It is also immiscible with the stabilizer chains. Not much is known about the mechanism of anchoring, but one frequently considers that a shell of stabilizer is formed about a core of the insoluble homopolymer. Hence these particles are frequently called "core-shell" materials.

Most non-aqueous dispersions are prepared from recipies reported in the patent literature. They are prepared from industrial polymers which frequently are not well characterized, and sometimes involve steps which seem to have no rationale. The diversity of choice is staggering. The individual recipies have been formulated with an eye to optimizing some ultimate application (eg. paint viscosity) rather than for generating well characterized discrete structures. One has to begin somewhere. Croucher and I decided to devote our initial efforts to looking at poly(methyl methacrylate) [PMMA] particles stabilized by polyisobutylene [PIB]. We chose to modify the published recipie by incorporating fluorescent derivatives of methyl methacrylate [MMA] along with MMA in the final step of the synthesis.

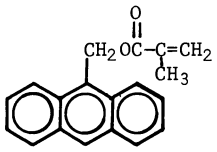
Labelled particles were prepared in the following way (Ref. 4): Initially a graft copolymer of PIB-PMMA was prepared by carrying out PMMA polymerization in the presence of butyl rubber containing ca. 2% unsaturation. This stabilizer was then added to a reaction mixture containing MMA, a chromophore-containing comonomer, an initiator, and an alkane solvent in which PMMA is insoluble. When this mixture was heated, particles formed after

*This paper is part 7 in a series "Luminescence Studies of Polymer Colloids".

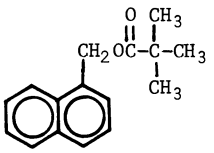
several hours. Particles were purified by repeated centrifugation followed by resuspension in fresh solvent. The particles could be stored in this fashion or freeze-dried from cyclohexane. Freeze-dried powder samples could be redispersed by mixing them with alkane solvent and then immersing the flask for a minute or two into a low power ultrasonic cleaning bath.



NMMA



AMMA



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Several chromophore-containing monomers were considered. Initial experiments used 1-naphthylmethyl methacrylate [NMMA] or 9-anthrylmethyl methacrylate [AMMA]. Thus we prepared particles with naphthalene [N] labels in the core (referred to as N2 and N10 for those containing 2 mol% and 10 mol% N groups) and particles with anthracene [A] labels in the core (referred to as A2 and A10). We also prepared the corresponding pivalate esters (e.g 1) to serve as model compounds for fluorescence from polymer bound chromophore.

Since the particles are not cross-linked, they could be dissolved in solvents like ethyl acetate or chloroform which are good solvents for PMMA. The composition of the particles could be characterized by ^{1}H nmr of their solutions in $CDCl_3$. In this way we learned that molar composition (IB/MMA/N) of two of the naphthalene containing particles were N2:13/100/2; N10: 13/100/10. The chromophore distribution in the PMMA chains can be estimated from the reactivity ratios of MMA and NMMA. In our case, these ratios are near unity; consequently we expect a statistical distribution of N groups along the chain. The fluorescence decay curves of solutions of the copolymer in ethyl acetate also indicate the absence of large blocks of N-containing segments.

We still know relatively little about the molecular weights of the polymers in the particles. The gel permeation chromatography [gpc] analyses of these materials are curious in that the apparent molecular weights are quite low. They are clearly less than 10^5. Peak retention times correspond to those of polystyrene standards of M = 2000 to 10000. Interpretation of these values is difficult, particularly since grafting of PMMA to PIB (which is poorly soluble in the gpc solvent THF) could induce contraction of the hydrodynamic volume of the polymer.

The classical picture of polymer colloid morphology is the "core-shell" model (Ref. 1,2). According to that model our particles should have a core of PMMA homopolymer surrounded by a shell of PIB. From the size and composition of N2 and N10, each 2 μm in diameter, we estimate that the radius of the PMMA core should be 9600Å, covered by a shell of PIB 370Å thick. One can see almost immediately a problem of the core-shell model for our system. The supposed thickness of the PIB layer is significantly greater than the random coil dimensions of the PIB in the molecule. Since any PIB not anchored to the particle would dissolve away, one has to consider whether significant amounts of PIB are trapped within the particle core.

FLUORESCENCE DECAY STUDIES OF N2 AND N10

Both N2 and N10 show typical naphthalene fluorescence spectra, Fig. 1. Part of the long wavelength tail in the spectra, more pronounced in N10 than N2, is due to naphthalene excimer emission. Even in N10 it contributes less than 10% to the total fluorescence. The fluorescence decay trace of an N10 dispersion in isooctane, measured at 337 nm, is shown in Fig. 2. There is a small component with a short lifetime (ca. 12 ns) and a larger component with a longer lifetime (ca. 39 ns).

The short component is due to emission from N groups located within spatial domains of high local N concentration (Ref. 4). These domains arise both from random fluctuations of N group concentrations as well as from sequences of adjacent N groups within individual chains. The fluorescence properties of PMMA-NMMA copolymers have been studied in detail (Ref. 5). If particle synthesis led to extensive formation of poly-N blocks, the 337 nm fluorescence decay curves would be dominated by the short component (τ_{sh}^{337}), and excimer formation would be more prominent than that seen in Figure 1.

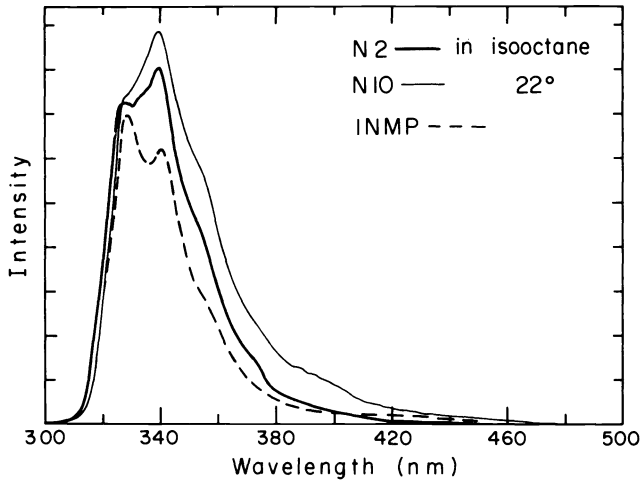

Fig. 1. Fluorescence spectra of N2 and N10 dispersions in isooctane at room temperature. The dotted line indicates the fluorescence of the model compound 1 at 10^{-5} M in isooctane.

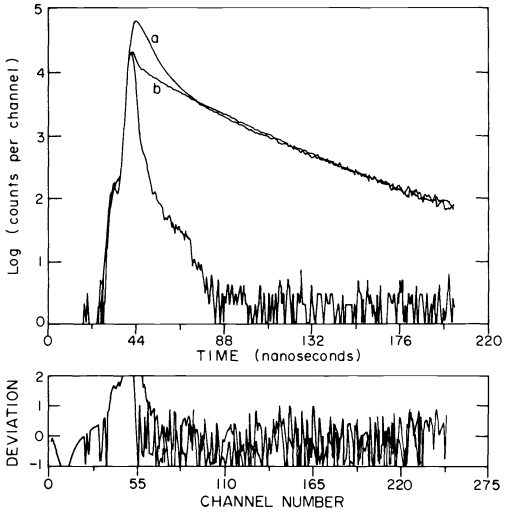

Fig. 2. A plot of log I(t) vs t for N10 in isooctane containing 1 x 10^{-3} M anthracene. The lowermost curve is the lamp excitation profile. Samples were excited at 280 nm. The middle curve (N fluorescence) is measured at 337 nm. The upper curve (A fluorescence) is measured at 450 nm.

The decay time of the long component (τ_ℓ^{337}) provides very important information about the particle structure. One observes first of all that the value of τ_ℓ^{337} is sensitive to the N concentration within the particle. It is 39 ns in N10, 42 ns in N2, and 44 ns for the model compound 1 at 10^{-5} M in isooctane or in a PMMA film at room temperature. Self-quenching occurs, equation (1), so that τ_ℓ^{337} becomes shorter in the presence of increasing N group concentration.

$$N^* + N \longrightarrow 2N \qquad (1)$$

Good models exist for describing static quenching of luminescence in rigid media. The most appropriate is that of Inokuti and Hirayama (Ref. 6). Following Perrin (Ref. 6b), they define an active sphere of radius R_0 about each excited chromophore. In their model, k_{sq} is taken to be distance dependent. For N* at large separation from a second N, $k_{sq} = 0$

and the decay time would be the unquenched value $\tau_{N,o}$ whereas for a chromophore separation equal to R_0, $k_{sq} = (\tau_{N,o})^{-1}$. This leads to the expression (for $[N](4\pi R_0^3 N_A')/3 << 1$)

$$\frac{\tau_\ell^{337}}{\tau_{N,o}} = 1 - [N](4\pi R_0^3 N_A')/3 \qquad (2)$$

where N_A' is (10^{-3} x Avogadro's number) and [N] is the local N concentration. A plot of $\tau_\ell^{337}/\tau_{N,o}$ vs [N] should be linear, and the slope proportional to R_0^3.

The values of [N] are not known and must be estimated. Since one knows the mole fraction of N in the PMMA and the density of the PMMA phase, one can calculate that [N] = 0.7M for N10 and 0.17M for N2. With these two points and the $\tau_{N,o}$ value of 44ns, one gets a good straight line for the plot according to equation (2). From the slope one calculates R_0 = 7Å, which is not unreasonable for naphthalene self-quenching (Ref. 7).

SWELLING AND CONTRACTION OF MICROPHASES

Freeze-dried powder samples of N2 or N10 were heated for three hours to various temperatures, and then allowed to cool to room temperature. When the annealing temperature was 60° or less, no change in τ_ℓ^{337} was observed. When the annealing temperature was greater than 60°, a pronounced decrease in τ_ℓ^{337} was found. A decrease in τ_ℓ^{337} implies a contraction within the PMMA phase, leading to an increase in the local concentration of N groups.

When this experiment is repeated with alkane dispersions of N10 or N2, the effects are startlingly different. For samples heated to temperatures up to 60° no changes in fluorescence decay time were observed. Samples annealed at higher temperatures showed an increase in τ_ℓ^{337}. An increase in τ_ℓ^{337} indicates local swelling within the PMMA phase, leading to a decrease in the local concentration of N. These results are summarized in Figure 3.

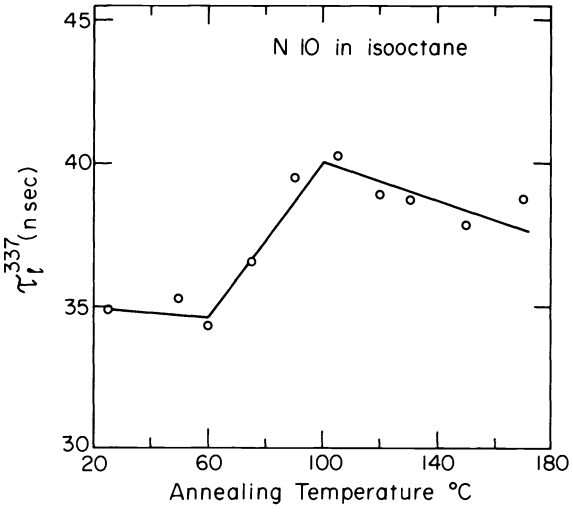

Fig. 3. A plot of the fluorescence lifetime τ_ℓ^{337} of N10 measured at 25° after samples were heated for 3 hours to the temperature indicated.

The data in Figure 3 represent the first application of fluorescence techniques to examine the swelling or contraction of a material. Three features of these experiments are particularly important. First, the spatial scale of the experiment is dictated by the R_0 value associated with self-quenching. Since R_0 is ca. 7Å, we can think of the N groups serving as a 5-10Å ruler for measuring volume changes. Second, the N groups are located exclusively within the PMMA phase of the particle. They provide a microscopic view of polymer relaxation within one phase of a composite material. Third, the changes in τ of the powder sample occur in the same temperature range as changes we observed by differential scanning calorimetry for this material. One has new insights via luminescence into a relaxation process of a glassy polymer.

There is one other feature of the data that is noteworthy. The tendency of the particle to swell is influenced by the nature of the alkane solvent in which the particle is

dispersed. This feature can be seen quite clearly in Figure 3. We do not yet have a good explanation for this phenomenon.

MEASURING SORPTION BY ENERGY TRANSFER.

Sorption is the process of small molecule uptake by a polymer. While it is traditionally measured by weight uptake for a polymer exposed to vapors of a substance (Ref. 8), we thought that fluorescence energy transfer [by the Förster mechanism (Ref. 9)] might provide a new method. With fluorescently labelled polymer dispersions serving as the donor, a small molecule energy acceptor could be dissolved in the continuous medium. Penetration of the small molecule into the particle would make energy transfer between donor and acceptor species possible.

$$N^* + A \longrightarrow N + A^* \qquad (3)$$

Anthracene [A] is an appropriate acceptor for energy transfer from excited naphthalene, equation (3). This process occurs over significant distances. Energy transfer from N* to A is characterized by an R_0 of 23Å. For static energy transfer, k_{ET} is a function of the distance r between the donor acceptor pair. The rate of energy transfer can be measured effectively for r values as small as $R_0/2$ and as large as $2R_0$. By definition, when $r = R_0$, $k_{ET} = 1/\tau_{N,o}$. Thus one can think of the N*/A pair as providing a 10 - 40Å ruler (Fig. 10). On the other hand, if A can diffuse a distance larger than R_0 during the lifetime of N*, k_{ET} provides a measure of the diffusion of A in the system.

When samples of N2 or N10 were dispersed in isooctane containing ca. 1 x 10^{-3}M A, energy transfer from N* to A could be observed when the N groups were preferentially excited at 280 nm. While this was difficult to quantify in the steady state fluorescence spectra, it could be demonstrated unambiguously in fluorescence decay measurements. For example, if dispersions of N2 and A were excited at 340 nm where only A absorbs light, and fluorescence of A monitored at 450 nm, an exponential decay with a lifetime of 5.4 ns was observed. When these same samples were excited at 280 nm, the A fluorescence showed two components, Figure 2. The short component (5 ns) in Figure 2 is due to direct excitation of A, whereas the long component (39 ns) is due to fluorescence from A excited by energy transfer from N*. Under these circumstances τ_ℓ^{450} (fluorescence from A*) was always found to be equal to τ_ℓ^{337} (fluorescence from N*).

$$\frac{1}{\tau_\ell^{450}} = \frac{1}{\tau_{\ell,o}^{337}} + k_{ET}[A] \qquad (4)$$

Quite to our surprise we discovered that the naphthalene fluorescence decay times in N2 and N10 were sensitive to the concentration of [A] in the continuous medium (Ref. 4). The decay rates followed Stern-Volmer kinetics, equation (4), where we use the subscript $_o$ in $\tau_{\ell,o}^{337}$ to indicate its value when [A] = 0. Plots of $1/\tau_\ell^{450}$ vs [A] are shown for both N2 and N10 in Figure 4. One observes parallel lines, indicating identical k_{ET} values. The different intercepts reflect N-group self-quenching effects on $\tau_{\ell,o}^{337}$, as discussed above.

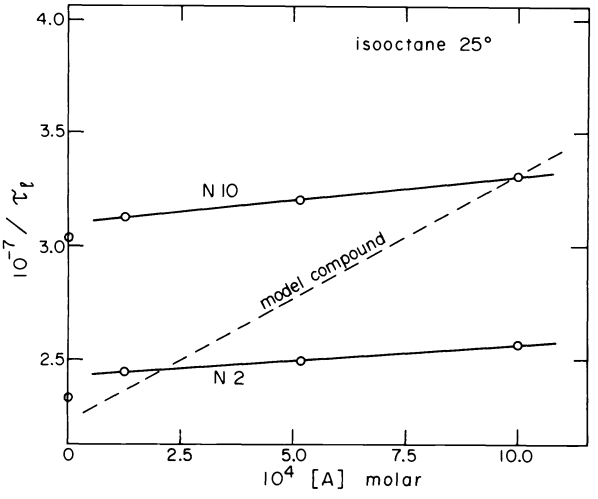

Fig. 4. Plots of $1/\tau_\ell$ vs [A] for N2 and N10 dispersions in isooctane, as well as for the model compound 1 at 10^{-5}M in isooctane (dotted line).

One of the problems in interpreting these experiments is that the concentration of [A] within the particle is not known. The system seems to reach equilibrium rather quickly, within the time of sample preparation (as short at 30 minutes). But the relative solubility of A in the particle and in the alkane solvent is unknown. If we assume a partition coefficient of unity, we calculate a value of 2.6×10^9 $M^{-1}s^{-1}$ for k_{ET}. This compares to a value of 1.8×10^{10} M^{-1} s^{-1} similarly determined for A and the model compound 1 in isooctane. The energy transfer rate within the particle is a factor of 7 slower than that involving the diffusion of small molecules in fluid solution.

Perhaps the most important point to make from these observations is that the A seems capable of communicating with equal probability with every N in the particle. Otherwise there would be an unquenchable fraction of N chromophores whose τ_ℓ[337] values would remain unaffected. From the k_{ET} values we can calculate appropriate diffusion coefficients. Thus for the pair 1 + A we calculate $D_{1,A} = 2.5 \times 10^{-5}$ cm^2 s^{-1} as the sum of their individual diffusion coefficents, a typical value for small molecules in isooctane. For N2 and N10 + A we calculate $D = 1.8 \times 10^{-6}$ cm^2 s^{-1}. Since the N groups are presumably immobile, this value describes the diffusion of A within the particle (Refs. 4,5,11). A value of $D \approx 10^{-6}$ cm^2 s^{-1} for A within the particle is very difficult to understand. There have been many studies of diffusion of small molecules in glassy polymers. Diffusion coefficients vary with the size of the diffusant (Ref. 12). Molecules the size of anthracene are characterized by D values typically 10^{-14} to 10^{-16} cm^2 s^{-1}. There is a factor of 10^8 to 10^{10} between the anticipated and experimental values of D.

This matter can be considered from another point of view: the diffusion time t varies with the square of the distance ℓ over which diffusion is detected. Diffusion to the centre of a 1 μm radius particle should take 10^{-2} s ($t = \ell^2/D$) for $D = 10^{-6}$ cm^2 s^{-1}, but 10^8 s (3 years) for $D = 10^{-16}$ cm^2 s^{-1}. If N groups throughout the particle are able to be excited by light at 280 nm, and if all the N* species are capable of transferring energy to A, the effective D value characterizing A sorption must be substantially larger than 10^{-16} cm^2 s^{-1}.

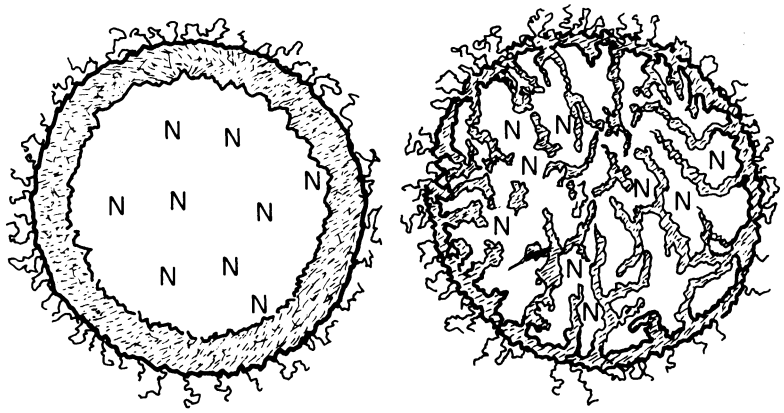

Fig. 5. The "core-shell" and "microphase" models of polymer colloid structure. The hairy appendages represent the swollen coils of the stabilizer chains at the particle surface which provide steric stabilization against particle flocculation.

THE MICROPHASE MODEL.

One of the ways to resolve the problems raised in the preceding sections is to discard the core-shell model for the PIB-stabilized PMMA particles we prepared. We replace it with a new model, which we call the "microphase model" (Ref. 5). According to the microphase model, substantial quantities of the stabilizer chain are found in the interior of the particle. Since this polymer (eg. PIB) is immiscible with the core polymer (ie. PMMA), it forms phase-separated microdomains.

If the PIB domains within N2 and N10 form a thread-like interconnecting network, we have the means to explain the fluorescence energy transfer experiments. One can imagine that alkane solvents, good solvents for PIB, would rapidly penetrate into the PIB phase and carry A molecules with it. In this phase, A would be very mobile. If one were to think of the PIB microphase as a network penetrating throughout the particle, ennervating it like capillaries within muscle, one can imagine that many of the N groups within the PMMA phase would be within 20 - 40 Å of a PIB-PMMA interface. Consequently communication would be possible between these N and A molecules in the PIB phase. A sketch of the microphase model is shown in Figure 5.

ANNEALING EFFECTS ON SORPTION.

When dispersions of N2 and N10 in isooctane containing A are heated, the τ_ℓ^{337} values decrease and the k_{ET} values determined from equation (4) increase. This is not surprising, since diffusion rates should increase with an increase in temperature. What is unusual is that when the samples are allowed to return to room temperature, the τ_ℓ^{337} values and the k_{ET} values do not return to their original value.[12]

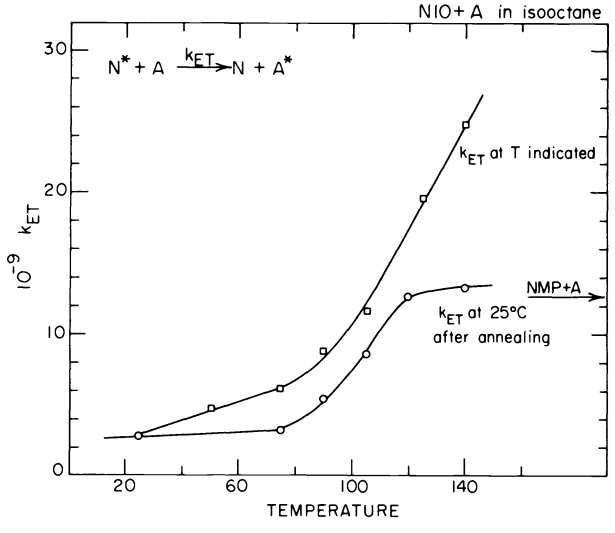

Fig. 6. Values of k_{ET}^{25} for N10 + A in isooctane determined at 25° after the samples were heated for three hours at the temperature indicated. The upper line depicts values of k_{ET} from analysis of fluorescence lifetimes measured at the temperatures indicated.

For samples annealed at temperatures below 60°, changes in k_{ET} are undetectably small. Samples annealed at temperatures above 60° show an increase in k_{ET} when lifetimes are remeasured at room temperature. A plot of k_{ET} vs annealing temperature is shown in Figure 6. The plot is sigmoidal. It suggests an irreversible relaxation of polymer morphology when the particles are heated in the presence of solvent. The increase in k_{ET} indicates that the morphology change is one of particle swelling.[12] A similar conclusion was reached on the basis of studies of naphthalene self-quenching.

In the context of the microphase model this swelling occurs within the PMMA microphases. It is likely that in the presence of alkane solvent, the PIB-PMMA interface becomes more diffuse and that the alkane (a non-solvent for PMMA) penetrates into the PMMA domains. These processes must operate to increase the local fluidity within the particle core. The mobility of A has been increased, and it is possible that segmental motion within the PMMA microphases permit relatively large amplitude motion of the N groups. Whatever the details of the process, the net effect is to make the kinetics of energy transfer within the particle as fast as that between the small molecules 1 and A in homogeneous solution.

CONCLUSIONS

Non-aqueous dispersions of PMMA particles, sterically stabilized by PIB, have been studied by fluorescence decay measurements. These measurements were carried out on particles labelled with naphthalene groups by incorporating an N-containing monomer into the monomer feed during particle synthesis. Several unusual observations were made. Fluorescence energy transfer studies indicated that anthracene molecules in the continuous phase could penetrate into the particles and diffuse ca. 10^8 to 10^{10} times faster than expected. Annealing the particles at temperatures above 60° caused local contraction within PMMA microdomains in dry powder samples, but swelling in these phases if the particles were dispersed in an alkane non-solvent for PMMA. These observations are inconsistent with a core-shell structure for the particles. A new model, based upon a phase-separated microphase structure for the particle was proposed.

These experiments pose far more questions than they answer. The most serious question is about the generality of the microphase model. The core-shell structure has been invoked for many materials. One has to establish experimental criteria for various morphologies of two-component and multi-component polymer systems. My collaborators have posed many questions about the detailed mechanism of anthracene sorption and diffusion within the particles, and our answers have not yet progressed much beyond the semi-quantitative description given here.

One feature of these experiments is clear. The luminescence techniques have provided rich information about a polymer system that otherwise would have been unavailable. In this sense we hope the experiments will serve not only as a stimulus for new luminescence experiments, but also as a focus for ideas to be tested by other complementary techniques.

Acknowledgements - This work was carried out in collaboration with Dr. M.D. Croucher of the Xerox Research Centre of Canada, initiated by a Co-op grant by NSERC Canada. Partial support was also provided by the Petroleum Research Fund administered by the American Chemical Society. The experiments described here are largely the work of Professor Onder Pekcan, Department of Physics, Haceteppe University, Ankara, Turkey, while on leave at the University of Toronto. His contributions are detailed in the publications cited. Additional assistance and valuable comments from Luke Egan and Brett Williamson in my research group were important to the development of this work.

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