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The 4-Å Ruler, Using Exciplex Fluorescence To Study Small-Molecule Diffusion into Nonaqueous Dispersions of Polymer Colloids

The kinetics of small-molecule penetration into dispersions of colloidal polymer particles is commonly determined by weight uptake[1] or by particle swelling.[2] Other methods such as radiolabeling are possible. These methods share in common the fact that they determine the gross features of the uptake process. In this paper we pose the question of whether one could unveil details of the diffusion process with techniques capable of ca. 5-Å resolution. One might imagine complexities in the diffusion of small molecules into multicomponent particles, particularly sterically stabilized dispersions composed of two linked but mutually incompatible polymers.

Fluorescence techniques, particularly fluorescence quenching interactions, provide high-resolution methods for studying diffusion processes. If one were to prepare polymer particles containing small amounts of a fluorescent dye covalently bound to one particular polymer phase, one could use fluorescence quenching techniques to study the rate of penetration of small molecules with quenching capabilities into that phase.

The kind of information one gets depends upon the choice of chromophore and the nature of the quenching process. Consequently, fluorescence studies of different pairs of interacting groups could provide complementary descriptions of the detailed mechanism of the diffusion process.

As a prototype system, we chose poly(methyl methacrylate) (PMMA) particles sterically stabilized by polyisobutylene (PIB) dispersed in various alkane solvents. In our first experiments[3,4] we examined 2-μm-diameter particles covalently labeled with naphthalene (N) groups in the PMMA chains. Fluorescence energy-transfer experiments were carried out in which we measured the rate of energy transfer from the N* groups in the particle core to anthracene (A) molecules dissolved in the isooctane medium.[3] We learned that A penetrates quickly into the particles (less than 30 min) and that energy transfer from N* to A seems to occur with equal probability from all or most of the excited N groups.

These conclusions were based upon fluorescence decay measurements in which we found that varying the concentration of A in isooctane from 1×10^{-3} to 5×10^{-3} M increased linearly the decay rate of the naphthalene chromophores. A diffusion model permitted the diffusion constant of A in the particle to be calculated. Its value of 2×10^{-6} cm^2 s^{-1} is 8–10 orders of magnitude too large

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for diffusion of A in PMMA below its glass transition temperature. Thus our results are difficult to reconcile with the classical "core–shell" picture of sterically stabilized polymer colloids.

Energy transfer from N* to A can occur over substantial distances, 10–40 Å (R_0 = 23 Å).[3,5] Thus it is possible for N* in a glassy PMMA phase to communicate across an interface to A molecules dissolved in a rubbery PIB phase. We proposed a new model for polymer colloid morphology, the microphase model,[3b] which depicts a core structure containing threads of PIB forming an innervated network throughout the core, much as capillaries penetrate muscle. In this way most of the N groups could be within 40 Å of a PIB–PMMA interface.

The energy-transfer experiments were based upon a spectroscopic process that occurs over considerable distances. We felt it would be interesting to examine a different spectroscopic process, exciplex formation, which requires donor and acceptor chromophores to be within 3–4 Å of one another.[5] Many such pairs of chromophores are possible. We chose to examine the anthracene–*N,N*-dimethylaniline exciplex, since it has been studied in great detail.[5,6] The process can be written as

$$\underset{\text{fluorescence at 380 nm}}{A^* + DMA} \xrightarrow{k_1} \underset{\text{fluorescence at 470 nm}}{(A/DMA)^*} \qquad (1)$$

Exciplex formation decreases (quenches) the intensity of A fluorescence, and the exciplex fluorescence is seen as a new broad structureless emission centered at 470 nm in alkane solvents. This suggests that if an alkane dispersion of a polymer labeled covalently with A groups in its core were exposed to DMA, exciplex emission could be used to minitor the penetration of DMA into the particle. Anthracene-labeled PMMA–PIB particles were prepared, using 9-anthrylmethyl methacrylate as comonomer with methyl methacrylate in the particle-forming step. These particles were identical in size and composition with the N-labeled particles studied previously, except that they contained 10 mol % A groups (A10) instead of N groups. Unlike the "10–40-Å ruler" energy-transfer experiments in which energy transfer could be observed immediately after sample preparation, exciplex formation (the "4-Å ruler") required hundreds of hours.

Dispersions containing 6 mg/mL of A10 in hexadecane were prepared in 6-mm-o.d. Pyrex tubes fitted with ground glass joints. Appropriate amounts of DMA were then added to give a final concentration of 0.5 M. The dispersions were degasses by three freeze–pump–thaw cycles and sealed under vacuum. The particles tended to settle on standing. They were redispersed by touching the sample tubes to a vortex mixer or by 30-s exposure to an ultrasonic bath.

A10 has a fluorescence spectrum somewhat distorted from that typical of 9-alkylanthracene derivatives. The 0–0 band is missing from the fluorescence spectrum. The high concentration of A groups in the core of the particle (0.8 M) leads to reabsorption of photons emitted at this wavelength and, possibly, to ground-state aggregates of A as well. An example is shown in Figure 1. The upper part of Figure 1 compares the fluorescence of A10 in hexadecane with that of an identical dispersion containing 0.5 M DMA 3 h after the sample was prepared. The difference spectrum shows a small band at long wavelengths which may be due to a trace of exciplex fluorescence.

The same samples are reexamined in Figure 2 after sitting at 22 °C in the dark for 333 h. It is clear that a significant amount of exciplex has formed. In the upper portion of Figure 2, the A10 spectrum and A10/DMA

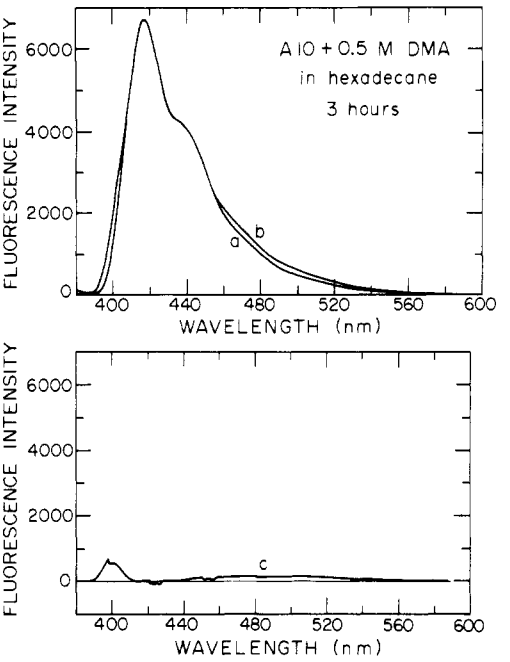

Figure 1. Fluorescence spectra of anthracene-labeled PMMA particles A10 dispersed in hexadecane in the absence (a) and presence (b) of 0.5 M *N,N*-dimethylaniline (DMA) 3 h after the DMA was added and the sample was degassed and sealed. Curve c is the difference spectrum.

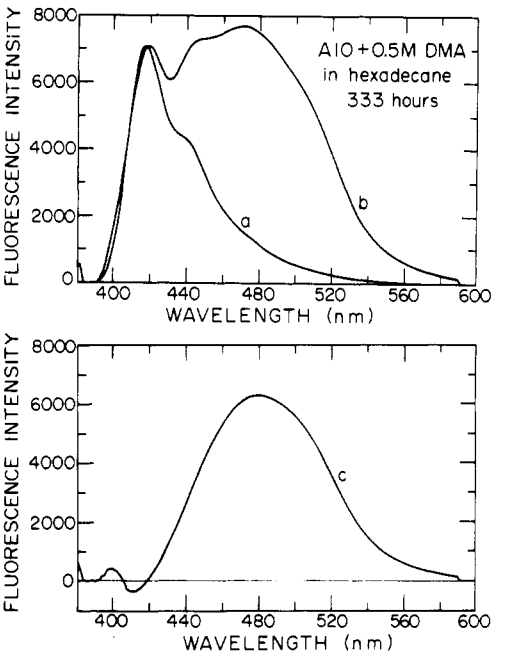

Figure 2. Fluorescence spectra of the same samples as in Figure 1 after sitting 333 h at room temperature (22 °C): (a) A10 in hexadecane; (b) A10 + 0.5 M DMA in hexadecane; (c) their difference spectrum.

spectra are normalized at 418 nm. Their difference spectrum, the exciplex emission, is shown in the bottom portion of Figure 2.

The kinetics of DMA entry into the particle are more difficult to explain. They stand in strong contrast to the results obtained from energy-transfer experiments with N-labeled particles.

The important variable in these experiments is the ratio I_E/I_M of the intensities of exciplex (I_E) and anthracene (I_M) fluorescence. It provides a measure of the fraction of A groups that have a nearest neighbor DMA when light is shone on the sample. The fluorescence lifetime of A* in A10 is only 2 ns,[7] which means that diffusion of DMA

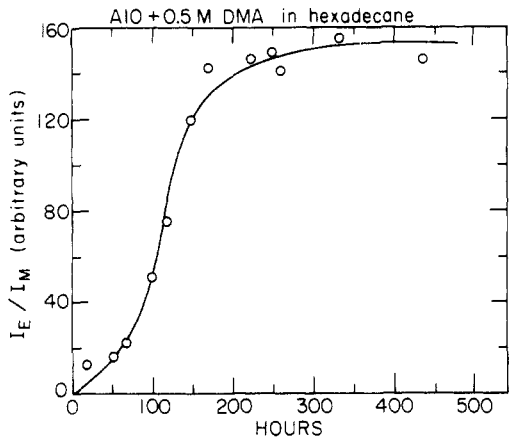

Figure 3. Plot of I_E/I_M vs. incubation time for the samples shown in Figures 1 and 2.

during the excited-state lifetime of A is relatively unimportant.

One of the curious features of the exciplex-forming process is its time dependence. As Figure 3 demonstrates, there is a long induction period, followed by a rapid rise in exciplex fluorescence, with an inflection at 110 h, leveling off after 300 h. The same kind of behavior is obtained with different concentrations of DMA and with different alkane solvents. There are important differences, however, in the rates of DMA penetration and in the equilibrium I_E/I_M values. These results will be reported in more detail elsewhere. We believe that the equilibrium I_E/I_M values measure a partitioning of DMA between the solvent and polymer particle phases.

The anthracene groups are located within the PMMA phase of the colloid. Previous work on naphthalene-labeled PIB–PMMA particles[3,4] indicate that the core has a microphase structure with threads of PIB penetrating throughout the particle. The PMMA regions are glassy. There are indications both from luminescence measurements and from differential scanning calorimetry (DSC) of a glasslike transition in the PMMA microphase at 60–80 °C. These results suggest that the slow rate of exciplex formation reflects the need for DMA to diffuse into a glassy PMMA environment.

The diffusion process has an interesting consequence. If after the system reaches equilibrium, the sample is diluted with solvent, the exciplex intensity decreases immediately. If the sample is centrifuged, the solvent, removed, and the particles are redispersed in fresh hexadecane, the exciplex emission disappears entirely. Thus penetration of DMA into the PMMA microphases is accompanied by morphological changes that make it possible for the DMA to exit almost instantaneously. We cannot at this time be more precise about the nature of these changes in particle morphology. Further experiments are needed.

We explain the slow diffusion of DMA into the particle in the following way: DMA is a good solvent for PMMA and a poor solvent for PIB. We therefore anticipate that PMMA is a good medium for DMA, whereas DMA should be poorly soluble in PIB. From this point of view the rate of penetration of DMA into the particle is affected not only by the glassy nature of the PMMA microphases but also by its poor solubility in the PIB layer that encapsulates the particle. Once large-scale penetration of DMA into the PMMA phase occurs, these microphases are plasticized and considerable hexadecane enters into the PMMA microdomains. Under these circumstances small-molecule diffusion is rapid, and the DMA molecules both inside and outside the core are in rapid equilibrium.

The morphological changes we detect may have interesting consequences on other properties of these dispersions. Further experiments are under way to explore the scope of luminescence techniques in these systems and to explain the phenomena that we report.

Summary. Exciplex formation is an effective method for studying the kinetics and mechanism of dimethylaniline (DMA) diffusion into alkane dispersions of sterically stabilized PMMA particles containing covalently bound anthracene groups. DMA diffusion is a cooperative process, with a strong induction period. It is accompanied by morphological changes within the particles.

Registry No. PMMA, 9011-14-7; PIB, 9003-27-4; DMA, 121-69-7; 9-anthracenylmethyl methacrylate, 31645-35-9.

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