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Luminescence Techniques in Polymer Colloids. 1. Energy-Transfer Studies in Nonaqueous Dispersions

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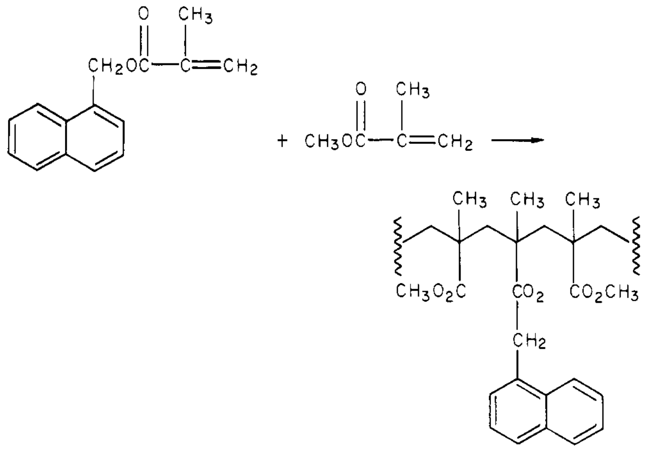
ABSTRACT: Nonaqueous dispersions (1–3-μm diameter) of a polymer colloid were prepared containing naphthalene (N) groups covalently attached to the poly(methyl methacrylate) (PMMA) core. Cilia of polyisobutylene grafted onto PMMA served as the steric barrier to stabilize the dispersions. Typical naphthalene fluorescence was observed when isooctane suspensions of these colloids were irradiated at 280 nm. When anthracene (A) was added to the solvent, energy transfer $N^* + A \rightarrow N + A^*$ was observed. The rate constant for this process was 70 times slower than for the corresponding reaction between excited 1-naphthylmethyl pivalate and anthracene. These results are interpreted in terms of a diffusion model in which both anthracene diffusion and exciton diffusion play a role.

This paper describes results on the use of fluorescent labels to study the properties of nonaqueous dispersions of polymer colloids. Fluorescence techniques have seen wide applicability in biochemistry as tools to study the molecular morphology and molecular dynamics of complex systems.[1] More recently, these techniques have been applied to polymers. Several reviews on the subject have appeared.[2] Among the topics in polymer science studied by fluorescence techniques are molecular orientation and molecular motion in amorphous polymers,[2,3] chain interpenetration,[4] the thermodynamics of mixing in polymer blends,[5] and a wide spectrum of solution properties of polymers.[2,3] For example, our research group has developed a fluorescence technique for measuring the slowest internal (Rouse–Zimm) relaxation time of polymer chains in dilute and concentrated polymer solution.[6]

In this paper, we focus our attention on the fluorescence properties of polymer colloids[7a] that are sterically stabilized by cilia of polyisobutylene (PIB) and which contain naphthalene (N) groups covalently attached to the poly(methyl methacrylate) (PMMA) that comprises the core of the particle. These colloids form stable dispersions in alkane solvents and clear, homogeneous solutions in solvents such as chloroform and ethyl acetate, which can dissolve PMMA. We have examined the fluorescence of these dispersions in aliphatic alkanes, exciting the samples at 280 nm, where the N groups absorb. In subsequent experiments, we added anthracene (A) to the alkane dispersion medium for the colloid, since we wished to investigate the possibility that A might approach sufficiently close to the colloid's core surface to accept energy from a photoexcited N. Quenching of N* and sensitized A* fluorescence would result.

Scheme I



The PIB sterically stabilized PMMA colloids were prepared in a two-step procedure.[7b] In the first step, short PMMA sequences were grafted onto a PIB sample of nominal molecular weight 10^4. These PIB samples contain sites of unsaturation for reaction with either initiator radicals or growing PMMA chains. Polymerization is terminated before the PMA sequences become sufficiently long as to render the polymer insoluble in the cyclohexane reaction mixture. This short graft copolymer, called the "dispersant", is precipitated from solution with ethanol and purified.

In the second step of the preparation, the dispersant, methyl methacrylate (MMA), an initiator, and a methacrylate derivative of the desired chromophore are combined in cyclohexane solution and refluxed overnight. A white dispersion forms. The reaction is stopped before all the monomer is incorporated into the dispersion. This procedure produces spherical particles of relatively narrow distribution of sizes. Using 1-naphthylmethyl methacrylate

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(NMMA) as the comonomer yielded dispersions containing 1-alkylnaphthalene groups covalently bound to the core (Scheme I). Colloids were prepared containing in the core 2 mol % naphthalene (N) and 10 mol % N. These are referred to as N-2 and N-10, respectively. These materials could be freeze-dried from cyclohexane, stored as a powder, and resuspended in isooctane (2,2,4-trimethylpentane) by subjecting the mixture in a flask to a few seconds in an ultrasonic cleaning bath.

Scanning electron microscope studies indicated that N-2 and N-10 were spherical particles with a diameter of 1–3 μm. Surface area studies carried out by the BET technique[15] gave a value of 2.5 $m^2\ g^{-1}$ for N-2, consistent with nonporous spheres of 2-μm mean diameter. The compositions of these materials were determined by NMR and UV absorption studies of their solutions in $CDCl_3$ and ethyl acetate, respectively. Mole ratios of PIB:PMMA:N determined for these samples are 13:100:11 for N-10 and 13:100:2 for N-2. For comparison, we also prepared a sample of 1-naphthylmethyl pivalate (NMP), a model for our fluorescent probe which is soluble in alkanes.

Fluorescence spectra were normally run at right-angle geometries. Some experiments using front-face fluorescence gave similar results. The tendency for the colloid particles to settle over the course of several hours made quantitative interpretation of steady-state fluorescence spectra difficult. The emission spectra of N-2, N-10, and NMP are typical of 1-alkylnaphthalene derivatives. We also observed a weak tail at $\lambda > 400$ nm in the N-2 and N-10 spectra due to naphthalene excimer formation.[8]

Anthracene is strongly fluorescent. Dissolved in isooctane, it has a fluorescent lifetime of 5.4 ns. When anthracene is added to the isooctane solvent in which the colloids are suspended and the samples are irradiated at 280 nm, a superposition of naphthalene and anthracene fluorescence is observed in the fluorescence spectrum. Some of this emission is due to direct absorption of light by anthracene at 280 nm.

In order to distinguish between direct excitation and energy transfer from N*, we examined the fluorescence decay curves of N* at 337 nm and of A* at 425–480 nm. The fluorescence decay of N* was nonexponential. While it could be fit reasonably to the sum of two exponential terms, more work is necessary before the short component ($\tau_2 \approx 10$ ns) can properly be interpreted. The long component in the naphthalene fluorescence was cleanly exponential. It had a decay time $\tau_1 = 34$ ns for N-10 and 43 ns for N-2. We focus our attention on the interaction of anthracene with this long component in the N* fluorescence.[9]

Fluorescence decay curves of N-10 in isooctane in the presence of 3.0×10^{-4} M anthracene are presented in Figure 1. Curve a, measured at 420–480 nm, is due to anthracene fluorescence [$I_A(t)$]. It has two exponential components in its decay. The short component, τ_{short}^{450}, has the value 5.4 ns, exactly the value of A* in isooctane. In addition, one sees a long component, τ_{long}^{450}, which in this instance has a decay time of 31.6 ns. Curve b, measured at 337 nm, has a long-time (channel numbers 57–220) decay time τ_{long}^{337} of 32.1 ns. Here, the excitation wavelength is 280 nm and the emission at 337 nm [$I_N(t)$] is due to naphthalene. The short component in curve a is due to A*, which absorbs light at the excitation wavelength. The equivalence at long times of the decay constants in curves a and b establishes that some A* are produced by energy transfer from N*.

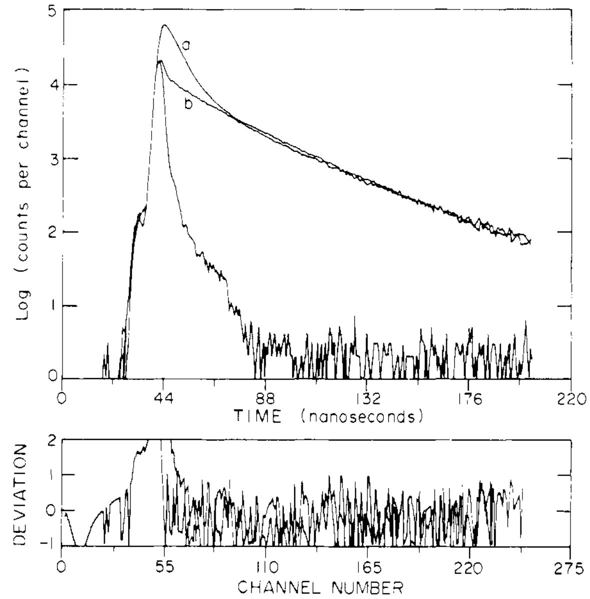
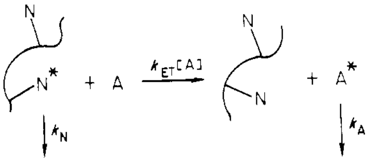


Figure 1. Fluorescence decay of an N-10 dispersion in isooctane in the presence of 3×10^{-4} M anthracene. Upper curve measured at λ = 420–480 nm (anthracene emission); lower curve measured at 337 nm. Their respective long-time decay times are 31.6 and 32.1 ns.

These observations are consistent with the simple model in Scheme II, where k_{ET} is the second-order rate constant for energy transfer from N* (in colloid core) to A. The terms k_N and k_A describe, respectively, the reciprocal lifetimes of N* in the colloid and A* in isooctane solution.

Scheme II



The kinetic equations derived from Scheme II predict that

$$I_N(t) = a_1 \exp\{-(k_N + k_{ET}[A])t\} \qquad (1)$$

$$I_A(t) = a_2 \exp(-k_A t) + a_3[\exp\{-(k_N + k_{ET}[A])t\} - \exp(-k_A t)] \qquad (2)$$

Since the a_2 term arises from prompt excitation of A at 280 nm, the ratio a_2/a_3 depends only on the relative concentration of A and colloid.

Scheme II makes a number of interesting predictions. It predicts that at all concentrations of [A], for both N-2 and N-10, τ_{long}^{337} should equal τ_{long}^{450}. Our measurements confirm this behavior. It also suggests that τ_{long}^{-1} should decrease with increasing [A]

$$1/\tau_{long} = k_N + k_{ET}[A] \qquad (3)$$

with a slope equal to k_{ET}. Much to our surprise, this prediction also was confirmed by our experiments. This result indicates that the majority of excited N* transfer energy to A with equal probability. We find a value of $2 \times 10^9\ M^{-1}\ s^{-1}$ for k_{ET}.

Energy is transferred from N* to A by a (Förster) dipole–dipole mechanism.[10] It can occur over substantial distances, with the rate and efficiency of energy transfer varying as the inverse sixth power of the interchromophore distance r. The theory permits one to define a critical distance R_0 (assuming random orientations) for a pair of nondiffusing chromophores at which the rate of energy transfer is equal to the decay rate (here k_N) of the excitation donor. When the donor and acceptor are immobile,

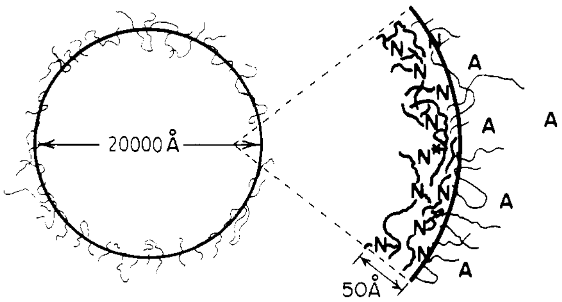


Figure 2. Pictorial representation of the surface of a polymer colloid nonaqueous dispersion with anthracene molecules (A) in the bulk solvent phase and naphthalene chromophores (N) in the core. The lighter lines imply PIB chains; heavier lines, PMMA chains. Our results indicate either that excitons migrate effectively to the surface or, more likely, that A penetrates efficiently into the core of N-2 and N-10 when these are dispersed in isooctane.

k_{ET} is a function of time and depends as well on $(R_0/r)^6$. R_0 can be calculated from the spectroscopic properties of the participating molecules. For example, for 1-methylnaphthalene transferring energy to anthracene, R_0(static) = 23 Å.[10] When diffusion can occur, the effective R_0 [$(R_0)_{eff}$] is increased because mass diffusion during the donor (N*) lifetime allows the interchromophore distance to vary. One can define a critical concentration according to eq 4. This concentration c_0 corresponds to 76% efficiency in energy transfer.

$$c_0 = 3000/2\pi^{3/2}NR_0^3 \qquad (4)$$

ciency in energy transfer. When mass diffusion can occur, c_0 is lowered and $(R_0)_{eff}$ replaces R_0. From experiments with NMP and A in isooctane, we find $k_{ET} = 1.34 \times 10^{10}$ $M^- s^{-1}$, $c_0 = 5.3 \times 10^{-3}$ M, and $(R_0)_{eff}$ = 43 Å. In a fluid solvent like isooctane our value of $(R_0)_{eff}$ is nearly twice as large as R_0.

These results are important because they establish that energy transfer can occur effectively between naphthalene groups in the colloid core and anthracene in the solvent without the anthracene necessarily penetrating into the PMMA core. For nondiffusing molecules energy transfer can be measured for chromophores separated by up to 1.5–1.8 times R_0. This means that the anthracene need approach to within 30–40 Å of an excited naphthalene group in the core for energy transfer to be detectable. A simplified model depicting this process is shown in Figure 2.

Excitation energy absorbed by naphthalene can be transferred directly to anthracene in a single step if $r \lesssim 1.5R_0$. In addition, excitation can, in principle, hop between naphthalenes ("energy migration"), also by a Förster mechanism.[9] The R_0(static) for this process is ca. 8 Å.[11] Since the data follow eq 3, we presume that diffusional processes are rate limiting in the energy-transfer process, i.e., that k_{ET} is diffusion controlled. In the Smoluchowski model,[10] the magnitude of k_{ET} is related to the diffusion coefficients of the interacting species, viz.

$$k_{ET} = 4\pi NDR_f/1000 \qquad (5)$$

where D is the appropriate diffusion coefficient and N is Avogadro's number. For NMP + A in isooctane, $D \equiv D_{AN} = D_A + D_{NMP}$, the sum of the diffusion coefficients A and NMP, respectively, in isooctane.

The exact meaning of R_f has been a matter of discussion for some time in the chemical literature. Birks[13] takes $R_f = R_0/2$ since at $r = R_0$ there is a 50% probability of energy transfer. A more complete treatment, by Gösele et al.[12] demonstrates that R_f depends upon D. When the mean diffusion length [$r = (2Dt)^{1/2}$] is much larger than R_0, R_f decreases with increasing D, approaching a value typical of molecular dimensions at large D. According to Gösele et al.

$$R_f \approx 0.676(\alpha/D)^{1/4} \qquad (6a)$$

$$\alpha = R_0^6/\tau^0 \qquad (6b)$$

where τ_0 is the fluorescence lifetime of the energy donor in the absence of acceptor. Using this approach, we calculate a value of R_f = 7.3 Å and $D = 2.4 \times 10^{-5}$ cm^2/s for A and NMP in isooctane.

The colloidal system is more complex. Three species can diffuse. Anthracene can diffuse within the surface (PIB steric barrier) environment of the colloid and perhaps penetrate into the core. These processes can be described by $D_{A,s}$. The naphthalenes in the core might undergo segmental motion, with a segmental diffusion coefficient D_{seg}. In addition, we can define Λ_N as the diffusion coefficient for exciton migration among naphthalene groups. The value of D_{coll} obtained experimentally represents the sum of these three processes: $D_{coll} = A_{A,s} + D_{seg} + \Lambda_N$.

In N-2 and N-10 the τ_0 values for N* are shorter than for NMP in isooctane due to self-quenching, being 42 and 34 ns, respectively. Using $k_{ET} = 2.0 \times 10^9$ M^{-1} s^{-1} for both, we calculate $R_f^{N\text{-}2}$ = 14 Å and $R_f^{N\text{-}10}$ = 15 Å, which are within experimental error of one another. This leads to a value of $D_{AN} = 1.8 \times 10^{-6}$ cm^2 s^{-1}. Thus the reduction of 7-fold in k_{ET} in colloidal dispersions corresponds to a 13-fold reduction in the corresponding diffusion coefficient.

Figure 2 is drawn to emphasize that N* in the core can transfer energy to A in solution at the colloid interface. Our observation that the naphthalene lifetimes decrease with increasing [A] according to eq 3 forces us to modify this picture. Since the particles are nonporous (see above), we assume that the A molecules penetrate into the N-2 and N-10 particles, immersed in isooctane. This explanation is consistent with Miller's observation[14] that T_g for polystyrene latexes are reduced from 105 to 50 °C by immersion in decane, a nonsolvent for polystyrene. Under these circumstances, it may not be unreasonable to ascribe the value of $D_{coll} = 1.8 \times 10^{-6}$ cm^2 s^{-1} to the self-diffusion coefficient $D_{A,s}$ of A in the core of the colloids, swollen by isooctane.

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Registry No. Anthracene, 120-12-7; NMP, 72681-59-5; PIB:PMMA:N, 84802-24-4.

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Notes

Differential Scanning Calorimetry Characterization of Polypropylene. Dependence of T_g on Polymer Tacticity and Molecular Weight

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Whereas the dependence of the glass transition temperature (T_g) on polymer tacticity has been well defined for certain polymers, notably the poly(alkyl methacrylates), the situation for polypropylene (PP) is still ambiguous.[1,2] This may in part stem from a failure to study polymer samples that have been carefully characterized with respect to both molecular weight and tacticity and in part to lack of consistency in T_g measurements.

Molecular weight determination is crucial since earlier work[3] has shown that the T_g value for atactic PPs falls dramatically in the low molecular weight region ($M_n <$ 50000). Furthermore, as illustrated below, the steric purity of PPs is rarely complete, being determined by catalyst type as well as reaction conditions. Consequently, an absolute method[4] for tacticity determination such as ^{13}C NMR must be considered mandatory for establishment of the stereochemical configuration.

We now report T_g values derived from standardized DSC measurements for well-characterized PP samples of varying tacticity.

Experimental Section

Polypropylene samples of varying stereoregularity and molecular weight were prepared with titanium and vanadium catalyst systems as follows: samples 1-4, $TiCl_4/C_6H_5COOC_2H_5/MgCl_2-Al(C_2H_5)_3$ system at 314 K; sample 5, $TiCl_4/C_6H_5COOC_2H_5/MgCl_2-NaAl(C_2H_5)_4$ system at 314 K; samples 6-8, $V(acac)_3-Al(C_2H_5)_2Cl$ system at 195 K; sample 9, $V(acac)_3-Al(C_2H_5)Cl_2$ system at 195 K; sample 10, $V(acac)_3-Al_2(C_2H_5)_3Cl_3$ system at 195 K; sample 11, $Ti(OC_4H_9)_4-Al(C_2H_5)Cl_2$ system at 313 K, sample 12, $Ti(OC_4H_9)_4-Al(C_2H_5)_2Cl$ system at 294 K; sample 13, $VCl_4-Al(C_2H_5)_2Cl$ system at 195 K; sample 14, $VCl_4-Al(C_2H_5)_3$ system at 195 K. Details of the polymerization procedure and purification of the polymers were previously described.[5-7] The stereoregularities of the samples were determined by ^{13}C NMR measurements using JEOL FX-200 and JEOL JNM PS-100 spectrometers on 15-30% (w/v) dichlorobenzene solutions at 413 K as detailed elsewhere.[5-7] The molecular weights of the samples were measured by GPC (Water Associates, Model 200) using five polystyrene gel columns (10^7, 10^6, 10^5, 10^4, and 10^3-Å pore sizes) and *o*-dichlorobenzene as solvent at 408 K.

DSC measurements were made with a Perkin-Elmer Model DSC-2C instrument equipped with a liquid nitrogen subambient accessory. In order to ensure good reproducibility, the liquid nitrogen reservoir was filled 2 h before calibration and maintained approximately three-fourths full throughout measurement. The temperature scale was calibrated against mercury (234.28 K), water (273.15 K), and indium (429.78 K) at a scan rate of 10 K/min.

Polymer samples (ca. 5 mg) were encapsulated in aluminum pans. Samples were pretreated at 473 K for 5 min, quenched (320 K/min) to about 60 K below T_g, and scanned through T_g at 10 K/min. Highly isotactic samples were found to crystallize under these quench conditions and consequently they were heated at 473 K outside the instrument, were quenched by dropping directly into liquid nitrogen, and were then inserted into the DSC sample holder below T_g and scanned as above.

Values of T_g were calculated with the Perkin-Elmer standard TADS program. The reproducibility of duplicate runs of samples with well-defined T_g was better than ±0.2 K.

Results and Discussion

The thermograms of samples representative of atactic, syndiotactic, and isotactic PP are displayed in Figure 1. The glass transition temperatures of the atactic and syndiotactic samples were found to be well defined whereas invariably the magnitude of the base line shift associated with the glass transition was much smaller for the isotactic samples and furthermore the transition was partially obscured by the onset of crystallization. It seems probable that the highly isotactic samples were not completely amorphous despite quenching directly into liquid nitrogen. The rapidity of crystallization for the highly isotactic PP samples is illustrated by Figure 2, which shows the onset of crystallization at 395 K despite quench cooling at 320 K/min. During the course of the heating scan the pre-

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