Direct Energy-Transfer Studies on Doped and Labeled Polymer Latex Particles

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We have used the direct energy-transfer method to study the internal morphology of a nonaqueous-dispersion-polymerization latex. These 1-μm particles contain 97 mol% poly(methyl methacrylate) (PMMA) and 3 mol% polyisobutylene (PIB). Phenanthrene (donor) and anthracene (acceptor) were doped selectively into the PIB phase. These dyes sample length scales up to 34 Å and indicate an "effective local dimension" $\bar{d}=2$, a result which conveys important information about the PIB phase in this material.

The technique of direct nonradiative singlet-singlet energy transfer (DET) has been used to characterize the distribution of probe molecules embedded in restricted geometries, with particular attention paid to porous glass[1,2] and silica.[3-5]

In this paper[6] we report results of DET experiments on micron-size polymer particles prepared by nonaqueous dispersion polymerization.[7,8] These nonaqueous-dispersion latex materials have many applications in the paint industry. In their simplest form they are composed of two different and incompatible polymer materials. The major (core) component, comprising 90%+ of the dry weight, is commonly in the form of an amorphous glass. The minor component is normally a rubbery material, very soluble in the kind of hydrocarbon media in which the particles are formed. For the particle to maintain its integrity, the core polymer must be insoluble in the dispersion medium. A thin (monomolecular) layer of the rubbery polymer is thought to cover the particle surface and provide colloidal stability by steric stabilization.[7,8]

Here we examine poly(methyl methacrylate) (PMMA) particles containing polyisobutylene (PIB) as the minor component. The particles are dense and free of voids. The PIB is present in the form of a graft copolymer with PMMA. Much of it is buried inside the particle and forms an interconnected network.[9-12] A representation of the gross morphology is shown in Fig. 1. The detailed mechanisms of particle formation is not well understood. Nevertheless it is clear that the formation of covalent grafts between PIB and PMMA limits the extent of phase separation, and is responsible in some important way for the morphology which is formed.

Anthracene-labeled PIB-PMMA particles were prepared from butyl rubber (PIB containing 2% isoprene units to promote grafting), methyl methacrylate, and 9-anthrylmethyl methacrylate as previously described.[9]

These particles can be dissolved in polar solvents such as chloroform and ethyl acetate. A combination of ^{1}H NMR and uv analyses indicate that these particles contain 6 mol% PIB and 0.01, 0.052, and 0.10 mmol anthracene groups per gram of polymer. We refer to these particles as A01, A05, and A1, respectively. The unlabeled (UL) particles used here contain 3 mol% PIB. Both sets of particles are spherical in shape with a particle size narrowly distributed about a diameter of 1 μm. Twice-recrystallized 9-anthrylmethyl pivalate was used as the acceptor in the UL samples. Phenanthrene (Aldrich) was in the form of zone-refined crystals.

Two kinds of experiments were carried out. In the first, UL particles were allowed to imbibe a pentane solution of phenanthrene (Phe, the energy donor) and an anthracene derivative, 9-anthrylmethyl pivalate (AMP, the energy acceptor), and then the solvent was removed. In the second set of experiments, particles covalently labeled in the PMMA phase with an anthracene derivative were allowed to imbibe a pentane solution of phenan-
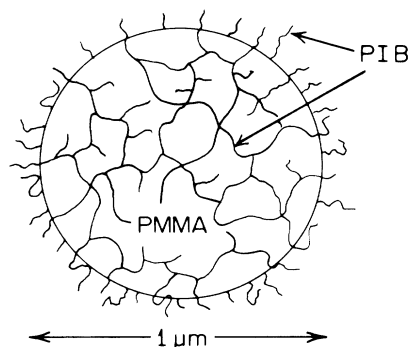

FIG. 1. Gross morphology of PMMA particles containing PIB as a minor component.

threne, and then dried. These conditions allow the dyes to penetrate into the particle interior via the PIB component, but do not permit the dyes to enter the PMMA phase.

Particles were doped by our exposing them to pentane solutions of dyes (2 h) inside 12-mm-i.d. quartz tubes, and then the solvent was removed, first on a rotary evaporator, and then under vacuum (10^{-1} Torr, 48 h). In this way a thin film of doped particles coated the inner surface of the tubes. Following the fluorescence decay measurements, each sample was dissolved in ethyl acetate, and the chromophore concentration measured by uv absorption spectroscopy. Films were then cast from this solution, and the fluorescence decay profiles were remeasured for these film samples. In the UL particles, [Phe] was typically 0.03 ± 0.01 mmol g^{-1} and [AMP] ranged from 0.017 to 0.084 mmol g^{-1}. Phe was doped into the A01, A05, and A1 particles to give concentrations of 0.005 to 0.05 mmol g^{-1}. Except for the amount of scatter observed at early times, fluorescence decay traces were unaffected by the Phe concentration.

Fluorescence decay profiles were measured by the time-correlated single-photon counting technique employing a pulsed lamp source (Edinburg Instruments, 0.5-atm D_2 gas) and a Hammamatsu model 928 photomultiplier. Samples were excited at 295 nm and emission detected at 344 nm. Data were collected over three

decades of decay and fitted by a nonlinear least-squares routine with use of the δ-function convolution method, with BBOT [2,5-bis(5-tert-butyl-2-benzooxazolyl)-thiophene] in ethanol as a standard. Data analysis allowed for a small correction due to scattered light[13] (the scatter parameter varied between 0.1 and 1.0). The uniqueness of the fit of the data by the model is determined by x^2 ($x^2 \le 1.5$), the distribution of the weighted residuals, and the autocorrelation of the residuals. The decay dynamics of the Phe-AMP system was measured by convolution of the survival probability of Phe [Eq. (1)] with the system response profile. An example is shown in Fig. 2.

The model used for data analysis is that of Förster energy transfer[14] in restricted geometries. The survival probability $\phi(t)$ of the donor (Phe*) is described by the Klafter-Blumen equation[15,16]

$$\phi(t) = \exp[t/\tau_0 - P(t/\tau_0)^\beta], \qquad (1)$$

with $\beta = \bar{d}/s$ and $s = 6$ for dipole-dipole interactions. τ_0 is the unquenched lifetime of the donor, and $\bar{d}$ is the fractal dimension. The proportionality factor P is given by

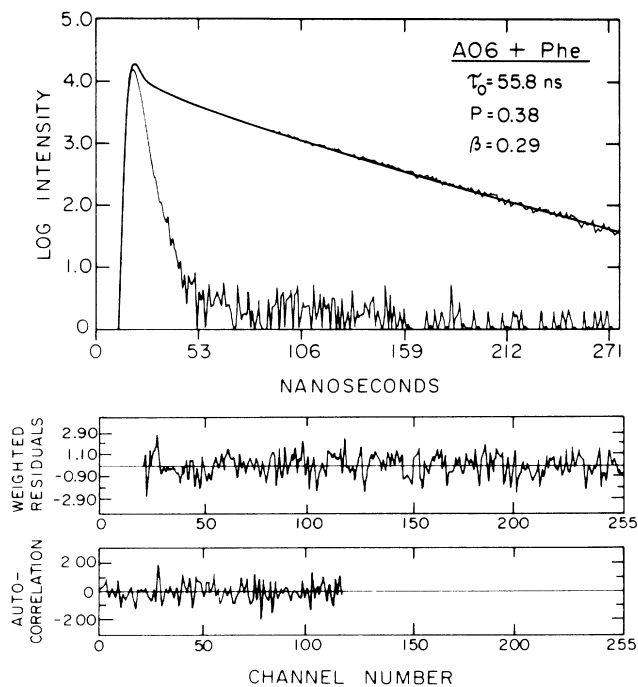$$P = A(\bar{d}/d)\Gamma(1 - \beta)(R_0/a)^{\bar{d}}. \qquad (2)$$

FIG. 2. Fluorescence decay of Phe* in A06 particles doped with Phe (0.05 mmol/g). Solid line, fit by the model [Eq. (1)]: $\tau_0 = 55.0$ ns (fixed), $\beta = 0.27 \pm 0.01$, $P = 1.35 \pm 0.06$, $x^2 = 1.03$, scatter parameter=0.73.
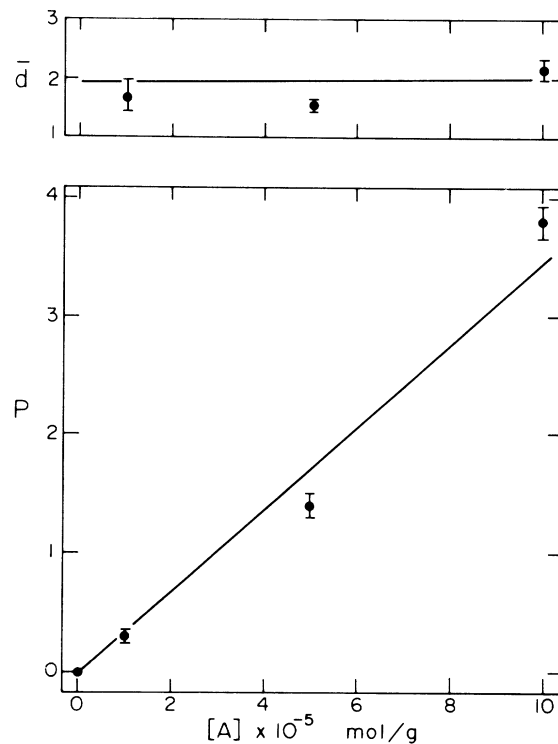
FIG. 3. Plots of P and $\bar{d}$ from Eq. (1) vs anthracene-group concentration (mmol g^{-1}) for the particles labeled with anthracene in the PMMA phase and doped with Phe. The standard deviation is calculated from three independent measurements for each point.

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Here A is the fraction of the sites occupied by the acceptors $(A \ll 1)$, d is the dimension of the embedding Euclidean space, a is the size of the acceptor molecule, and R_0 is the critical radius for DET.

To test the reliability of our experimental procedure for the determination of β, we prepared films of PIB and of PMMA containing either Phe, or Phe plus various concentration of AMP. The films contained typically 3×10^{-6} mol Phe per gram of polymer and the AMP concentration was varied from 3.7×10^{-6} to 1.0×10^{-5} mol/g. By itself Phe showed an exponential decay with lifetimes of 53.2 ns in PMMA and 53.6 ns in PIB. Phe+AMP decay curves, fitted by Eq. (1), gave a value of $\beta = 0.50 \pm 0.05$, which is in good agreement with the Förster result[14] for DET in three dimensions. Values of P were proportional to the AMP concentration, and from the Förster equation, $P = 4\pi^{3/2} N_A R_0^3 [A]/3000$, we obtained $R_0 = 26.5 \pm 1.0$ Å for experiments both in PIB and in PMMA.

Analysis of the Phe decay curves in the samples A01, A05, and A1 yields $\beta = 0.31 \pm 0.03$, which corresponds to $\bar{d} = 1.86 \pm 0.18$ for the anthracene-labeled colloids. As shown in Fig. 3, P is found to be linear in anthracene concentration, in accord with Eq. (2). Similar results are obtained for the (Phe+AMP)-doped unlabeled particles, where we find $\beta = 0.30 \pm 0.04$. This corresponds to a dimensionality of $\bar{d} = 1.80 \pm 0.24$ for this system. Fig-
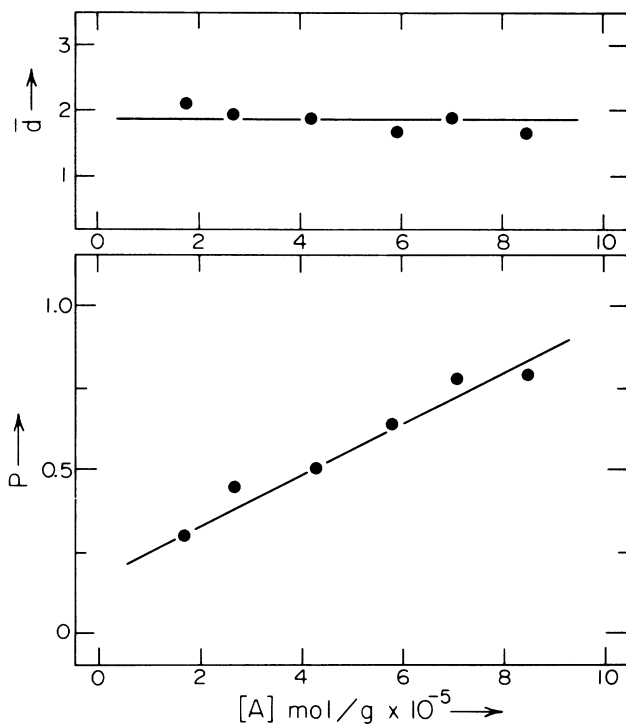

FIG. 4. Plots of P and $\bar{d}$ from Eq. (1) vs AMP concentration (mmol g^{-1}) for unlabeled particles doped with Phe and AMP.

ure 4 shows the linear dependence of P upon [AMP] and the $\bar{d}$ values for the UL particles. In both systems β is independent of [Phe] over the range studied, indicating that single-step DET is involved. If the particle morphology were known, we could use the information to interpret the $\bar{d}$ values found in the DET experiments. For example, the finding that $\bar{d} \approx 2$ for the UL particles doped with Phe+AMP would be easy to understand if the particle structure were that of a sphere of PMMA covered by a monolayer shell of PIB. The experiment is sensitive to a distance scale (r_{max}) set by R_0, τ_0, and the time scale of the measurement. We estimate $r_{max} = R_0(t_{max}/\tau_0)^{1/6}$, with $t_{max} = 255$ ns, and obtain $r_{max} = 34$ Å. The surface of a 1-μm sphere is locally flat on a scale of 34 Å.

We know, however, that a substantial fraction of the PIB is trapped as a continuous network within the particle interior. Briefly stated, the connected nature of this PIB network was deduced from transport experiments involving particles labeled with naphthalene groups in the PMMA phase.[9-11] When AMP was added to a cyclohexane dispersion of these particles, quenching of all the naphthalene was detected within minutes, whereas diffusion of AMP into solid PMMA over distances of 500 nm is expected to take years.[17] This implies the existence of pathways, channels of PIB swollen with solvent, penetrating deeply within the particle. When Phe and AMP are doped into the UL particles with use of pentane, they can penetrate into the particle through the PIB paths, and remain trapped in this phase when the solvent is removed. Hence the result that $\bar{d} \approx 2$ pertains to both the internal and surface PIB components.

Evidence from quite different sources suggests that polymer latex particles form by a mechanism involving coagulation of smaller particles.[18-20] One view of this process is the following: Polymerization of MMA in solution is competitive with hydrogen abstraction from PIB leading to graft copolymer formation. In the early stages of the reaction when little graft copolymer is present, primary PMMA particles are not stabilized against aggregation. As the reaction proceeds, graft copolymer adheres to the surface of both primary particles and aggregates. These are swollen with monomer, and after 10% conversion, much of the subsequent polymerization of MMA occurs inside the swollen polymer phase.[21] Particle growth exposes new surface area and promotes aggregation of units containing a monolayer coverage of the PIB-PMMA graft copolymer. As a consequence, some of the PIB component becomes trapped within the aggregates and forms the PIB network in the final particle. The dimension $(\bar{d} = 1.80 \pm 0.24)$, suggests that the donor and acceptor molecules are distributed on local surfaces of the primary PMMA building blocks and their aggregates. This surface might be locally flat, or, alternatively, the result $\bar{d} \approx 2$ might indicate a crossover: The β value determined in the

fluorescence decay experiment may represent the effective exponent between regimes of $\bar{d} = 3$ at early times and $\bar{d} = 1$ at long times. For example, a value of $\bar{d} = 1.8$ could be explained if the internal PIB were present as a network of thin cylinders ca. 25 Å in diameter.[22]

One unanswered question concerns the magnitude of the P values shown in Fig. 4, which seems small. As a control experiment each of the samples shown in Figs. 2 and 3 were dissolved in ethyl acetate, and cast as films. This process conserves material but destroys morphology and allows the dopants to dissolve in the PMMA as well as the PIB component. DET measurements on both the UL samples and the anthracene-labeled samples gave results consistent with Förster energy transfer in three dimensions with P values identical to those calculated from bulk chromophore concentrations. Further work is needed to understand why the P values for the intact particles are so small.

While the results on the unlabeled particles are consistent with formation of the macroscopic structure through self-assembly of primary polymer particles, the results on the labeled particles are curious and comment on the nature of the interface between the PIB and the PMMA phases. The anthracene groups are statistically distributed along the PMMA chains. If they were distributed uniformly in space, one would expect a three-dimensional distribution of acceptor groups, and a value of $\beta = 0.5$. This is clearly not the case. No crossover model with the donor in the minor phase and the acceptor distributed throughout a surrounding phase leads to $\bar{d} < 3$. We propose as a possible explanation of this result that during the time when the hydrocarbon solvent is removed and the particles are dried, anthracene groups near the interface can partition between the phases and are selectively concentrated in the PIB network. While such a statement is difficult to prove, a variety of other experiments on labeled particles[23,24] indicate that PMMA chains near the interface become mobile when the particles are dispersed in a liquid hydrocarbon (here pentane). They suggest that chromophore groups in this region partition between the PMMA and PIB phases and tend to concentrate in the latter. Other anthracene groups, buried deeper in the PMMA phase, are presumably too far from the Phe molecules to serve as efficient energy acceptors.

In conclusion, in these experiments we have shown that the long-range single-step energy-transfer process can be used to probe geometrical details of a self-assembling polymer latex particle.

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[1]U. Even, K. Rademann, and J. Jortner, Phys. Rev. Lett. **52**, 2164 (1984).

[2]W. D. Dozier, J. M. Drake, and J. Klafter, Phys. Rev. Lett. **56**, 197 (1986).

[3]P. Levitz and J. M. Drake, Phys. Rev. Lett. **58**, 686 (1987).

[4]N. J. Turro, M. B. Zimmt, and I. R. Gould, J. Am. Chem. Soc. **107**, 5826 (1985).

[5]D. Rojanski, D. Huppert, H. D. Bale, Xie Dacai, P. W. Schmidt, D. Farin, A. Seri-Levy, and D. Avnir, Phys. Rev. Lett. **56**, 2505 (1986).

[6]This paper is number 19 in our series of papers on fluorescence studies of polymer colloids.

[7]A. J. Barrett, *Dispersion Polymerization in Organic Media* (Wiley-Interscience, New York, 1975).

[8]D. Napper, *Polymeric Stabilization of Colloidal Dispersions* (Academic, London, 1983).

[9]O. Pekcan, M. A. Winnik, and M. D. Croucher, J. Polym. Sci. Polym. Lett. **21**, 1011 (1983).

[10]M. A. Winnik, Pure Appl. Chem. **56**, 1281 (1984).

[11]M. A. Winnik, in *Polymer Surfaces and Interfaces*, edited by J. Feast and H. Munro (Wiley, London, 1987).

[12]T. P. Russell, B. Williamson, and M. A. Winnik, Macromolecules **20**, 899 (1987).

[13]J. M. G. Martinho, L. Egan, and M. A. Winnik, Anal. Chem. **59**, 861 (1987).

[14]T. Forster, Discuss. Faraday Soc. **27**, 7 (1959).

[15]J. Klafter and A. Blumen, J. Chem. Phys. **80**, 875 (1984).

[16]J. Klafter and A. Blumen, J. Lumin. **34**, 77, 2632 (1985).

[17]A. R. Berens and H. P. Hopfenberg, J. Membrane Sci. **20**, 183 (1982).

[18]P. J. Feeney, D. H. Napper, and R. G. Gilbert, Macromolecules **17**, 2520 (1984).

[19]M. J. Ballard, R. G. Gilbert, D. H. Napper, P. J. Pomery, and J. H. O'Donnell, Macromolecules **17**, 504 (1984).

[20]R. M. Fitch and C. H. Tsai, in *Polymer Colloiods*, edited by R. M. Fitch (Plenum, New York, 1971).

[21]B. Williamson, R. Lukas, M. A. Winnik, and M. D. Croucher, J. Colloid Interface Sci. **119**, 559 (1987).

[22]A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses*, edited by I. Zschokke (Reidel, Dordrecht, Holland, 1986).

[23]L. S. Egan, M. A. Winnik, and M. D. Croucher, Langmuir **4**, 438 (1988).

[24]O. Pekcan, L. S. Chen, M. A. Winnik, and M. D. Croucher, Macromolecules **21**, 55 (1988).