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Phase Separation and Polymer Diffusion in Poly(vinyl acetate−butyl acrylate) Latex Films Prepared by Batch Miniemulsion Polymerization

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ABSTRACT: A series of poly(vinyl acetate−butyl acrylate) P(VAc−BA) latex particles, with a 4:1 weight ratio of VAc and BA, unlabeled and labeled with phenanthrene (Phe) as the donor and with 4′-(dimethylamino)benzophenone (NBen) as the acceptor, were prepared by batch miniemulsion polymerization in the presence and absence of a chain transfer agent. The latex particles were characterized by a phase-separated morphology, and the dyes appeared to be localized in the BA-rich domains. One set of samples, which we refer to as “gel-free”, had a negligible gel content, whereas the gel-containing samples for the energy-transfer studies of polymer diffusion had a gel content of ca. 34%. For gel-free samples, diffusion led to complete mixing of donor- and acceptor-labeled polymer during the drying process, at even 4 °C, suggesting that the PBA-rich domains were continuous. For the gel-containing samples, the diffusion rate (for molecules not part of the gel network) was negligible at 22 °C but became significant at temperatures above 60 °C, suggesting that the BA-rich domains were trapped as occlusions dispersed in a PVAc-rich continuous phase.

Introduction

Many latex copolymers prepared by batch emulsion polymerization undergo phase separation during the reaction. Phase separation normally occurs throughout the particles, giving rise to structured latex with a morphology, as inferred by electron microscopy measurements, often characterized by occlusions with one composition dispersed in a matrix formed by the other phase. Films formed from these particles often have interesting mechanical properties that arise from synergistic interactions between the different domains. For example, in pressure-sensitive adhesives, hard domains distributed in a soft matrix provide mechanical reinforcement. In coatings, the soft domains can provide low-temperature film formation and toughness in a tack-free film.

While we have a global understanding of how domains in films interact to provide interesting properties, we have a much poorer understanding of how structured latex particles coalesce to form films. On a length scale defined by the particle diameters, particles deform as the dispersion dries, leading to an essentially void-free film made up of polyhedral (Voronoi) cells formed from the individual latex particles. The mechanical strength of the film increases over time as polymer chains diffuse across the intercellular boundaries to enhance the adhesive strength of these interfaces. For structured latex particles, film formation can be more complex because one has to consider the possibility of coalescence of dispersed domains from different particles as the film forms and ages. Additional complexities can arise if the latex particles themselves have a significant gel content. The gel network itself will not diffuse, but it can act as a barrier to diffusion of components of the matrix phase and the dispersed phase within the film.

As a first step toward developing an understanding of coalescence and polymer diffusion in films formed from structured latex particles, we have undertaken a study of poly(vinyl acetate−butyl acrylate) (PVAc−BA) copolymer latex particles in which dispersed domains are a prominent feature of the particle morphology. P(VAc−BA) is widely used in architectural coatings in North America. We would hope that a deeper understanding of coalescence and film formation for this material will eventually lead to better coatings with improved performance.

Poly(vinyl acetate) is as a classic example of a latex polymer characterized by the presence of long chain branches. The propagating radical in VAc polymerization is highly reactive. Through hydrogen abstraction from polymer in the reaction mixture, radical sites are created that lead to extensive branching.[1] This branching becomes more extensive in its copolymers with monomers such as BA, which introduce a more reactive C−H bond into the polymer backbone. In these polymers, branching is accompanied by gel formation. Branching reactions themselves will not create gel, but gelation can occur through termination reactions involving either coupling or addition of the propagating VAc radical to terminal double bonds formed by disproportionation.

The characteristic feature of free-radical copolymerization of VAc with BA is a poor match in their reactivity ratios. The reactivity ratios of VAc and BA have values on the order of $r_{\mathrm{VAc}} \approx 0.02-0.07$ and $r_{\mathrm{BA}} \approx 3.07-8.00$, respectively.[2] Such a big difference in reactivity ratios leads to phase separation for bulk copolymerization of VAc with BA. This tendency for rapid polymerization of BA followed by polymerization of VAc, leading to phase separation, also occurs in batch-emulsion copolymerization of VAc with BA. The Vanderhoff group[3] has shown that domains of BA-rich copolymers form and become dispersed in a PVAc-rich continuous phase during batch conventional emulsion polymerization. These domains could be seen in transmission electron

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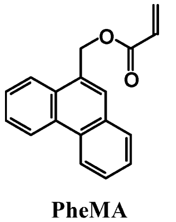
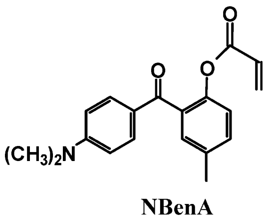
microscopy (TEM) images of sectioned and stained films. In addition, two glass transition temperatures could be detected by differential scanning calorimetry (DSC): a low T_g associated with the BA-rich domains and a higher T_g associated with the VAc-rich domains. This group also showed that semicontinuous emulsion copolymerization of these monomers under monomer-starved condition gave homogeneous latex particles with little phase separation.[4] Thus, P(VAc−BA) represents a useful example in which the extent of phase separation depends on how the polymerization reaction is carried out.

In this article, we describe polymer diffusion in P(VAc−BA) latex films with a weight ratio of 4:1 of VAc/BA as studied by fluorescence resonance energy transfer (ET). The latex copolymers were prepared by batch miniemulsion polymerization. Miniemulsion polymerization differs from batch emulsion copolymerization in that transport of the monomers through the aqueous medium plays a much less important role in determining copolymer composition. In traditional bulk emulsion polymerization, the monomers must pass from the large monomer droplets to the locus of growing particles as the reaction proceeds. If the water solubility of the monomers differs, this will affect the rate at which each is incorporated into the growing polymer. In miniemulsion polymerization, small monomer droplets are created prior to the onset of the reaction and stabilized against coalescence and Ostwald ripening. Under ideal circumstances, each droplet is converted to a latex particle. Polymer composition is determined only by the reactivity ratios of the monomers. Thus, miniemulsion polymerization closely resembles copolymerization in bulk. We note that the El-Aasser group (Delgado et al.)[5] has studied miniemulsion copolymerization of 1:1 molar mixtures of VAc and BA.

In our experiments we used 1 mol % 9-acryloxymethylphenanthrene (PheMA) as the comonomer to introduce the Phe group as the donor (D) chromophore into the donor-labeled latex particles. For labeling P(VAc−BA) latex particles with an acceptor (A) chromophore, we used 0.3 mol % 4′-(dimethylamino)-2-acryloxy-5-methylbenzophenone (NBenA). The structures of these dye comonomers are shown below. A particularly interesting feature of the ET experiments with these latex particles arises as a consequence of the selective incorporation of the donor and acceptor into the BA-rich microdomains. We can use energy-transfer experiments to get insights into film morphology, and we can follow polymer diffusion of the components of this BA rich domain as the films age or are annealed.



PheMA



NBenA

Films prepared from latex particles synthesized in the absence of a chain transfer agent show a significant gel content, ca. 35 wt %. We denote these latex polymers prepared by miniemulsion polymerization as G−P_{me}(VAc−BA). When 1-dodecanethiol (C_{12}−SH, 1.5 wt % based on monomer) was introduced into the reaction as a chain transfer agent, no insoluble polymer could be detected from a traditional gel content determination. We refer to these samples as “gel free” and denote them as GF−P_{me}(VAc−BA). We prepared various latex samples, unlabeled, labeled with Phe and with NBen, and doubly labeled with both Phe and NBen in both the G and GF series. These samples allow us to examine the influence of gel content on polymer diffusion in these latex films. We have used these donor−acceptor pair previously to study polymer diffusion in latex films.[6−8] A plot of the UV absorption spectrum of NBen and the fluorescence spectrum of Phe showing the overlap region can be found in Figure 1 of ref 9. For this D/A pair in P(VAc−BA) films, R_0 = 2.7 nm.

Table 1. Recipe for the Synthesis of Gel-Containing Latex Sample G−P_{me}(VAc−BA)−NBen by Batch Miniemulsion Polymerization at 80 °C

ingredients (g)	G−P_{me}(VAc−BA)−NBen
water	116.5
SDS	0.023
$NaHCO_3$	0.35
TX305	0.188
KPS	0.125
VAc	6.0
BA	1.5
hexadecane	0.05
NBenA	0.075,[a] 0,[b] 0.37[c]
PheMA	0,[a] 0.20,[b] 0.10[c]

[a] NBen-labeled particles, 0.3 mol % of the total monomer. [b] Phe-labeled particles, 1.0 mol % of the total monomer. [c] Doubly labeled particles, 0.15 mol % NBen, 0.50 mol % Phe.

To place the results reported here in a proper context, we compare these results with those previously published[6] describing polymer diffusion in P(VAc−BA) latex films of similar composition, in which the latex particles were prepared by semicontinuous emulsion polymerization under monomer-starved conditions, here denoted as P_{sc}(VAc−BA).

Experimental Section

Materials. Sodium dodecyl sulfate (SDS), sodium bicarbonate ($NaHCO_3$), hexadecane (HD), and 1-dodecanethiol (C_{12}-SH) were used as received from Aldrich. Vinyl acetate (VAc, Aldrich) and butyl acrylate (BA, Aldrich) were distilled at reduced pressure, and those purified monomers were stored at 0 °C until use. Water was purified by a Milli-Q ion-exchange filtration system. Dye comonomers PheMA and NBenA were synthesized as described elsewhere.[9,10]

Latex Preparation. Batch latex dispersions in this paper were prepared by miniemulsion polymerization reactions carried out at 80 °C with KPS as the initiator. In the reactions, most of the ingredients including water, emulsifier, pH buffer, monomers, and hexadecane as the costabilizer were sonified to form a stable miniemulsion. The emulsion was heated to 80 °C, and then the initiator solution was added. As an example, the recipe for the synthesis of “gel-containing” G−P_{me}(VAc−BA)−NBen latex sample is summarized in Table 1. The specific procedure is described below: SDS (0.023 g), TX305 (0.188 g), and $NaHCO_3$ (0.2 g) were dissolved in water (61.5 g) in 100 mL beaker. A mixture of the monomers (VAc 6 g, BA 1.5 g) including NBenA (0.075 g, 0.3 mol % of the total monomers) and HD (0.05 g) was added to the aqueous solution. miniemulsion was prepared using a Branson 250/450 digital sonifier. The above mixture was cooled in an ice bath, sonified for 60 s at 50% amplitude with pulse-on 1 s and pulse-off 1 s. The stable miniemulsion was then transferred to the polymerization flask. The polymerization was carried out in a 250 mL three-necked round-bottom flask provided with a stirrer, a thermometer, and an N_2 inlet. The flask was immersed into an oil bath. The system was then thoroughly purged with nitrogen while the reaction mixture was heated to 80 °C.

Table 2. Characteristics of the Batch Latex Particles

latex[a]	d^c [nm]	T_g [°C]	gel content [%]
gel-free[a]			
GF−P_{me}(VAc−BA)	181		0
GF−P_{me}(VAc−BA)−Phe−NBen	166		0
GF−P_{me}(VAc−BA)−Phe	186		0
GF−P_{me}(VAc−BA)−NBen	196	−2.3, 40.3	0
gel-containing[b]			
G−P_{me}(VAc−BA)	170		4
G−P_{me}(VAc−BA)−Phe−NBen	178		25
G−P_{me}(VAc−BA)−Phe	196		39
G−P_{me}(VAc−BA)−NBen	181	−15.8, 38.7	26

[a] Prepared in the presence of 1.5 wt % of C_{12}-SH. [b] Prepared without C_{12}-SH. [c] Particle diameter.

During this time the initiator was dissolved in water. After the reactor temperature stabilized at 80 °C, the initiator solution was added at the rate of 2 mL/min. After the addition of the initiator solution was complete, the system was maintained at 80 °C for 3 h. The reaction was cooled to room temperature, and then sodium bicarbonate solution (0.15 g in water 50 g) was added. This reaction produced a dispersion with 5.7 wt % solids content with a mean particle diameter of 181 nm and a narrow size distribution.

The reactions carried out differed in the amount of C_{12}-SH (0 or 1.5 wt %) added as a chain transfer agent. For each type of latex, we prepared four samples: unlabeled latex without dye comonomers; Phe-labeled latex by adding 1 mol % PheMA (based on total monomers); NBen-labeled latex by adding 0.3 mol % NBenA; and doubly labeled latex by adding 0.5 mol % PheMA and 0.15 mol % NBenA. For many experiments, salts and surfactants were removed from the dispersion by treatment with previously purified ion-exchange beads (AG-501-X8 mixed-bed resin, Bio-Rad).[11] We refer to these dispersions as “purified” latex. The characteristics of these materials and our notation for naming the samples are presented in Table 2.

Characterization of Latex Particles. Particle diameters were measured by dynamic light scattering at a fixed scattering angle of 90° at 20 °C with a Brookhaven Instruments model BI-90 particle sizer equipped with a 10 mW He−Ne laser. The solids contents of the latex dispersion were determined by gravimetry. The molar mass distribution was measured by gel permeation chromatography (GPC) using polystyrene as molar mass standards. These experiments were performed with a Waters liquid chromatograph equipped with a Waters 480 tunable UV−vis absorbance (UV) detector and a Waters 480 R410 differential refractometer (RI) detector. Three Waters AM Gel columns (500/10, 10^4/10, and 10^5/10 in series, designed to measure molar mass up to 2 000 000 g/mol) were used with THF as the elution solvent at a flow rate of 0.8 mL/min. For all latex samples, only the sol fraction of the polymers (see below) was examined. Each polymer solution was passed through a 0.2 μm filter prior to injection in the GPC.

The glass transition temperatures (T_g) of the copolymers were measured with a TA Instruments DSC 2920 MDSC V2.6A differential scanning calorimeter over a temperature range of −70 to 120 °C at a heating rate of 10 °C/min. Each sample was taken through three runs. T_g values were calculated from the third run. The purified dispersions above were freeze-dried at −80 °C and then further dried at 30 °C in a vacuum oven for 2 days.

To determine the gel content of each polymer, a dried sample (ca. 0.2 g, W_1) was stirred with 1,4-dioxane (10 mL) in a centrifuge tube.[12] The solution was spun to sediment the gel fraction. The clear supernatant was separated. More dioxane was added, and the process was repeated. The remaining insoluble fraction was dried (110 °C for 5 h) to a constant weight (W_2).

$$\text{gel content (\%)} = (W_2/W_1) \times 100 \tag{1}$$

The sol fraction extracted from latex polymers was examined by dynamic light scattering (DLS) using an ALV/DLS/SLS-5000 system with a 633 nm laser. A 10 mm diameter cell was carefully flushed with acetone and dried before filled with sample solutions. Samples of the sol fraction in 1,4-dioxane were filtered into the cells using a 0.45 μm PTFE filter. The signals were detected using the ALV/APD detector system at 90° for a 300 s time period and analyzed by the ALV-5000/E/WIN software.

Film Formation and Fluorescence Measurements. Latex films for energy-transfer experiments were prepared from a 1:1 weight ratio mixture of the purified donor- and acceptor-labeled dispersions. For each film, an aliquot of the mixture (two or three drops) was placed on a quartz plate (1 × 2.5 cm) and spread with a glass rod. Latex films were allowed to dry for 12 h at room temperature. All of them were transparent and homogeneous, with a film thickness of 30−40 μm. The films on their quartz substrates were annealed by placing them directly on a high mass (2 cm thick) aluminum plate in a preheated oven. Under these conditions, we estimate that it takes less than 1 min for the film to reach the preset oven temperature.

Fluorescence decay measurements were made by the single photon timing technique.[13] A pulsed flash lamp was used as excitation source. Each film was placed in a quartz tube and degassed with N_2 for 10 min before the measurement. The excitation wavelength was 300 nm, and the emission was collected from 350 to 400 nm. A 335 nm cutoff filter was mounted in front of the emission monochromator to minimize the amount of scattered light from the sample entering the detection system. Data were collected to 5000 counts in the maximum channel, and these data were fitted by nonlinear least squares using the delta function convolution method.[13]

Data and Data Analysis. Films of the Phe-labeled latex gave exponential fluorescence decays (I_D) with an unquenched lifetime of 41 ns in the polymer prepared by miniemulsion polymerization and 43 ns in the polymer prepared by semicontinuous emulsion polymerization. In the presence of an energy transfer acceptor, the fluorescence-decay curves became nonexponential. The shape of the curve depends on the details of the donor−acceptor (D/A) pair distribution. In a system with uniformly distributed donors and acceptors in three dimensions in the absence of diffusion, the donor fluorescence intensity decay $I_D(t')$ following instantaneous excitation is described by the Förster equation:[14]

$$I_D(t') = A \exp\left[-\frac{t'}{\tau_D} - P\left(\frac{t'}{\tau_D}\right)^{0.5}\right] \tag{2}$$

where

$$P = \frac{4}{3}\pi^{3/2}\left(\frac{3}{2}\langle\kappa^2\rangle\right)^{1/2} N_A {R_0}^3[\mathrm{Q}] \tag{3}$$

Here, P is proportional to the acceptor (quencher) concentration [Q]. R_0 is the Förster radius for energy transfer, and N_A is Avogadro's number (6.023 × 10^{23} number/mol). The orientation factor $\langle\kappa^2\rangle$ describing the average orientation of dipoles of donor and acceptor molecules has a value of $^2/_3$ in fluid solution, where rotation is rapid. It takes a value of $\langle\kappa^2\rangle = 0.476$ for a random distribution of immobile chromophore in three dimensions,[15] a situation typical of dyes in polymer matrices.

The quantum efficiency of energy transfer $\Phi_{ET}(t)$ is defined by the middle term in the expression

$$\Phi_{ET}(t) = 1 - \frac{\int_0^\infty I_{DA}(t')\,dt'}{\int_0^\infty I_D(t')\,dt'} = 1 - \frac{\text{area}(t)}{\tau_D} \tag{4}$$

where t is the annealing time after sample preparation, t' is the fluorescence decay time, and area(t) refers to the normalized area under the fluorescence decay curve of a sample annealed for time t. To obtain an accurate area for each decay profile, we fitted each decay curve to the empirical eq 5 and then evaluated the integral analytically from the magnitude of the fitting parameters, A_1, A_2, and p.

$$I_D(t') = A_1 \exp[-t'/\tau_D - p(t'/\tau_D)^{1/2}] + A_2 \exp(-t'/\tau_D) \quad (5)$$

A useful measure of the extent of polymer diffusion is the parameter f_m in eq 6. This parameter represents the fractional growth of ET in the system and is defined in such a way that it corrects for the energy transfer in the nascent films. In eq 6, $[\Phi_{ET}(t) - \Phi_{ET}(0)]$ represents the change in energy-transfer efficiency between the freshly prepared film and that annealed for time t. The denominator describes the difference in energy transfer efficiency between the initial and the fully mixed films.

$$f_m = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} = \frac{\text{area}(0) - \text{area}(t)}{\text{area}(0) - \text{area}(\infty)} \quad (6)$$

Results and Discussion

Preparation and Characterization of the Latex Samples. A series of unlabeled P(VAc−BA) latex samples and those labeled with dyes were prepared by batch miniemulsion polymerization. Unlabeled P(VAc−BA) samples were prepared in the absence of dye comonomers. To prepare Phe-labeled latex samples, 1 mol % PheMA was used. To prepare NBen-labeled latex samples, 0.3 mol % NBenA was used, and to prepare doubly labeled latex samples, both 0.5 mol % PheMA and 0.15 mol % NBenA were added to the monomer mixture. The latex particles have diameters of ca. 180 nm. In the absence of a chain transfer agent, the latex polymer has a substantial gel content. In some experiments, 1.5 wt % C_{12}-SH was added to the reaction recipe in an attempt to moderate or eliminate the gel content.

Gel Content. Our protocol for measuring gel content uses centrifugation to separate the soluble from insoluble components of a polymer. To carry out this experiment, we took freeze-dried latex polymer in a centrifuge tube. We added solvent, stirred, and then centrifuged the solution to sediment the “insoluble” material. There are some subtle features of this methodology that require comment. First, the gel that is formed during the reaction is localized within individual particles; i.e., it is produced in the form of microgel. From the work of Tamai et al.,[16] we know something about the nature of films formed from pre-cross-linked particles. When the latex film dries, a mechanically coherent film is formed, in which the dangling ends from the microgel contribute to adhesion between adjacent cells in the film. These films when dry show good mechanical properties, but they exhibit poor solvent resistance. Our protocol depends on the tendency of these films to form fragments upon exposure to good solvents that are large enough to sediment under normal high-speed centrifugation. Individual solvent-swollen microgel particles can disperse in a good solvent, and these dispersions would not be expected to sediment under our centrifugation conditions. Thus, the gel content values, which we report below, refer only to the sedimented fraction of any gel that might be present.

P(VAc−BA) particles prepared by miniemulsion polymerization in the absence of 1-dodecanethiol exhibited a significant gel content that appeared to depend on which dye was incorporated into the recipe. We refer to these gel-containing samples as G−P_{me}(VAc−BA). Using the protocol described above, we obtained 39% gel for G−P_{me}(VAc−BA)−Phe but 26% gel for G−P_{me}(VAc−BA)−NBen. In an attempt to confirm this difference, we measured the gel content of a 1:1 mixture of the two polymers and obtained 34% gel for this film. We also obtained 25% gel for G−P_{me}(VAc−BA)−Phe−NBen and 4% gel for unlabeled G−P_{me}(VAc−BA). These results imply that the presence of even these small amounts of dye comonomer significantly enhances gel formation during polymerization. In addition, Phe-labeled latex particles have higher gel content than NBen-labeled latex samples. Similar results were found in other latex samples prepared by semicontinuous emulsion polymerization. As reported in our previous paper,[17] we obtained 77% gel for G−P_{sc}(VAc−BA)−Phe and 5% for G−P_{sc}(VAc−BA)−NBen. We do not know why NBen-labeled samples have a higher gel content than the unlabeled samples. That Phe-labeled samples have a higher gel content than others may be due to active propagating VAc radicals abstracting a hydrogen from the benzyl group of Phe derivatives attached to the copolymers. In all experiments in which 1.5 wt % C_{12}-SH based on monomer was introduced into the miniemulsion polymerization, we obtained latex polymer in which no gel could be detected by centrifuging dry films exposed to 1,4-dioxane (see Table 2). This result indicates that the presence of C_{12}-SH can suppress formation of gel even in the presence of dye comonomers. We refer to these samples as “gel-free” (GF−P_{me}(VAc−BA)).

To gain further insights into the contribution of gel content on polymer diffusion in P(VAc−BA) latex films, we took some of the gel-containing samples and separated them into their sol and gel fractions as described in the Experimental Section. To test the effectiveness of this separation, we carried out dynamic light scattering (DLS) measurements in 1,4-dioxane on the sol fractions of the latex samples. The DLS experiments provide evidence for small amounts of solvent-swollen microgel particles in the sol component. We also observed the presence of microgels even in the “gel-free” latex. These results indicate that the chain transfer agent is not able to suppress gel formation completely. We have also seen the presence of these microgels in P(VAc−BA) latex particles prepared by semicontinuous emulsion polymerization.[17] However, it proved to be very difficult to quantify the amount of microgel in the sol component. For both the gel-free sample and the sol fraction of the gel-containing sample, filtered solutions gave $M_w \sim 150\,000$ g/mol.

Phase Separation. In this section we describe experiments that provide information about phase separation in P(VAc−BA) latex particles prepared by batch miniemulsion polymerization. The results of DSC measurements are presented in Table 2. In each of the samples, we observe two T_g values and conclude that two separate domains are present.

This result is consistent with the findings of the Vanderhoff group (Misra et al.[3,4]), who showed that VAc−BA latex copolymers prepared by conventional batch emulsion polymerization have two T_g values. They investigated particles prepared from a 63:37 (w/w) mixture of VAc/BA without any added chain transfer agent. These authors also investigated the morphology of the films formed by these latex particles, using transmission electron microscopy in combination with hydrazine vapors followed by OsO_4 as a selective stain for butyl acrylate. They found domains of a BA-rich phase dispersed in a continuous BA-lean matrix and inferred that the latex particles themselves consisted of a PVAc-rich continuous phase containing a dispersion of BA-rich droplets. Several years later, this group

(Delgado et al.[5,18]) extended their studies to miniemulsion polymerization of a 30:45 w/w mixture (1:1 molar ratio) of VAc and BA. On the basis of dynamic mechanical measurements of films of these latex, the authors conclude that there is more mixing between the BA-rich domains and the PVAc-rich domains in the particles formed in conventional batch polymerization than in the particles formed by miniemulsion polymerization. Kinetics studies showed that in miniemulsion the BA monomer was consumed more rapidly, as one would expect for the reactivity ratios, and that the remaining VAc was incorporated into the particles in the later stages of the reaction.[5] In addition, they showed that there was a substantial gel content in the polymer produced by miniemulsion polymerization, whereas the polymer produced under conventional batch emulsion polymerization conditions appeared free of gel.

We have no direct information about the morphology of the individual particles produced in our miniemulsion reactions, but on the basis of results in the literature summarized in the preceding paragraph, and the fact that BA is the minor component in our reactions, we assume that these particles consist of low-T_g BA-rich domains in a PVAc-rich matrix. We did investigate the influence of chain transfer agent on the thermal response of our polymers and found that the lower T_g value appeared to increase with a decrease in the gel content of the copolymers. For example, this T_g value is −2.3 °C for GF−P_{me}(VAc−BA)−NBen and −15.8 °C for G−P_{me}(VAc−BA)−NBen. One implication of this result is that there is a higher VAc content in the BA-rich phase of the "gel-free" latex than in the gel-containing latex.

Another experiment was carried out to examine the reaction profile as a function of polymerization time in a batch miniemulsion polymerization of VAc + BA in the presence of 1.5 wt % C_{12}−SH and 0.3 mol % NBenA. This reaction was run on a larger scale to facilitate taking 10 mL aliquots during the polymerization to measure monomer conversion, mole ratio of VAc/BA, T_g, and molar mass distribution from the UV and RI signals of the GPC measurements. We note that polymer samples taken during polymerization are "gel-free". The mole ratios of VAc/BA in copolymers were determined by ^{1}H NMR in DMSO-d_6. To analyze these spectra, we used the peak at 4.9 ppm, corresponding to the methine group of VAc, and the peak at 4.0 ppm, corresponding to the methylene group adjacent to carboxyl group in the butyl ester of BA, to calculate the mole ratio of VAc to BA in the copolymer.

In Figure 1, we plot monomer conversion of VAc and BA against overall monomer conversion. One can clearly see that BA is converted to polymer more rapidly than VAc. This rapid conversion of BA leads to the formation of PBA-rich domains with the lower T_g value. By 34% overall monomer conversion, over 80% of the BA has reacted. In later stages of the reaction VAc reacts to form the PVAc-rich phase with the higher T_g value. These results are in good agreement with those cited above by Delgado et al.[5]

In Table 3, we present the characteristics of the samples as a function of polymerization time. We found that the mole ratio of VAc to BA increases along with monomer conversion. We observe that there are two T_g values for polymer formed throughout the reaction but that these T_g values increase as the reaction proceeds: −28.1 and 4.5 °C at 10 min (34% conversion), −2.5 and 35 °C at 15 min (52% conversion), and −2.5 and 40 °C at 60 min (90% conversion). We infer from these data that after most of the BA monomer was consumed, PBA-rich domains formed at the beginning of polymerization were gradually swollen by PVAc-rich polymer, as the polymerization proceeded. As a result, the lower T_g values increase from −28 to −2.5 °C.

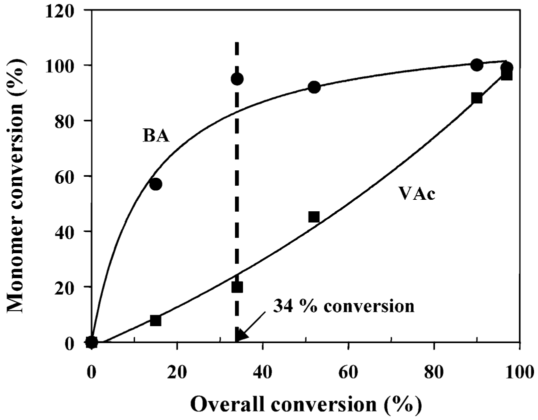


Figure 1. Monomer conversion of VAc and BA against overall monomer conversion in miniemulsion polymerization in the presence of 1.5 wt % C_{12}-SH and 0.3 mol % NBenA of the total monomers.

Table 3. Monomer Conversion, Mole Ratio of VAc/BA, and T_g Values as a Function of Polymerization Time in Batch Miniemulsion Polymerization at 80 °C in the Presence of 1.5 wt % of C_{12}-SH and 0.3 mol % of NBenA

polymerization time (min)	conv [%]	mole ratio of VAc/BA[a]	T_g [°C][b]
7	15	0.82/1	
10	34	1.00/1	−28.1, 4.5
15	52	2.90/1	−2.5, 34.7
60	90	5.16/1	−2.3, 40.3
90	97	5.71/1	

[a] Measured by ^{1}H NMR in DMSO-d_6. All solutions were transparent. [b] Measured by DSC.

Location of the Dyes. Since phase separation during miniemulsion polymerization leads to the formation of BA-rich and VAc-rich domains, we need to consider whether the fluorescent dyes are preferentially incorporated into one of these domains. Since both the Phe and NBen monomers are simple acrylates, we imagine that their reactivity ratios with the other monomers will be similar to those of simple acrylates.

Molar Mass Distributions in GPC Measurements. In monomer conversion studies, we focus on the incorporation of the NBenA monomer into the copolymer. In Figure 2, we show the molar mass distributions obtained by GPC from the UV and RI signals for copolymer samples taken during miniemulsion polymerization in the presence of 1.5 wt % C_{12}-SH and 0.3 mol % NBenA. The UV signal in the low molar mass region appearing at ca. 20 mL elution volume indicates that at very low conversion there is a significant fraction of dye in the sample not bound to the polymer. This peak disappeared approximately 10 min (34% conversion) after the polymerization began, which indicates that most of the NBenA monomer was consumed over this time. Near the end of the reaction (60 min in Figure 2), the strong difference in the UV signal (due to the NBen chromophore) and the RI signal due to polymer is clear evidence that the dye is not uniformly distributed in the latex polymer. We infer that the NBenA monomer copolymerized with BA to become incorporated primarily into the PBA-rich domains. We assume that the Phe

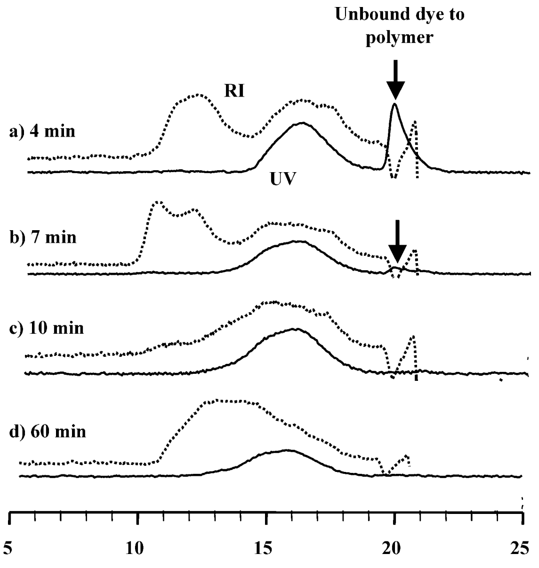


Figure 2. Evolution of apparent molar mass distributions from the UV and RI signals of GF−P_{me}(VAc−BA) samples as a function of polymerization time in miniemulsion polymerization with 1.5 wt % of C_{12}-SH and 0.3 mol % of NBenA. For measurements of the UV signals, we employed $\lambda_{ex} = 350$ nm.

dye is localized in a similar fashion. Further insights into the location of the dye into the polymer are possible through energy-transfer measurements.

Doubly Labeled Latex Particles. To help resolve questions about the location of the dyes in the film, we examined films formed from a doubly labeled "gel-free" latex sample GF−P_{me}(VAc−BA)−Phe-NBen and "gel-containing" latex sample G−P_{me}(VAc−BA)−Phe−NBen (see Table 2). In these samples the dye content was chosen to be half the amount for each dye compared to the individual Phe- and NBen-labeled latex particles. In this way, the bulk dye concentration is comparable to what one would expect from full mixing of the polymers in a 1:1 P(VAc−BA)−Phe plus a P(VAc−BA)−NBen film. Solvent-cast doubly labeled films were cast from a solution of freeze-dried polymer particles in dichloromethane, dried at room temperature for 12 h, and then annealed at 120 °C for 1 h. As an example, a measured donor fluorescence decay profile for this film is shown in Figure 3. From the weighted residual plot and the autocorrelation of the residuals, one can see that this decay curve did not give a good fit to eq 2. This result is not surprising because of preferential localization of the dyes in the BA-rich phase. The derivation of eq 2 assumes a macroscopically uniform, but locally random, distribution of donors and acceptors in the polymer. On the other hand, this curve gives a good fit to eq 5 (see the lower plot of weighted residuals in Figure 3), which has an extra fitting parameter to accommodate a long-time tail in the fluorescence decay. The fitting parameters for decay curves are presented in Table 4.

Estimation of Local Concentration of Dyes. We can gain insights about particle morphology from these data. First, without resorting to models, we can see that the quantum efficiency of energy transfer in both the "gel-free" solvent-cast films ($\Phi_{ET} = 0.83$) and the "gel-containing" films ($\Phi_{ET} = 0.81$) is substantially higher than that ($\Phi_{ET} = 0.70$) one would expect for randomly distributed acceptors in the polymer. This value was calculated with $R_0 = 2.7$ nm and eq 3, for which $[NBen]_{bulk}$ would equal 21.9 mM. We note here that the value of the Förster ET distance ($R_0 = 2.7$ nm) was determined from model experiment with free dyes randomly distributed in P(VAc−BA) films based on latex particles prepared by semicontinuous emulsion polymerization, in which we assume that the latex polymer is homogeneous and uniform.[17] This result indicates that the dyes have a local concentration higher than their bulk concentration; i.e., they are localized within dye-rich domains. One can also see that the value of Φ_{ET} for the "gel-free" film is similar to that for the "gel-containing" film, even though there is the presence of gel. This result tells us that the formation of gel does not affect the distribution of dyes in the sample.

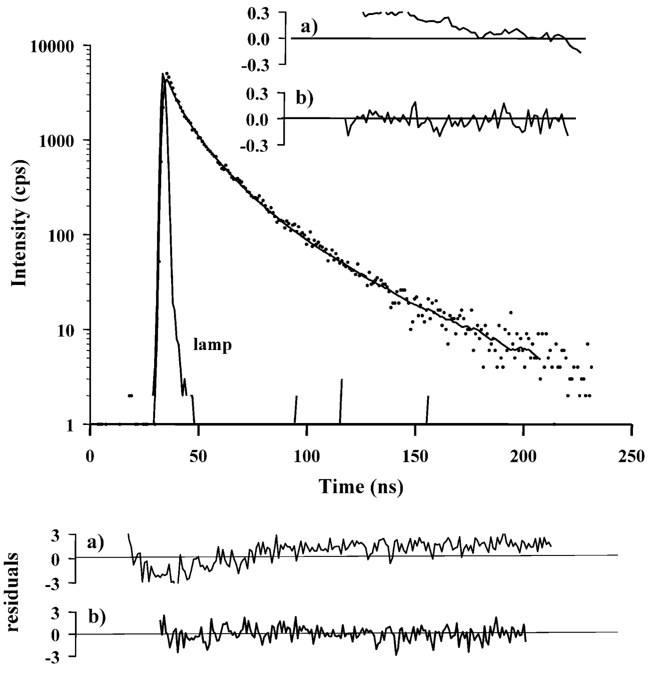


Figure 3. Fluorescence decay profile of a "gel-free" GF−P_{me}-(VAc−BA)−Phe−NBen latex film doubly labeled with 0.5 mol % of PheMA and 0.15 mol % of NBenA. Weighted residuals and autocorrelation of the residuals of the fits to (a) eq 2 and (b) eq 5. The rapidly decaying peak at short times (lamp) is the time profile of the excitation source.

Table 4. Fitting Parameters for $I_D(t')$ Profiles of Solvent-Cast Films Based on P_{me}(BA−VAc)−Phe−NBen Latex Particles[a]

parameters	gel-free	gel-containing
A_1[b]	0.989	0.988
A_2[b]	0.011	0.012
P_{local}	2.82	2.6
Φ_{ET}(lim)	0.83	0.81
$[NBen, mM]_{local}$[c]	38	35

[a] Solvent-cast films were cast from solutions of freeze-dried latex polymers in dichloromethane, dried at room temperature for 12 h, and then annealed at 120 °C for 1 h. [b] A_1 and A_2 values are normalized. [c] Calculated based on eqs 2 and 3, using the $R_0 = 2.7$ nm and P_{local} values. [d] $k' = [NBen]_{local}/[NBen]_{bulk}$, where $[NBen]_{bulk} = 21.9$ mM.

Additional information is available from the fitting parameters if we make some assumptions about the data. First, we assume that most of the dyes are associated with these dye-rich domains and that the long tail of the donor decay is due to a small fraction of donors that are unable to communicate with acceptors. As seen in Table 4, the A_2 terms contribute only ca. 1.2% to the donor fluorescence in both the "gel-free" and "gel-containing" doubly labeled latex films. We now assume that we can use the expression for P given in eq 3 to interpret the value of this parameter obtained from the first term of eq 2. Using $R_0 = 2.7$ nm, we calculate a local acceptor concentration $[\mathrm{NBen}]_{\mathrm{local}}$ that is 38 mM for the "gel-free" latex films, 35 mM for the "gel-containing" latex films, and 36.5 mM on average for both samples (see Table 4). These results meant that local concentration of dye is approximately 1.7 times higher on average for both "gel-free" and "gel-containing" samples than its bulk-averaged concentration.

From these various experiments, we see that in the miniemulsion polymerization reaction more than 90% of the dye is incorporated into the copolymer during the first 34% conversion. This BA-rich polymer does not by itself constitute the entire BA-rich domain. It is swollen by polymer produced at somewhat later stages of the reaction. From the model used to interpret the $I_D(t)$ decay profile for the doubly labeled latex, we infer that the dye-containing domain represents about somewhat larger than half ($1/1.7 = 0.6$) the volume fraction of the overall polymer.

Polymer Diffusion. In this section we examine polymer diffusion in films formed by $\mathrm{P_{me}}$(VAc–BA) latex prepared by miniemulsion polymerization. We compare these results to similar experiments carried out on D- and A-labeled latex films in which the latex samples were prepared by semicontinuous emulsion polymerization under monomer-starved conditions. Both sets of latex contained respectively 1 mol % PheMA and 0.3 mol % NBenA in the D- and A-labeled particles. Films were prepared from 1:1 weight ratio mixtures of Phe- + NBen-labeled P(VAc–BA) latex samples. Some of these films were cast at 4 °C and dried at this temperature for 12 h. Others were formed by more rapid drying at room temperature, 22 °C. After an initial fluorescence decay measurement (at 22 °C) on each film, the films were then placed in an oven on a high mass aluminum slab to bring the temperature rapidly to the annealing temperature.

A curious result is that the phenanthrene decay profiles in films of the donor-labeled polymer prepared by miniemulsion polymerization were exponential. We are accustomed to finding exponential phenanthrene decays for Phe-labeled homopolymers and copolymers without phase separation.[6–8,17,19] The Phe lifetime can vary between 41 and 46 ns in these films. Here we find 41 ns for the miniemulsion polymer and 43 ns for the more uniform polymer prepared by semicontinuous emulsion polymerization. The fact that we find simple exponential profiles in films of the miniemulsion polymer, known to have domains of different composition, is likely an indication that the actual lifetimes of the donor in each domain are rather similar.

Gel-Free $\mathrm{P_{me}}$(VAc–BA) Films. We have previously described energy transfer experiments on films formed from the latex GF–$\mathrm{P_{sc}}$(VAc–BA) prepared by semicontinuous polymerization, with nominal polymer molar mass $M_w \approx 75\,000$, $M_w/M_n \approx 4$.[6] Those experiments were on the whole "normal" in that the decay profiles of films formed from the donor-labeled latex were exponential, and the initial quantum efficiency of 1:1 donor- and acceptor-labeled films newly formed at 4 °C were small ($\Phi_{\mathrm{ET}}(0) = 0.05$). Similar films formed at room temperature were characterized by a larger value ($\Phi_{\mathrm{ET}} = 0.25$). These results indicate that little polymer diffusion accompanies particle deformation at 4 °C to form a void-free film, whereas in films formed at 22 °C, some polymer diffusion across the intercellular boundaries occurred as the film dried. When these films were annealed at temperatures ranging from 45 to 65 °C, Φ_{ET} values increased until they reached 0.58, the limiting value expected for solvent-cast films consisting of the donor- and acceptor-labeled polymers.

For the GF–$\mathrm{P_{me}}$(VAc–BA) samples prepared by miniemulsion polymerization in the presence of 1.5 wt % $\mathrm{C_{12}}$-SH, we also found that the films from the donor-labeled latex had a simple exponential form with a lifetime (42 ns) similar to those described above. We then prepared latex films from a 1:1 mixture of the GF–$\mathrm{P_{me}}$(VAc–BA)–Phe and GF–$\mathrm{P_{me}}$(VAc–BA)–NBen latex dispersions. Here we found very different results. Irrespective of whether these films were prepared at 4 or 22 °C, the newly formed films exhibited extensive energy transfer, with an area(0) = 10.9 ns, corresponding to $\Phi_{\mathrm{ET}}(0) = 0.74$. When these films were annealed at 120 °C for 2 h, these Φ_{ET} values remained essentially unchanged. To try to understand the origin of this difference, we prepared solvent-cast films. These films were prepared by taking a 1:1 mixture of GF–$\mathrm{P_{me}}$(VAc–BA)–Phe and GF–$\mathrm{P_{me}}$(VAc–BA)–NBen particles, purified by ion exchange to remove salt and surfactant, and dissolving it in dichloromethane. Aliquots of this solution were cast onto quartz plates and allowed to dry at room temperature for 12 h. For this sample, we obtained also $\Phi_{\mathrm{ET}}(\mathrm{lim}) = 0.74$. This value did not change upon annealing the films. We conclude that for both the latex films and for the solvent-cast films, diffusive mixing of the donor- and acceptor-labeled polymer took place as the films formed, and that no further mixing occurred when the films were heated.

We note that the value $\Phi_{\mathrm{ET}}(\mathrm{lim}) = 0.74$ is less than that in the films formed from the "gel-free" doubly labeled latex ($\Phi_{\mathrm{ET}} = 0.83$). This result indicates that the dye distribution in films formed from the mixture of GF–$\mathrm{P_{me}}$(VAc–BA)–Phe + GF–$\mathrm{P_{me}}$(VAc–BA)–NBen is somewhat different than that of the doubly labeled latex. When both dye comonomers are added to a single reaction, they can become distributed statistically in the reaction in a manner that depends only on their reactivity ratios, which we imagine are very similar to those of butyl acrylate. When they are attached to polymers in separate particles and mix through polymer diffusion, their ability to randomize is limited by the influence of correlation effects on polymer mixing.

Gel-Containing $\mathrm{P_{me}}$(VAc–BA) Films. As in the case of gel-free latex films, donor fluorescence decays for G–$\mathrm{P_{me}}$(VAc–BA)–Phe films in the absence of acceptor dye were well fit with a single-exponential term. These films gave an unquenched lifetime of 41.4 ns. To examine polymer diffusion in these latex films, a 1:1 mixture of G–$\mathrm{P_{me}}$(VAc–BA)–Phe + G–$\mathrm{P_{me}}$(VAc–BA)–NBen was prepared and then purified by treating it with an ion-exchange resin to remove all ionic species, including salts and surfactants. When we attempted to prepare films in the cold room at 4 °C, the films we obtained were cracked and turbid, indicating that film formation was incomplete. Therefore, aliquots of the mixed latex films were cast onto quartz plates and allowed to dry for 12 h at room temperature (22 °C). This procedure led to transparent crack-free films. Representative donor fluorescence decays for these films are shown in Figure 4. From the newly formed film of the D- + A-labeled latex we find an area(0) of 39.6 ns, corresponding to $\Phi_{\mathrm{ET}}(0)$ of 0.04. The difference in behavior of this set of films prepared from the gel-

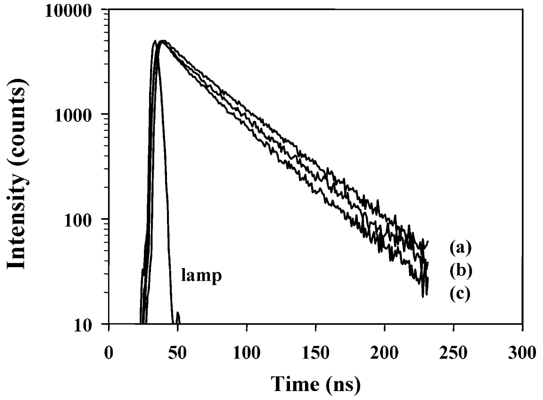


Figure 4. Phenanthrene (donor) fluorescence decay curves ($I_D(t)$) for latex films consisting of a 1:1 weight ratio of G–P_{me}-(VAc–BA)–Phe + G–P_{me}(VAc–BA)–NBen. (a) The newly formed film dried at 22 °C, (b) the same film shown in (a) annealed for 150 min at 09 °C and (c) the solvent-cast film cast from sol polymers extracted from a 1:1 mixture of the two freeze-dried polymers and then dried at 110 °C for 4 h.

containing latex and that described above for the gel-free sample could not be more striking. We infer from the low value of $\Phi_{ET}(0)$ that little or no polymer diffusion takes place during film formation for these samples.

When these latex films were annealed at elevated temperatures and then cooled to room temperature, the area under the donor fluorescence decay curve decreased, an indication of an increase in ET due to polymer diffusion. To evaluate the extent of mixing f_m, defined by eq 6, we need a value for $\Phi_{ET}(\infty)$, which corresponds to full mixing of the D- and A-labeled latex polymers. If "full mixing" corresponded to a state in which the two dyes were distributed in a globally uniform manner throughout the polymer film, we could define $\Phi_{ET}(\infty)$ in terms of eqs 2 and 3, in which [Q] is set equal to the acceptor concentration calculated from the composition of the latex film. This is a reasonable strategy if the polymer films have a homogeneous composition with little or no phase separation.[16] The situation is very different for films formed from latex particles characterized by domains of different chemical composition, as is the case for P_{me}(VAc–BA). Here the concentration of the dyes is enriched in one of the domains, and the limiting value of Φ_{ET} is likely to be larger than that predicted by eq 3 for acceptors randomly distributed in the matrix. This was the case for the gel-free sample of P_{me}(VAc–BA), for which $\Phi_{ET}(\mathrm{lim}) = 0.74$, when the predicted value of $\Phi_{ET}(\infty)$ as defined above is 0.7. From films of the doubly labeled latex particles, in which D and A groups can be bound to the same polymer chain within the PBA-rich phase, Φ_{ET} reached 0.83. For these systems, it may make more sense to define an effective extent of mixing f_{eff} in terms of the limiting extent of ET observed in solvent-cast or thermally aged latex films

$$f_{eff} = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\mathrm{lim}) - \Phi_{ET}(0)} = \frac{\mathrm{area}(0) - \mathrm{area}(t)}{\mathrm{area}(0) - \mathrm{area}(\mathrm{lim})} \quad (7)$$

where area(lim) refers to the integrated area of the donor decay profile for a film that has reached its maximum extent of mixing. Because f_{eff} is defined differently from f_m, we will have to exercise caution in comparing the rates and extents of diffusion in films characterized by different extents of phase separation. This is the situation we face in trying to compare polymer diffusion in films of P_{me}(VAc–BA) with the corresponding films consisting of P_{sc}(VAc–BA) latex synthesized by semicontinuous emulsion polymerization.

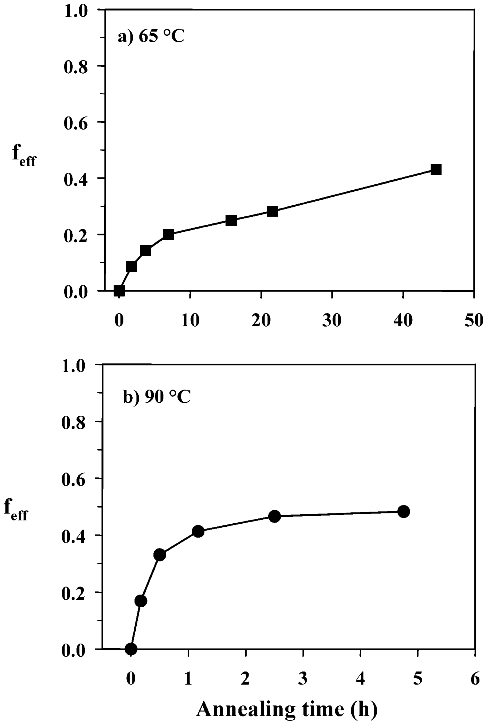


Figure 5. Plots of effective extent of mixing f_{eff} vs annealing time for films of G–P_{me}(VAc–BA)–Phe + G–P_{me}(VAc–BA)–NBen miniemulsion latex annealed at 65 and 90 °C.

Table 5. Characteristics of Solvent-Cast Films from 1:1 Mixture of G–P_{me}(VAc–BA)–Phe + G–P_{me}(VAc–BA)–NBen Prepared by Batch Miniemulsion Polymerization without C_{12}-SH

fractionation	area(lim)	$\Phi_{ET}(\mathrm{lim})$
gel + sol	29.1	0.30
sol	25.4	0.39

To establish values of $\Phi_{ET}(\mathrm{lim})$ for G–P_{me}(VAc–BA), we prepared a solution of the D- and A-labeled polymer in dichloromethane. A solvent-cast film was dried at room temperature for 12 h and then annealed at 120 °C for 2 h. For this solvent-cast film, we obtained area = 29.1 ns, corresponding to $\Phi_{ET} = 0.3$. This low quantum efficiency, compared to that of the gel-free polymer, points to limited mixing of the D- and A-labeled polymer in this film. To obtain further insights into factors that limit the extent of mixing in solvent-cast films, we took a 1:1 mixture of the Phe-labeled and NBen-labeled G–P_{me}(VAc–BA) polymers and attempted to separate it into sol and gel fractions. An aliquot of the sol fraction in 1,4-dioxane was cast onto quartz plates. The films were then dried at 110 °C for 3 h until solvent had completely evaporated. For this sample, we obtained area = 25.4 ns, corresponding to $\Phi_{ET} = 0.39$. This value is larger than that found for the starting polymer but substantially smaller than the value of $\Phi_{ET} = 0.81$ found for the "gel-containing" doubly labeled latex polymer. The results are presented in Table 5.

In Figure 5, we plot f_{eff} values as a function of annealing time for films consisting of G–P_{me}(VAc–BA)–Phe + G–P_{me}(VAc–BA)–NBen miniemulsion latex annealed at 65 and 90 °C. To calculate the values of f_{eff}, we used the value of area(0) = 39.6 ns corresponding to $\Phi_{ET}(0) = 0.04$ and the value area(lim) = 25.4 ns

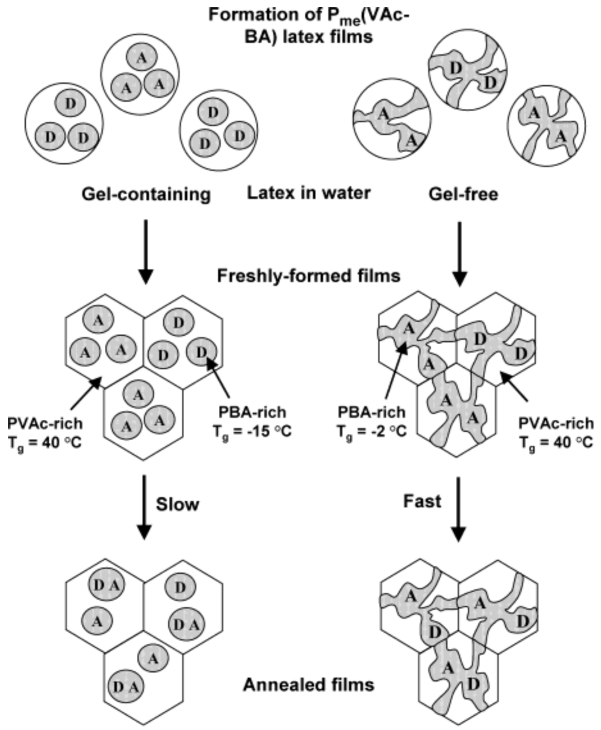


Figure 6. Proposed morphology of latex films based on (a) gel-containing G−P$_{me}$(VAc−BA) and (b) gel-free GF−P$_{me}$(VAc−BA).

corresponding to Φ_{ET}(lim) = 0.39 for the sol fraction as a model for maximum mixing of polymers for this sample. We note that in all of our experiments three films were annealed in parallel, and the average value was taken. The data in Figure 5 indicate that f_{eff} increases with annealing time, as Phe- and NBen-labeled polymers diffuse across the intercellular boundaries. We also see that temperature has an important effect on the rate of polymer diffusion. The important feature for polymer diffusion in gel-containing G−P$_{me}$(VAc−BA) latex films prepared by batch miniemulsion polymerization is that the maximum amount of mixing that can be attained is only 76% (based on the solvent-cast film) due to the large amount of gel. This value is calculated from the limiting value of Φ_{ET} = 0.3 for (sol + gel) polymers and Φ_{ET} = 0.39 for the sol polymers. For a latex film, annealed for several hours at 90 °C, we obtain an f_{eff} value of 0.5. We imagine that network polymers do not diffuse, whereas the sol polymers can diffuse between cells and contribute to the mixing.

Morphology and the Effect of Phase Separation on Polymer Diffusion. We now attempt to explain the difference of polymer diffusion in films prepared from the “gel-containing” latex and from the “gel-free” sample. Because these differences are so striking, we suggest that they reflect morphological differences in the samples with and without a significant gel content. We depict our ideas in Figure 6. We have established that the donor and acceptor dyes are associated with the low-T_g PBA-rich domains. In the case of the gel-free latex, where complete mixing of the donor- and acceptor-labeled polymer occurs rapidly on the time scale of latex film preparation, we imagine that the PBA-rich domains form a continuous phase within each of the particles. The overall morphology is likely to be bicontinuous. This idea is shown on the right-hand side of Figure 6. When the particles come into contact and pack into polyhedral cells during film formation, polymers in these low-T_g domains are able to diffuse rapidly across the cell boundaries. The D and A dyes undergo rapid mixing, and annealing the films does not lead to any additional increase in Φ_{ET}.

To explain the observation that polymer diffusion occurs much more slowly in the gel-containing samples, we imagine that gel formation during particle synthesis traps the dye-labeled PBA-rich domains as occlusions. This idea is shown on the left-hand side of Figure 6. When the particles form a film, some polymer cannot diffuse because it is part of a cross-linked network. D and A dyes linked to these microgel networks remain within cells formed by their original particles. The diffusion of the un-cross-linked polymer component can take place, but these molecules must pass through domains of a different (PVAc-rich) composition.

To test the idea that the PVAc-rich domains act as a barrier to diffusion in films of the gel-containing latex polymer prepared by miniemulsion polymerization, we compare their diffusion rate with a sample prepared by semicontinuous emulsion polymerization. Both samples have the same overall monomer composition and dye content. A detailed description of the synthesis and characterization of the P$_{sc}$(VAc−BA) samples is given in ref 17. For 1:1 mixtures of D- and A-labeled polymer, the P$_{me}$(VAc−BA) latex films have a gel content of 34%, whereas the P$_{sc}$(VAc−BA) latex films have a gel content of 40%. Films were cast from 1:1 weight mixtures of D- and A-labeled latex samples, dried at room temperature for 12 h, and then annealed at temperatures of 65 and 90 °C. To calculate the values of f_{eff} for the semicontinuous latex film, we used area(0) = 41.4 ns corresponding to Φ_{ET}(0) = 0.05 and area(lim) = 21.1 ns corresponding to Φ_{ET}(lim) = 0.51 for the sol fraction of the solvent-cast films. In Figure 7, we compare f_{eff} values as a function of annealing time for miniemulsion batch and semicontinuous latex films annealed at 65 and 90 °C. The data indicate that phase separation retards significantly the rate of polymer diffusion. This result is consistent with our model that in P$_{me}$(VAc−BA) latex films the continuous PVAc-rich phase acts as a barrier to diffusion of the dye-labeled low-T_g component.

Summary

We synthesized four different sets of P$_{me}$(VAc−BA) copolymer latex particles by batch miniemulsion polymerization. These copolymers include donor-labeled latex samples prepared in the presence of 1 mol % of PheMA, acceptor-labeled latex samples prepared with 0.3 mol % of NBenA, doubly labeled latex samples prepared with both 0.5 mol % of PheMA and 0.15 mol % of NBenA, and an unlabeled latex sample. In some syntheses, dodecyl mercaptan was introduced as a chain transfer agent to reduce the polymer molar mass and to suppress gel formation during polymerization. In this way we prepared latex samples with no detectable gel content (GF−P$_{me}$(VAc−BA)). In the gel-containing samples (G−P$_{me}$(VAc−BA)), the gel content was enhanced by the presence of dye comonomer in the reaction. For polymer diffusion studies by ET, the gel content of these films was 34%. Because of the unfavorable reactivity ratios for VAc and BA, all of the samples were characterized by separate domains of a low-T_g PBA-rich phase and a higher-T_g PVAc-rich phase. The dyes were selectively incorporated into the BA-rich domain. From ET measurements on the doubly labeled

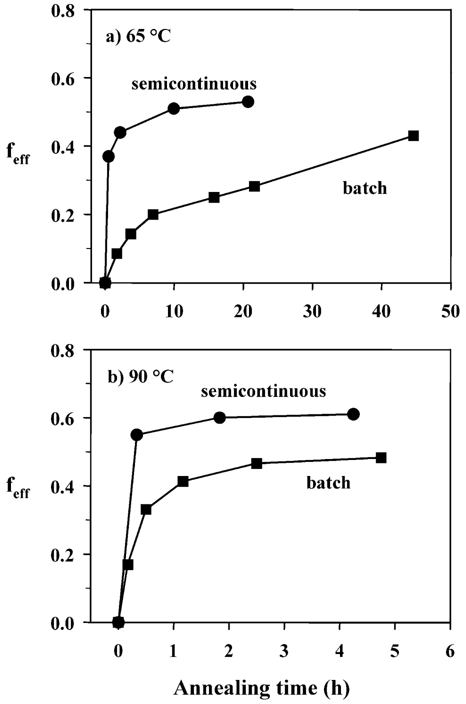


Figure 7. Comparison of effective f_{eff} values calculated from eq 7 as a function of annealing time for miniemulsion batch P$_{\mathrm{me}}$(VAc−BA) (gel = 34%) and semicontinuous (gel = 40%) P$_{\mathrm{sc}}$(VAc−BA) latex films annealed at 65 and 90 °C. To calculate f_{eff} values in semicontinuous latex films, $\Phi_{\mathrm{ET}}(0) = 0.05$ corresponding to area(0) = 41.4 ns and $\Phi_{\mathrm{ET}}(\mathrm{lim}) = 0.51$ corresponding to area(lim) = 21.1 ns for solvent-cast films were used.

samples, we estimated the local concentration of the NBen dye (ca. 36.5 mM), suggesting that the dye is localized in about 60 vol % of the latex polymer.

ET experiments on films cast from 1:1 mixtures of Phe- and NBen-labeled latex particles were employed to examine polymer diffusion across intercellular boundaries. Experiments on the gel-free samples showed that polymer diffusion was so rapid that mixing of donor- and acceptor-labeled polymer was complete on the time scale for film drying, even at 4 °C. This result was interpreted in terms of a model for a bicontinuous particle morphology in which the BA-rich and PVAc-rich domains were interconnected. In films of these latex particles, the low-T_g BA-rich polymer could diffuse without interference from the other phase in the film. In contrast, experiments on the G−P$_{\mathrm{me}}$(VAc−BA) sample showed that diffusion was slow even at 65 and 90 °C. This diffusion was limited to the fraction of polymer not part of the gel component in the sample. The sol component diffused more slowly in these films than the sol component in latex films with a uniform composition of the same monomers and a similar gel content. These homogeneous samples were prepared by semicontinuous emulsion polymerization and were characterized by a single T_g. On the basis of these results, we proposed a model in which the G−P$_{\mathrm{me}}$(VAc−BA) sample was characterized by a morphology in which the low-T_g BA-rich domains were separated by PVAc-rich domains that served as a barrier to diffusive mixing of donor- and acceptor-labeled PBA-rich domains.

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