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Molar Mass Effect on the Rate of Polymer Diffusion in Poly(vinyl acetate-*co*-butyl acrylate) Latex Films

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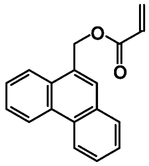
ABSTRACT: The effect of molar mass and gel content on the rate of polymer diffusion in film based on poly(vinyl acetate-*co*-butyl acrylate) P(VAc-BA) latex particles with a 4:1 weight ratio of VAc and BA is examined by fluorescence decay measurements of nonradiative energy transfer (ET). P(VAc-BA) latex particles labeled with phenanthrene (Phe) as the donor and with 4′-(dimethylamino)benzophenone (NBen) as the acceptor were prepared by semicontinuous emulsion polymerization in the presence of different amounts of chain transfer agent to modify the mean molar mass and gel content of the latex particles. We synthesized three sets of samples, which we refer to as high M, medium M, and low M. The high M sample had about 40% gel content, and the sol fraction extracted from the polymer had a nominal M_w (GPC) of 125 000. The medium M and low M samples had a negligible gel content and corresponding values of $M_w \approx 75\,000$ and 42 000, with a broad size distribution. The rate of polymer diffusion in these films was found to increase strongly with decreasing mean molar mass. The diffusion rate increased with annealing temperature. For the high M sample, we found that the diffusion rate was characterized by an apparent activation energy $E_a = 37$ kcal/mol. This value is somewhat larger than that ($E_a = 34$ kcal/mol) reported previously for the medium M sample determined both by ET experiments and by viscoelastic relaxation measurements. The extent of mixing parameter f_m showed a power law dependence on diffusion time, with $f_m \sim t^z$, with z values on the order of 0.12−0.18.

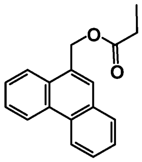
Introduction

Films prepared from aqueous dispersion of latex particles are widely used as coatings.[1] These latex films are formed from small polymer particles formed initially as a colloidal dispersion in water. As the dispersion dries, the particles come into contact and deform to form a transparent film made up of polyhedral cells. The newly formed film often has poor mechanical properties, but these evolve and improve over time, as the boundaries between the individual cells in the newly formed film disappear, and a mechanically coherent film is formed. We now understand that in this maturation process polymer molecules diffuse across the intercellular boundary and create entanglements that provide mechanical strength to the film.

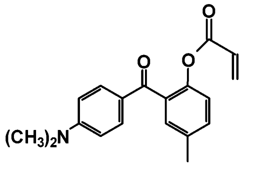
Our group has used fluorescence resonance energy transfer (ET) to study polymer diffusion in latex films.[2] For these studies, the latex polymers were labeled with appropriate dyes. In most of our experiments, phenanthrene (Phe) was used as the donor dye and anthracene (An) was used as the acceptor dye.[3] To extend these studies to latex polymers based on poly(vinyl acetate) (PVAc), we were obliged to seek a new acceptor dye, since anthracene derivatives strongly inhibit VAc polymerization. We found that dyes based on the 4-(N,N-dimethylamino)benzophenone (NBen) chromophore are good acceptors for ET from Phe and are compatible with VAc polymerization. For example, 4′-(dimethylamino)-2-acryloxy-5-methylbenzophenone (NBenA) can successfully be incorporated into VAc copolymer latex particles.[4] The donor-labeled latex particles were synthesized in the presence of 9-acryloxymethylphenanthrene (PheMA).[5] We also prepared the propionate ester NBenP as a model for the acceptor dye and PheMP as a model for the donor dye.



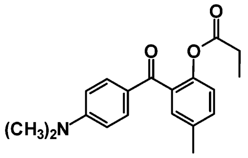
PheMA



PheMP



NBenA



NBenP

The NBen chromophore provides two advantages over An as an ET acceptor for Phe. It has a higher extinction coefficient (ϵ) in the region of Phe emission, leading to a somewhat larger characteristic ET distance R_0 (2.7 nm, see below) than that (2.4 nm) for ET from Phe to An in poly(vinyl acetate-*co*-butyl acrylate) P(VAc-BA) films.[6] In addition, NBen is nonemissive. We can monitor the donor fluorescence decay signal over the entire

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Phe fluorescence spectrum. For An as the acceptor, we had to use narrow-band-pass filter to avoid contamination of the $I_D(t')$ signal with emission from the acceptor.[7] As a consequence, we were able to use smaller levels of acceptor dye labeling (0.3 mol % NBen vs 1 mol % An) in recent experiments on latex films of VAc copolymers with butyl acrylate (BA)[8] and with dibutyl maleate[9] as well as in poly(butyl methacrylate) (PBMA) latex films.[10]

In our previous paper on P(VAc-BA) latex films, we described the temperature dependence of the diffusion rate for a single latex polymer, a material with no gel content and $M_w \approx 75\,000$ g/mol,[8] prepared by semicontinuous emulsion polymerization. Here we turn our attention to the influence of molar mass and gel content on the rate of polymer diffuison in P(VAc-BA) latex films. We examined the behavior of three samples prepared in the presence of three different concentrations of chain transfer agent (dodecyl mercaptan, C_{12}-SH), which we refer to as the low *M*, medium *M*, and high *M* samples. Poly(vinyl acetate) and its copolymers are characterized by the presence of long chain branches,[11] and our high *M* sample has a significant gel content. We use ET experiments to monitor how these factors affect the rate and extent of polymer diffusion between adjacent cells in films formed from these latex dispersions.

In the present paper, we examine molar mass effect on polymer diffusion in P(VAc-BA) latex films via energy transfer measurements. Films consist of a copolymer of VAc and BA with a weight ratio of 4:1. Both donor (D) and acceptor (A) labeled latex were prepared from a common unlabeled seed particle in seeded semicontinuous polymerization reactions under monomer-starved conditions. The donor-labeled latex samples were prepared in the presence of 1 mol % of PheMA. The acceptor-labeled latex samples were prepared in the presence of 0.3 mol % of NBenA based on second stage monomers. The average molar mass of these copolymers was varied by adding different amount of C_{12}-SH. Three sets of films of different molar mass (low, medium, and high) were prepared. The low and medium *M* films showed no significant gel, while high *M* films contained a significant amount of gel (over 40%). We also explore the effect of that gel on the extent of polymer mixing and the rate of diffusion. We show that we can follow interparticle polymer diffusion in films formed from a 1:1 mixture of D- and A-labeled particles. We employ a simple diffusion model to estimate apparent diffusion coefficients and use these values to calculate effective activation energy E_a for the diffusion process in high *M* films. In addition, the rate of polymer diffusion in the lower molar mass films was examined. The results are compared with those for medium *M* films.

Experimental Section

Materials. Potassium persulfate (KPS), sodium dodecyl sulfate (SDS), sodium bicarbonate ($NaHCO_3$), and 1-dodecanethiol (C_{12}-SH) as a chain transfer agent 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.[4,5]

Latex Preparation. All latex dispersions were prepared by semicontinuous emulsion polymerization reactions carried out at 80 °C, with KPS as the initiator and subsequent addition of monomer and surfactant as a preemulsion under monomer-starved conditions as previously described.[8] As an example, the recipe for the synthesis of H-P(VAc-BA)-NBen is summarized in Table 1. The same seed latex was employed for the synthesis of the high *M*, medium *M*, and low *M* latex except for the synthesis of H-P(VAc-BA)-Phe (Table 2). The reactions differed only in the amount of C_{12}-SH (0−2 wt %) added as a chain transfer agent in the second stage. For each type of latex, we prepared two samples: one containing 1 mol % Phe (based on total second-stage monomer) by adding PheMA to the second-stage preemulsion; the other, containing NBen, by adding 0.3 mol % NBenA. For many experiments, salts and surfactants were removed from the dispersion by treatment with previously purified[12] ion-exchange beads (AG-501-X8 mixed-bed resin, Bio-Rad). 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.

Table 1. Recipe for the Synthesis of Poly(vinyl acetate-*co*-butyl acrylate) Latex Particles (H-P(VAc-BA)-NBen) by Semicontinuous Emulsion Polymerization at 80 °C in the Presence of 0.3 mol % of NBenA

ingredients (g)	seed stage	second stage
unlabeled seed[a]		27.1
VAc	60	16.0
BA	15	4.0
NBenA[b]		0.2
SDS	0.45	0.14
$NaHCO_3$[c]	3.0	0.78
KPS	1.15	0.14
water	918.5	100.00

[a] The seed latex particle (diameter 98 nm and pH 7.5) was used for all emulsion polymerizations reported here. It represents 9 wt % of the second stage monomers based on solids. [b] The amount of NBenA is corresponding to 0.3 mol % based on total monomers of the second stage. [c] Sodium bicarbonate as a pH buffer.

Characterization of the Latex Particles. The sizes of latex particles in diameter 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 content of each latex dispersion was determined by gravimetry. The glass transition temperatures (T_g) of the copolymers was measured with a TA Instruments DSC 2920 MDSC V2.6A differential scanning calorimeter over a temperature range of −50 to 60 °C at a heating rate of 10 °C/min. The purified dispersions were freeze-dried at −80 °C until their water content was less than 0.2 wt % and then further dried at 30 °C in a vacuum oven for 2 days. Each sample was taken through three runs. T_g values were calculated from the third run.

To determine the gel content of each polymer, a dried sample (0.17−0.2 g, W_1) was stirred with 1,4-dioxane (10 mL) in a centrifuge tube.[13] 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).

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

The composition of the sol fraction extracted from the high polymers was characterized by ^{1}H NMR, recorded at 400 MHz using a Varian XL400 spectrometer with DMSO-d_6 (d 2.49 ppm) as reference standard. We also examined this material 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. These characteristics of the sol fraction of the high M P(VAc-BA) latex samples are presented in Table 3. We also note that the two lower mass samples have a negligible

Table 2. Characteristics of Latex Particles

latex[a]	solids [%]	d[e] [nm]	M_w (kg/mol)	M_w/M_n	T_g [°C]	gel content [%]
high molar mass[b]						
H-P(Vac-BA)-Phe	14.3	250	130	5.1	16.5	77
H-P(Vac-BA)-NBen	14.7	211	125	5.6	19.8	5
medium molar mass[c]						
M-P(VAc-BA)-Phe	12.7	183	77	5.1	10.7	1.5
M-P(VAc-BA)-NBen	13.8	205	73	4.0	11.8	1.2
low molar mass[d]						
L-P(Vac-BA)-Phe	13.7	187	36	3.4	7.5	0
L-P(VAc-BA)-NBen	13.8	197	47	3.8	9.1	0

[a] All Phe-labeled P(VAc-BA) latex samples were prepared in the presence of 1 mol % of PheMA and all NBen-labeled P(VAc-BA) latex samples were prepared in the presence of 0.3 mol % of NBenA. [b] Prepared without C_{12}-SH. [c] In these reactions, 0.85 wt % of C_{12}-SH on the second stage monomers is used for M-P(VAc-BA)-Phe and 0.5 wt % of C_{12}-SH is used for M-P(VAc-BA)-NBen. [d] In these reactions, 2 wt % of C_{12}-SH on the second stage monomers is used for L-P(VAc-BA)-Phe and 1.5 wt % of C_{12}-SH is used for L-P(VAc-BA)-NBen. [e] Particle diameter. The predicted diameter is 216 nm, based on the number and size of the seed particles as well as the amount of monomer added in the second stage. In the synthesis of H-P(VAc-BA)-Phe, a seed in different size (d = 105 nm) is used.

Table 3. Characteristics of Sol Polymers Extracted from High Molar Mass P(VAc-BA) Latex Samples

latex copolymers	mole ratio of VAc/BA[b]	d[c] [nm]
H-(PVAc-BA)-Phe	5.0/1	106
H-(PVAc-BA)-NBen	2.5/1	33
1:1 weight ratio mixture of H-(PVAc-BA)-Phe/H-P(VAc-BA)-NBen[a]	4.5/1	75, 280

[a] Gel content = 40%. [b] Measured by ^{1}H NMR spectrometry using 400 MHz Varian XL400 spectrometer with DMSO-d_6 (d 2.49 ppm) as reference standard. In the feed, mole ratio of VAc/BA = 5.9/1. [c] Measured by dynamic light scattering in 1,4-dioxane.

gel content when analyzed in terms of eq 1, but their filtered solutions show a microgel component by DLS. This component may be due to the seed particle, which was prepared in the absence of C_{12}-SH.

The molar mass distributions of the latex polymers were measured by gel permeation chromatography (GPC) using polystyrene as molar mass standards. GPC measurements were performed on 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 low and medium M latex samples, an aliquot of latex particles without further purification was dissolved in THF to form a solution, which was passed through a 0.2 μm filter prior to injection in the GPC. For high M latex samples, only the sol fraction of the polymers extracted with refluxing THF for 24 h was injected into the GPC.

A disappointing consequence of the presence of microgel even in the “gel-free” samples is that we could not determine the absolute molar mass of the polymer with a new Viscotek GPC equipped with a triple detector including light scattering. It proved difficult to filter solutions of these polymers through a 0.25 μm filter, a problem that may be connected to the high molar mass of the seed latex used in the synthesis. Thus, the masses (M) of copolymers that we report were determined by the GPC using the older Waters GPC by reference to polystyrene standards. We note here that these M values are likely very different from the true molar mass (M_w) values, since the R_H value of our branched P(VAc-BA) is different from that of linear polystyrene.

Film Formation and Fluorescence Measurements. Latex films for energy transfer experiments were prepared from a 1:1 weight mixture of the purified donor- and acceptor-labeled dispersions. Aliquots of the mixture were placed on quartz plates (1 × 2.5 cm). Low and medium M latex films were allowed to dry for 12 h at 4 °C. They were transparent but partially cracked. High M latex films were dried for 12 h at room temperature. They were transparent and homogeneous.

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 profiles of the films were measured at room temperature by the single photon timing technique.[14] 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 310–400 nm band-pass (BP) with 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 7000 counts in the maximum channel, and these data were fitted by nonlinear least squares using the delta function convolution method.[14]

Data and Data Analysis. For a dipole–dipole coupling mechanism, the rate of energy transfer $w(r)$ between a donor and an acceptor molecule depends on the inverse sixth power of their separation distance r.[15,16]

$$w(r) = \frac{\alpha}{r^6} \qquad \alpha = \frac{3R_0^{\,6}\kappa^2}{2\tau_D} \tag{2}$$

Here, R_0 is the characteristic (Förster) energy transfer distance, and τ_D is the unquenched donor lifetime. The term κ^2 is a dimensionless parameter related to the relative orientation of the donor and acceptor transition dipole moments.[17–19] As predicted by eqs 3 and 4, the donor decay in the absence of acceptor is exponential. Films of the Phe-labeled latex gave exponential fluorescence decays (I_D) with an unquenched lifetime τ_D = 43.3 ns for H-P(VAc-BA)-Phe and M-P(VAc-BA)-Phe, and τ_D = 41.5 ns for L-P(VAc-BA)-Phe. The goodness-of-fit parameter (chi-squared) for these single-exponential fits ranged from 1.2 to 1; for nonexponential decays (see below) the multiparameter fits gave chi-squared values ranging from 1.01 to 1.1.

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.[20]

$$I_D(t') = A \exp\left[-\frac{t'}{\tau_D} - P\left(\frac{t'}{\tau_D}\right)^{0.5}\right] \tag{3}$$

where

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

Here, P is proportional to the acceptor (quencher) concentration ([Q], mM). 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, a situation typical of dyes in polymer matrices.[19]

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

$$\Phi_{ET}(t) = 1 - \frac{\int_0^\infty I_{DA}(t')\,dt'}{\int_0^\infty I_D(t')\,dt'} = 1 - \frac{\text{area}(t)}{\tau_D} \qquad (5)$$

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 fit each decay curve to the empirical eq 6 and then evaluate the integral analytically from the magnitude of the fitting parameters, A_1, A_2, and p.

$$I_D(t') = A_1 \exp[-t'/\tau_D - p(t'/\tau_D)^{1/2}] + A_2 \exp(-t'/\tau_D) \quad (6)$$

A useful measure of the extent of polymer diffusion is the parameter f_m in eq 7. 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 7, $[\Phi_{ET}(t) - \Phi_{ET}(0)]$ 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.

$$f_m = \frac{\Phi_{ET}(t) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} = \frac{\text{area}(0) - \text{area}(t)}{\text{area}(0) - \text{area}(\infty)} \qquad (7)$$

To estimate a value for R_0 for ET from Phe to NBen in this polymer, we prepared films containing a known concentration (120 mM) of PheMP as a free dye and concentrations of NBenP varying from 0 to 13 mM. The films were prepared by solvent casting from dichloromethane solution, which should lead to a random dye distribution. Measured $I_D(t')$ profiles for these films fit well to eq 3, and a plot of the best-fit P values against [NBenP] was linear and passed through the origin. From the slope of the plot (not shown here), assuming $\langle\kappa^2\rangle = 0.476$, we calculate $R_0 = 2.7$ nm. We defer a deeper discussion of R_0 values for Phe and NBen in PVAc copolymer matrices to a future publication.[6]

Results and Discussion

Preparation and Characterization of the Latex Samples. We focus on poly(vinyl acetate-*co*-butyl acrylate) with a monomer weight ratio 4:1 (mole ratio = 5.9:1) as the base polymer for these studies. This copolymer has an estimated glass transition temperature (T_g) of 10 °C from the Fox equation.[21] Dye-labeled P(VAc-BA) latex samples were prepared by seeded semicontinuous emulsion polymerization. Both donor- and acceptor-labeled particles were prepared from a common seed latex. The seed particles themselves (98 nm diameter) were prepared without adding dodecyl mercaptan (C_{12}-SH) as a chain transfer agent. The seed consisted of a similar copolymer and represented 9 wt % of the final particles prepared by two-stage emulsion polymerization. The second stage emulsion polymerization reaction was carried out in the presence of seed particles, and the monomers including dye comonomer were fed into the reaction as a preemulsion along with the initiator KPS.

To vary the molar mass of the latex polymer, different amounts of C_{12}-SH as a chain transfer agent were added during the second stage polymerization. No C_{12}-SH was employed in the synthesis of the high M latex (denoted as H-P(VAc-BA)). This sample had a significant gel content. For some experiments, we separated the high M polymer into its sol fraction and its gel fraction as described in the Experimental Section. The sol fraction by GPC had $M_w \approx 125\,000$ g/mol with $M_w/M_n \approx 5.3$. For the medium M latex (M-P(VAc-BA)) with $M_w \approx 75\,000$ g/mol, we used 0.85 wt % C_{12}-SH for the Phe-labeled particles and 0.5 wt % for the NBen-labeled particles. The different amounts reflect the results of preliminary experiments in which we tried to match the GPC curves of the two latex polymers. For the low M latex (L-P(VAc-BA)) with $M_w \approx 42\,000$ g/mol, we used 1.5 wt % C_{12}-SH for the Phe-labeled particles and 2.0 wt % for the NBen-labeled latex.

The GPC measurements with tandem UV and RI detectors provide information about the dye distribution in the copolymers.[22] In each sample, the trace for the polymer, as monitored by the RI signal, and the trace for the dye, as monitored by the UV signal, had similar shapes and eluted at times consistent with the fact that the UV detector precedes the RI detector. We conclude that the dyes are uniformly incorporated into the second stage polymer and that there are no detectable dyes in the samples not bound to the polymer. In the syntheses for the Phe- and NBen-labeled latex particles where a 98 nm sized seed is used, the final latex samples are obtained with particle diameter in the range of 200 ± 20 nm and a narrow size distribution.

The T_g values determined by DSC are presented in Table 2. We observe that the T_g values appear to increase with molar mass of copolymers. We found, for example, $T_g = 8.3 \pm 0.8$ °C for L-P(VAc-BA), 11.2 ± 0.5 °C for M-P(VAc-BA), and 18.2 ± 1.5 °C for H-P(VAc-BA). Interestingly, we find that the T_g values of Phe-labeled copolymers are somewhat lower than those of corresponding NBen-labeled copolymers. In each of the samples, we observe only one T_g. This result is consistent with the findings of Misra et al.,[23] who have showed that semicontinuous VAc-BA latex copolymers have only one single T_g value, indicating that semicontinuous emulsion copolymerization of VAc with BA under monomer-starved condition gives homogeneous latex particles with little phase separation.

We note in Table 2 that there is no detectable gel for low M and medium M P(VAc-BA) latex samples. This is a consequence of the chain transfer agent used to lower the molar mass during the polymerization reactions. There was a measurable gel content for the high M latex samples that were substantially different for the donor- and acceptor-labeled polymer. We found 77% gel for H-P(VAc-BA)-Phe but only 5% gel for H-P(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 40 wt % gel. We are aware, however, that problems can arise when one tries to measure the gel content of a sample in which the gel is present in the form of microgel particles. Repeated steps of solvent swelling, centrifugation, and decanting of the supernatant can remove solvent-swollen microgel particles that do not settle during the centrifugation step. When we used the Soxhlet extraction method as described by Asua et al.[24] to determine the gel content of H-P(VAc-BA)-NBen, we obtained an average gel content (three measurements) of 51 wt %. We carried out ^{1}H NMR measurements of three samples polymers for three samples, H-P(VAc-BA)-Phe, H-P(VAc-BA)-NBen, and 1:1 weight mixture of H-P(VAc-BA)-Phe with H-P(VAc-BA)-NBen, using solutions of the sol component 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. The results are presented in Table 3. In each case, we obtained mole ratios of VAc/BA smaller than the monomer feed mole ratio of 5.9/1, which indicates that gels consist of mainly VAc-rich copolymers. We also carried out dynamic light scattering measurements in 1,4-dixoane for the sol fractions of H-P(VAc-BA)-Phe and H-P(VAc-BA)-NBen. The DLS experiments provide evidence for solvent-swollen microgel particles in the sol component. It is very difficult to know what fraction of the mass of the sol component is microgel.

ET Studies of Polymer Diffusion. In this paper we examine polymer diffusion in P(VAc-BA) latex films of different molar mass by FRET measurements. Three sets of latex films are employed according to the molar mass: low ($M_w \approx 42\,000$ g/mol), medium ($M_w \approx 75\,000$ g/mol), and high molar mass (>40% gel). Three 1:1 weight mixtures of Phe- and NBen-labeled P(VAc-BA) latex samples were prepared and then purified by treating them with an ion-exchange resin to remove all ionic species including salts and surfactants. Latex films were cast on quartz plates. The low and medium *M* latex films were allowed to dry for 12 h at 4 °C and were transparent but partially cracked. The high *M* latex would not form films at low temperature but formed films that were transparent and homogeneous when dried for 12 h at room temperature (22 °C).

Representative donor fluorescence decays for the films are shown in Figure 1. The top curve in each figure is that of a film containing only the Phe-labeled polymer. The unquenched lifetime was slightly smaller (41.5 ns) for L-P(VAc-BA)-Phe than for H-P(VAc-BA)-Phe and M-P(VAc-BA)-Phe (43.3 ns). The curves for H-P(VAc-BA) in Figure 1A show that only small changes occur in the decay profile for films annealed at 65 °C. For the medium *M* latex films shown in Figure 1B, the decay curves show more curvature after the samples were annealed at 45 °C. A similar evolution of the system takes place for the low *M* latex for films annealed at 35 °C.

One important parameter characterizing a latex film is $\Phi_{ET}(0)$, which describes the extent of ET in a newly formed film. If the particle deformation step during film drying is well separated from the onset of polymer diffusion, sharp boundaries will separate donor- and acceptor-labeled cells in the film. Only Phe and NBen groups close to but on opposite sides of the interface will contribute ET. We obtained $\Phi_{ET}(0) = 0.05$ for the high *M* latex film and $\Phi_{ET}(0) = 0.05$ for the medium *M* latex film. These small values are consistent with little or no polymer diffusion occurring during film preparation.[25] For the low *M* latex film, we obtained $\Phi_{ET}(0) = 0.24$, even though the film was formed at 4 °C, indicating that a significant amount of intercellular polymer diffusion took place during the drying step. When the low *M* and medium *M* latex films were prepared by drying the dispersions at 22 °C, we found dramatic increases in $\Phi_{ET}(0)$ for the newly dry films: 0.4 for the low *M* polymer and 0.24 for the medium *M* polymer. Under these conditions, polymer diffusion occurs as the films dry.

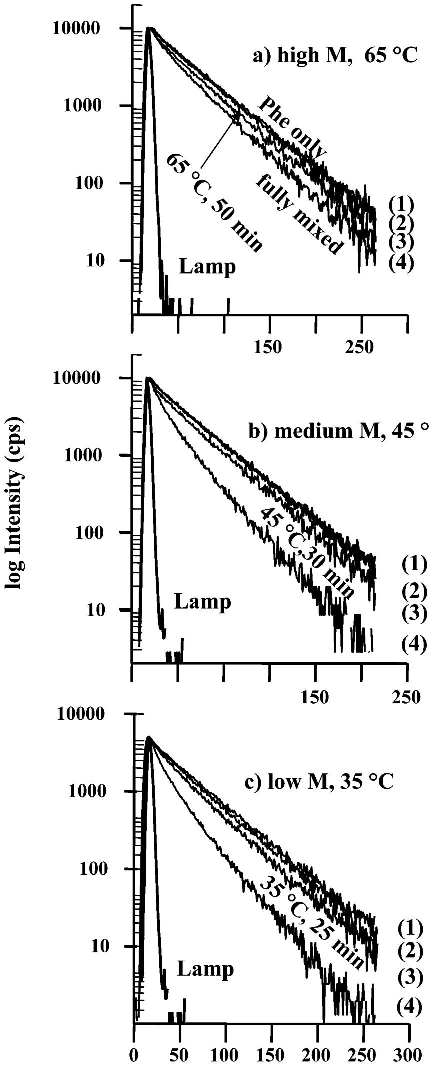

Figure 1. (a) Phenanthrene (donor) fluorescence decay curves ($I_D(t)$) measured at 65 °C for high *M* latex films. (1) The pure Phe-labeled latex, (2) the newly formed film dried at room temperature, consisting of a 1:1 ratio of H-P(VAc-BA)-Phe + H-P(VAc-BA)-NBen, (3) the same film shown in (2) annealed for 55 min at 65 °C, and (4) the solvent-cast film cast from a 1:1 mixture of two freeze-dried polymers dissolved in CH_2Cl_2 and then annealed at 110 °C for 1 h. (b) Corresponding decay curves obtained for medium *M* latex films, consisting of a 1:1 ratio of M-P(VAc-BA)-Phe + M-P(VAc-BA)-NBen, annealed for 30 min at 45 °C. (c) Corresponding decay curves obtained for low *M* latex films, consisting of a 1:1 ratio of L-P(VAc-BA)-Phe + L-P(VAc-BA)-NBen, annealed for 25 min at 35 °C. Note that curves 1 and 2 in (a) and (b) overlap.

Solvent-Cast Films. To evaluate the extent of mixing f_m, defined by eq 7, we need a value for $\Phi_{ET}(\infty)$, which corresponds to full mixing of the donor- and acceptor-labeled latex polymers. In the past, we have used a solvent-cast film as a model for complete mixing of donor- and acceptor-labeled polymer. For linear polymers, the decay curve for films prepared by the solvent casting fit well to the Förster equation (eq 2), and the *P* values obtained from the fit to eq 2 were approximately equal to that expected from the acceptor concentration calculated from the polymer composition. In addition, for linear polymers, we found that the Φ_{ET} values remained constant if the films are annealed at elevated temperature and then cooled back to room temperature.[26,27] We assumed that solvent casting led to a random distribution of polymer-bound donor and

Table 4. Characteristics of Solvent-Cast Films from 1:1 Weight Ratio Mixtures of P(VAc-BA)-Phe/ P(VAc-BA)-NBen of Different Molar Mass Prepared by Semicontinuous Emulsion Polymerization

P(VAc-BA) latex films	area(lim)[a]	Φ_{ET}(lim)[a]
low *M*	15.0	0.64
medium *M*	18.0	0.58
high *M* (sol + gel)	27.1	0.37
high *M* (gel)	32.7	0.24
high *M* (sol)	21.1	0.51

[a] In the calculations, $\tau_D = 43.3$ ns for the high and medium *M* films and $\tau_D = 41.5$ ns for the low *M* film.

acceptor chromophores. In calculating values of f_m, we set the limiting value of the ET efficiency equal to $\Phi_{ET}(\infty)$.

This strategy for data analysis breaks down for the polymers investigated here. Complications arise in more complex systems. The complications we encountered here appear to be due to extensive branching or gel content in the latex polymer. For example, we took freeze-dried samples consisting of purified 1:1 mixtures of Phe- and NBen-labeled particles and dissolved them in dichloromethane. These solutions were cast onto quartz plates and allowed to dry at room temperature for 12 h. We found unexpectedly that when these films were annealed at 110 °C and cooled to room temperature, Φ_{ET} increased. For a film of L-P(VAc-BA)-Phe + L-P(VAc-BA)-NBen, we obtained $\Phi_{ET} = 0.58$ for the solvent-cast film before annealing, and Φ_{ET} increased to 0.64 upon annealing. For a film of M-P(VAc-BA)-Phe + M-P(VAc-BA)-NBen, the solvent-cast film gave $\Phi_{ET} = 0.48$. After a similar annealing, Φ_{ET} increased to 0.58. Here we imagine that there is some local microphase separation that occurs in the solvent-cast film that is overcome upon annealing at a higher temperature.

In Table 4, we present the limiting values of the area (area(lim)) and Φ_{ET} (Φ_{ET}(lim)) obtained for solvent-cast films prepared from 1:1 mixtures of Phe- and NBen-labeled latex samples of the different molar mass after annealing at 110 °C. One can see that the magnitude of area(lim) decreases and that of Φ_{ET}(lim) increases with decrease in molar mass of copolymers, Φ_{ET}(lim) = 0.64 for the low *M* films, 0.58 for the medium *M* films, and 0.37 for the high *M* films. The order of Φ_{ET}(lim) values appears to follow the gel content of copolymer films. Consistent with the fact that the low and medium *M* latex films have little or no gel content, their films show only small differences in their Φ_{ET}(lim) values. The high *M* particles contain over 40% gel. As shown by Tamai and Winnik,[28] the gel content of the individual particles should prevent full mixing between Phe- and NBen-labeled copolymers.

To obtain further insights into factors that limit the extent of mixing in solvent-cast films, we took a 1:1 weight ratio mixture of the Phe-labeled and NBen-labeled high *M* solid polymers and separated it into its sol and gel fractions. We have commented above that the sol fraction is somewhat richer in BA and the gel fraction is somewhat richer in VAc than the monomer feed ratio used to synthesize the particles. Sol polymers from 1,4-dixoxane and gel polymers from dimethyl sulfoxide (DMSO) were cast onto quartz plates. We note here that the gel polymer is not soluble in 1,4-dioxane but appears to form a transparent "solution" in DMSO. The films were then dried at 110 °C for 3 h until the solvent had completely evaporated. We obtained $\Phi_{ET} = 0.51$ for the sol polymers and $\Phi_{ET} = 0.24$ for the gel polymers, bracketing the value $\Phi_{ET} = 0.37$ for the high *M* polymer before fractionation.

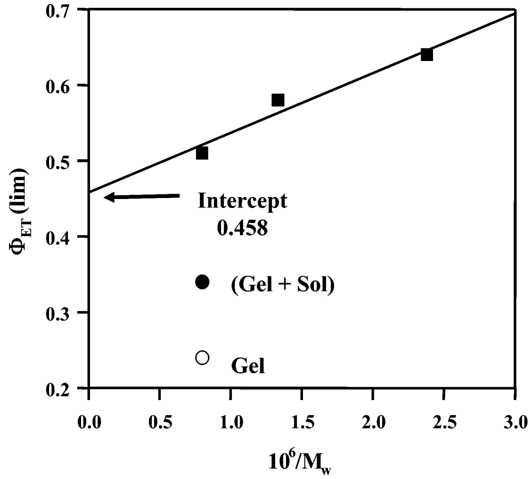

Figure 2. Plot of Φ_{ET}(lim) values against $1/M_w$ for films prepared from 1:1 mixtures of donor- and acceptor-labeled latex. The point on the line for the high *M* polymer refers to the value obtained for the sol fraction. The points below the line refer to the unseparated high *M* sample and to its gel fraction.

More interesting is the fact that the value $\Phi_{ET} = 0.51$ for the sol fraction with $M_w \cong 125\,000$ is smaller than the corresponding values for the low and medium *M* polymers. This trend prompted us to look for a molar mass dependence of Φ_{ET}(lim). In Figure 2, we note that a plot of Φ_{ET}(lim) against $1/M_w$ is linear, and the intercept predicts a value of 0.46 for the hypothetical case of an infinite molar mass soluble copolymer. The same data also give a linear plot of (ln Φ_{ET}(lim)) vs (ln M_w), with a slope of −0.21. This is the type of behavior expected for correlation effects (a "correlation hole")[29] in which there is a depleted concentration of acceptor dyes in the space defined by the radius of gyration of the donor-labeled polymer. This effect may be more severe because of the highly branched nature of PVAc copolymers, which can limit the extent of interpenetration of neighboring molecules in the bulk.

Choice of Meaningful Value for $\Phi_{ET}(\infty)$. In the previous section, we showed for solvent-cast films, of samples of nominal molecular weights $M_w \approx 42\,000$, 75 000, and 125 000 (GPC, polystyrene standards), that limiting Φ_{ET} values decreased with increasing molecular weight. For these samples, we found that a plot of Φ_{ET}(lim) against M_w was linear, with an intercept 0.46. These results indicate that some feature of the polymer architecture is limiting the extent to which the donor and acceptor dyes can reach a uniform random distribution in the film. When the latex polymer has a significant gel content, one expects that there will be little or no diffusion of these microgel networks, although the remaining polymer in the film will be free to undergo extensive diffusion. The limiting Φ_{ET} value should reflect the fact that D-labeled microgel in one cell in a latex film cannot mix with A-labeled microgel in an adjacent cell.

In this context, we return to the question of the most meaningful way to define $\Phi_{ET}(\infty)$ for the calculation of f_m values. For polymers characterized by a uniform chemical composition, the parameter f_m is meant to measure the progress of polymer diffusion from an initial state, in which D- and A-labeled polymers are confined to adjacent cells in a latex film, toward a final

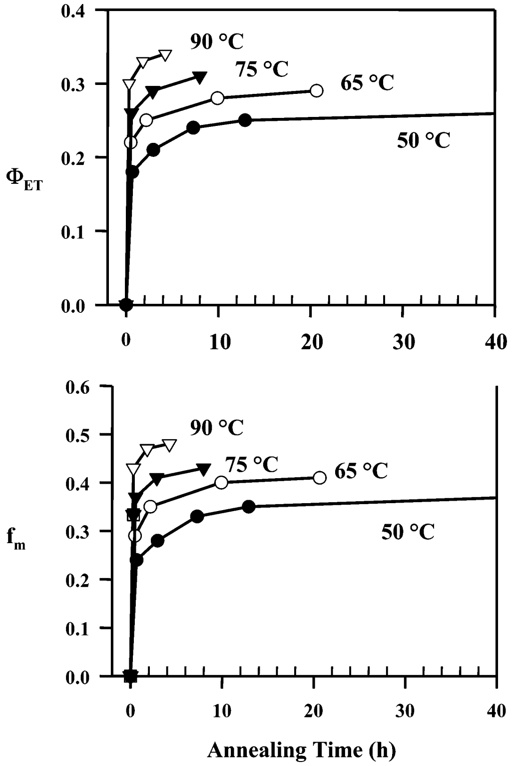

Figure 3. Plots of Φ_{ET} and f_m vs annealing time for high *M* latex films cast from a 1:1 ratio of H-P(VAc-BA)-Phe and H-P(VAc-BA)-NBen, annealed at 50, 65, 75, and 90 °C.

state in which the D and A chromophores are randomly distributed. Under these circumstances, it makes sense to 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. For the experiments described here with mixtures of Phe- and NBen-labeled latex polymer, the bulk acceptor concentration is 17.4 mM. Using the value $R_0 = 2.7$ nm, we calculate area(∞) = 16 ns, corresponding to a value of $\Phi_{ET}(\infty) = 0.63$. We note here that the limiting value of Φ_{ET}(lim) for low M P(VAc-BA) films is very close to this value. With a common choice of values for $\Phi_{ET}(\infty)$, we can now compare the growth of f_m for films consisting of polymers with different molecular weights, different extents of branching, or varying in gel content. Limiting values of $\Phi_{ET}(\text{lim}) < \Phi_{ET}(\infty)$ and thus $f_m < 1.0$ would be a signature of latex films in which features of the polymer architecture limited the extent of polymer intermixing.

Polymer Diffusion in High Molar Mass Latex Film at Various Temperatures. A series of H-P(VAc-BA)-Phe + H-P(VAc-BA)-NBen latex films were prepared at room temperature (22 °C). After the films were dried for 12 h, their fluorescence decay curves were measured. The initial quantum yield for energy transfer for these films was found to be area(0) = 41.4 ns corresponding $\Phi_{ET}(0) = 0.05$. On the basis of arguments in the previous paragraph, we choose the value area(∞) = 16 ns and $\Phi_{ET}(\infty) = 0.63$ as a model for complete polymer mixing.

In Figure 3 we plot Φ_{ET} and f_m values as a function of annealing time for high *M* latex films annealed at various temperatures ranging from 50 to 90 °C. The date in Figure 3 indicate that f_m 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. From the shapes of these curves in Figure 3, we infer that a large increase in f_m values occurs at early times, followed by a smaller increase at longer times. This behavior is consistent with a broad molar mass distribution ($M_w/M_n \approx 5.3$) and also a distribution of branching in the latex polymers. Faster diffusing species, of smaller molar mass and lower degree of branching, contribute to the early rapid diffusion, and larger molar mass copolymers and those with long-chain branches contribute to later diffusion.

The important feature for understanding polymer diffusion in the high *M* P(VAc-BA) latex film is the fact that the maximum amount of mixing that can be attained is only 60% ($f_m = 0.6$) due to the large amount of gel. This value is calculated for the solvent-cast film, based on the measured values of area(lim) = 27.1 ns and Φ_{ET}(lim) = 0.37. For a latex film annealed at 90 °C, f_m values increase rapidly at early times, and after 3 h f_m reaches a value of 0.48. We imagine that the gel component in the film does not diffuse, whereas the sol polymers can diffuse between cells and contribute to the mixing of donor- and acceptor-labeled polymer.

To quantify the temperature dependence of the diffusion process, we need to calculate a parameter like a diffusion coefficient, which is a measure of the diffusion rate of the polymer in the system. We have shown that it is possible to calculate apparent diffusion coefficients D_{app} from f_m values by making some rather strong assumptions about the nature of the diffusion in the system. The model we employ and its strengths and weaknesses are described in ref 30. D_{app} values calculated in this way represent an average over all the diffusion preceding a given f_m value. We have in the past used this approach to quantify the influence of changes in temperature[31,32] or the influence of plasticizing additives[33] on the rate of polymer diffusion. The approach works well as long as one is careful to compare D_{app} values for identical values of f_m. For a system characterized by a distribution of species with different diffusion rates, D_{app} values decrease with increasing f_m.

In Figure 4a we plot the calculated D_{app} values against f_m values for various annealing temperatures. For each sample, these D_{app} values decrease with increasing time as polymers with lower mobility make their contribution to the ET signal. For example, the film sample annealed at 65 °C gave a value of D_{app} = 0.19 nm^2/s after 30 min, 0.06 nm^2/s after 130 min, and 0.01 nm^2/s after 1240 min.[34] This large variation in the magnitude of D_{app} with the extent of mixing reflects a large span in the distribution of the diffusion rates. We also see that temperature has an important effect on the rate of polymer diffusion.

The temperature dependence of polymer diffusion can be described in terms of the Williams–Landel–Ferry (WLF) equation[35] with parameters close to those obtained from viscoelastic relaxation measurement.[36] Over a sufficient broad range of temperatures, for polymer diffusion, the WLF equation takes the form

$$\log (a_T) = \log \frac{DT_0}{D_0 T} = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \qquad (8)$$

where T_0 is an arbitrary chosen reference temperature and D_0 is the diffusion coefficient at that temperature. The magnitudes of the parameters C_1 and C_2 depend on the choice of T_0, but these values are easily trans-

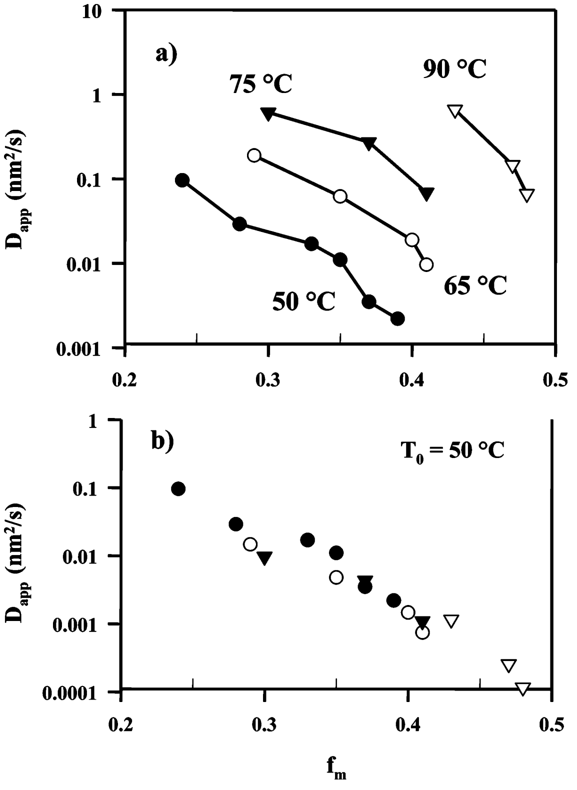

Figure 4. (a) Plots of the apparent diffusion coefficient (D_{app}) as a function of f_m at various temperatures for high M latex films (H-P(VAc-BA)-Phe + H-P(VAc-BA)-NBen). (b) The master curve of D_{app} values at 50 °C was calculated using $E_a = 37$ kcal/mol (154 kJ/mol) as a shift factor.

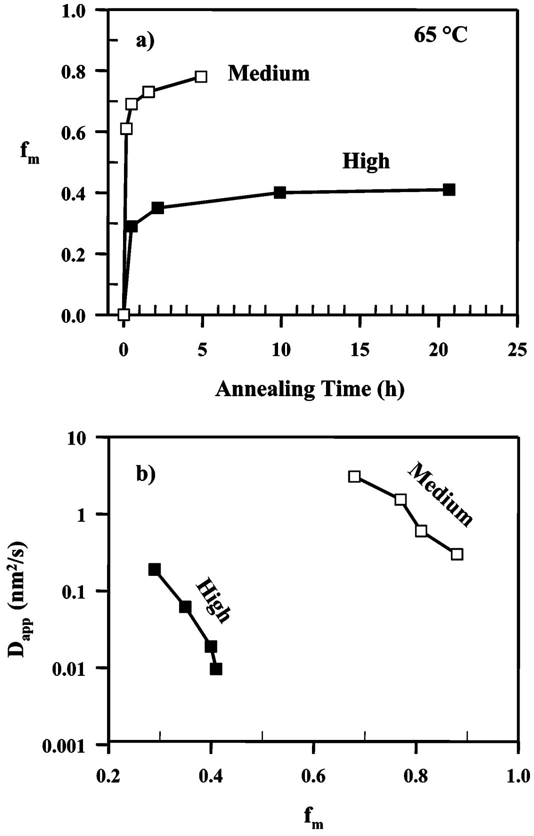

Figure 5. Comparison of f_m and D_{app} values as a function of annealing time for the medium M and high M films annealed at 65 °C.

ferred to other reference temperatures. Because of the greater precision in the individual measurements and the larger number of data points for rheological experiments compared to diffusion measurements, viscoelastic measurements normally provide values of C_1 and C_2 with greater precision than diffusion measurements.

Over a limited temperature range, a plot of ln D vs $1/T$ appears linear, and one can calculate an apparent E_a for polymer diffusion from slope of the plot. For example, a plot of ln D_{app} vs $1/T$ was linear for the data in Figure 4a at $f_m = 0.39$. From the slope we calculated an apparent $E_a = 37$ kcal/mol. This value is somewhat larger than that we reported ($E_a = 34$ kcal/mol) for medium M P(VAc-BA) latex films over the temperature range 35−75 °C.[8] We note that in a different system, with polystyrene latex films using small-angle neutron scattering, Klein et al. found higher apparent E_a values for polymer diffusion for samples of higher molar mass.[37] Since temperature affects the rate of diffusion by a change in the microscopic friction coefficient, the magnitude of the E_a should be independent of f_m. Therefore, we used the value of $E_a = 37$ kcal/mol (154 kJ/mol) as a shift factor to create a master curve of D_{app} values at 50 °C. The shifted values calculated in this way are shown in Figure 4b. We take the success in generating the master curve as strong support for the validity of our analysis to obtain D_{app} values.

Molar Mass Effects on Polymer Diffusion. We next consider the influence of polymer molar mass and gel content on the rate and extent of polymer diffusion. We begin by comparing the high M sample with its gel content and sol fraction molar mass $M_w \approx 125\,000$ g/mol with the medium M sample with $M_w \approx 75\,000$ g/mol. In Figure 5 we compare f_m and D_{app} values as a function of annealing time for medium with high M latex films annealed at 65 °C. To calculate f_m values for the medium M latex film, we used $\Phi_{ET}(0) = 0.05$ and $\Phi_{ET}(\infty) = 0.63$. The data in Figure 5 indicate that the molar mass affects significantly the rate of polymer diffusion and the presence of gel decreases significantly the extent of polymer mixing.

In Figure 6, we present the results of experiments on the low M latex film, with $M_w \approx 42\,000$ g/mol. Here we used $\Phi_{ET}(0) = 0.05$ and $\Phi_{ET}(\infty) = 0.63$ to calculate f_m values. In Figure 6a, we show that polymer diffusion for this sample at 35 °C is substantially faster than that of the medium M sample. In Figure 6b, we show that even at 22 °C significant polymer diffusion occurs on a time scale of days.

Time Dependence of Polymer Diffusion in P(VAc-BA) Latex Films. For Fickian diffusion, the mass transferred across an initially sharp interface increases as $t^{1/2}$. For linear polymers such as PBMA with $M_w/M_n \approx 2$ and with M_w not much larger than the entanglement molar mass, we found that f_m increased as $t^{1/2}$. The samples examined here have a much broader distribution of diffusing species. More out of curiosity than to test any theoretical models, we examined plots of ln(f_m) vs ln(t) to see whether there were any interesting trends. We find (Figure 7) that each of the samples gave simple power law plots, with exponents closer to 0.2 than 0.5.

In Figure 7a, we plot ln(f_m) vs ln(t, min) for polymer diffusion in low M latex films annealed at 35 °C and room temperature. One can see that all plots are linear with an average slope of 0.18. We also plot ln(f_m) vs ln(t, min)

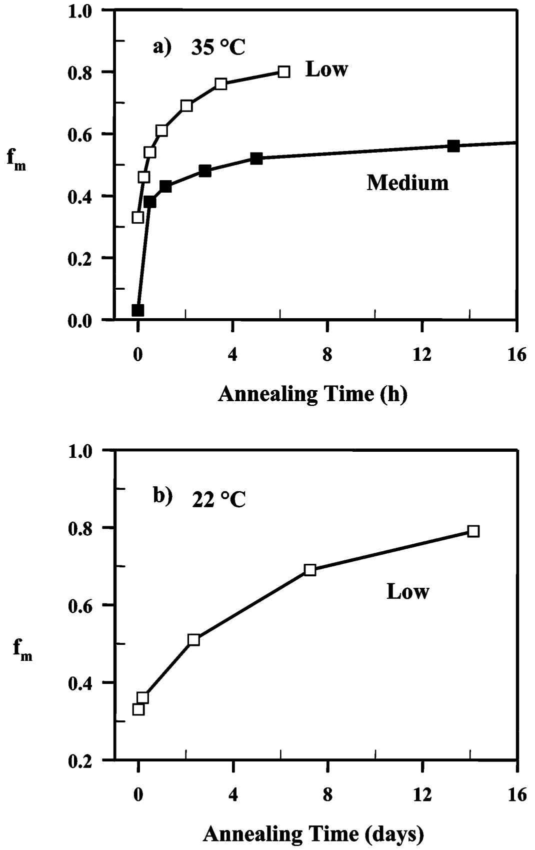

Figure 6. Plot of f_{m} values as a function of annealing time for low *M* films annealed at (a) 35 and (b) 22 °C, compared with those for the medium *M* film annealed at 35 °C.

for polymer diffusion in medium *M* latex films annealed at 35, 45, and 55 °C in Figure 7b and in high molar mass films annealed at 50 and 65 °C in Figure 7c. All plots are linear with an average slope of 0.12 for medium and 0.10 for high *M* films. Because of the distribution of species in each sample with different diffusivities, the decrease in the power law exponents with increasing polymer molar mass may only reflect that the diffusion is slower at longer diffusion time.

Suumary

We synthesized donor- and acceptor-labeled P(VAc-BA) copolymer latex particles by semicontinuous emulsion polymerization in the presence of unlabeled seed latex particles, using different amounts of chain transfer agent to modify the mean molar mass and gel content of the latex particles. The base polymer was a copolymer with weight ratio of VAc/BA = 4/1. Even the gel-free samples should consist of highly branched polymer. Donor-labeled latex samples were prepared in the presence of 1 mol % of PheMA as the dye-containing comonomer. Acceptor-labeled latex samples were prepared in the presence of 0.3 mol % of NBenA. In this way we prepared samples which we refer to as high *M*, medium *M*, and low *M*. The high *M* sample had about 40% gel content, and the sol fraction extracted from the polymer had a nominal M_{w} (GPC) of 125 000. The medium *M* and low *M* samples had a negligible gel content and corresponding values of $M_{\mathrm{w}} \approx 75\,000$ and 42 000. The latex particles had diameters of ca. 200 nm with a narrow size distribution.

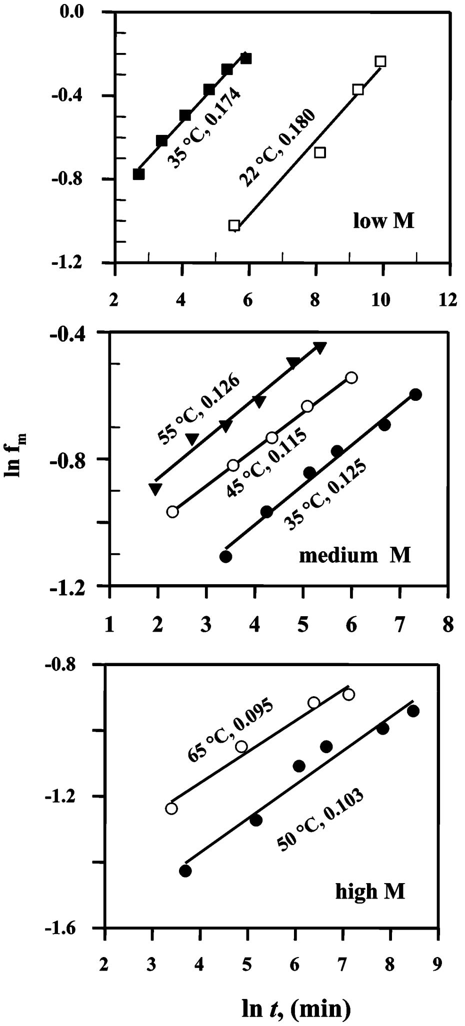

Figure 7. Plots of ln(f_{m}) vs ln(*t*) (a) for low *M* films annealed at 22 and 35 °C, (b) for medium *M* films annealed at 35, 45, and 55 °C, and (c) for high *M* films annealed at 50 and 65 °C.

Fluorescence resonance energy transfer measurements were used to follow polymer diffusion across interfaces in these latex films, prepared from 1:1 mixtures of Phe- and NBen-labeled latex particles. Low and medium *M* films formed films at 4 °C whereas the high *M* sample required room temperature drying. One interesting result is that the quantum efficiency of energy transfer for fully mixed films prepared by solvent casting decreased from $\Phi_{\mathrm{ET}}(\mathrm{lim}) = 0.64$ for low *M*, 0.58 for medium *M*, and 0.37 for high *M* films. For the high *M* sample, the sol and gel fractions were examined separately. There was much less mixing in the latter ($\Phi_{\mathrm{ET}}(\mathrm{lim}) = 0.24$) than in the former ($\Phi_{\mathrm{ET}}(\mathrm{lim}) = 0.51$).

The rate of polymer diffusion in these films was found to increase strongly with decreasing mean molar mass. All three polymers were characterized by a broad distribution of species with different diffusivities. The extent of mixing parameter f_{m} showed a power law dependence on diffusion time, with $f_{\mathrm{m}} \sim t^{z}$, with *z* values on the order of 0.12−0.18. The diffusion rate increased with annealing temperature. For the high *M* sample, we found that the diffusion rate was characterized by an apparent activation energy $E_{\mathrm{a}} = 37$ kcal/mol. This value is somewhat larger than that ($E_{\mathrm{a}} = 34$ kcal/mol) reported previously[8] for the medium *M* determined both by ET experiments and by viscoelastic relaxation measurements.

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