

Film Formation and Polymer Diffusion in Poly(vinyl acetate-*co*-butyl acrylate) Latex Films. Temperature Dependence

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ABSTRACT: We describe polymer diffusion measurements in a poly(vinyl acetate) copolymer latex film by fluorescence decay measurements of nonradiative energy transfer (FRET). The base monomer is a 4:1 weight ratio copolymer of vinyl acetate and butyl acrylate P(VAc–BA) with a glass transition temperature of ca. 12 °C. P(VAc–BA) latex particles labeled with phenanthrene (Phe) as the donor and with 4-(*N,N*-dimethylamino)benzophenone (NBen) as the acceptor were prepared by semicontinuous emulsion polymerization. Latex films were cast from a 1:1 mixture of Phe- and NBen-labeled latex samples. First, a series of films containing NBen-labeled latex samples with different NBen levels were annealed at 45 °C, showing that NBen levels have no influence on the rate of polymer diffusion in P(VAc–BA) latex films. From the fully mixed solvent-cast films, the characteristic distance for energy transfer between Phe and NBen (the Förster radius R_0) was obtained as 2.44 nm. Then, polymer diffusion was monitored as a function of annealing temperature in latex films containing Phe-labeled latex with 1 mol % PheMA and NBen-labeled latex with 0.3 mol % of the NBen chromophore. The temperature dependence of the diffusion rate (from 35 to 75 °C) was characterized by an effective activation energy $E_a = 34 \pm 0.5$ kcal/mol. In parallel, an effective $E_a = 34$ kcal/mol was obtained from viscoelastic relaxation measurements over a range of temperatures close to those of the diffusion experiments.

Introduction

For more than 20 years there has been a strong interest in the diffusion of polymer molecules across interfaces. From a practical point of view, this topic is of interest because of its importance in many processes as diverse as crack healing in plastics, welding of polymer slabs, the sintering of polymer powders by compression molding, and the formation and aging of latex films. From a theoretical perspective, the interesting features arise from the fact that the initial interface serves as a dividing surface with all polymer chains confined to either side. When the chains are long enough to be entangled, lateral diffusion is retarded or suppressed. As a consequence, the rate at which new polymer chains penetrate the boundary and the rate at which they diffuse across the interface are affected.^{1,2} These ideas are nicely summarized in the monograph by Wool.³ The challenge in each of these areas is to obtain information about the polymer diffusion rate and to connect this information to the evolution of the performance-related properties of the system.

For example, films prepared from aqueous dispersion of latex particles are widely used as coatings.⁴ 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 developed techniques based upon fluorescence resonance energy transfer (ET) to study polymer diffusion in latex films. Our ET measurements require us to first synthesize matched pairs of dye-labeled latex. The latex particles should be similar in size and contain polymers of nearly identical molar mass and molar mass distribution. One must be labeled with a donor (D) dye and the other with a corresponding acceptor (A) dye. Most of our previous experiments have focused on polymer diffusion in latex films consisting of linear polymer, particularly poly(butyl methacrylate).⁵ Recently we have begun to consider the consequences of chain architecture on the maturation of latex films.^{6,7} For example, the network present in films formed from cross-linked latex particles limits polymer diffusion across the interface to dangling ends at the edge of the microgel particle.⁸ Long chain branches introduce another level of complexity into the description of polymer diffusion. Such branches present in chains long enough to be entangled should slow the diffusion rate significantly.⁹ In some polymers, substantial changes in the temperature dependence of the polymer backbone motion have been attributed to long branches.¹⁰ A classic example of latex polymers characterized by the presence of long chain branches is poly-

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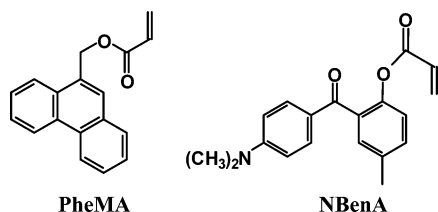
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(vinyl acetate) (VAc) and its copolymers. The propagating radical in VAc polymerization is highly reactive. Through hydrogen abstraction from polymer in the reaction mixture, radical sites are created that lead to extensive branching.¹¹ These experiments are more difficult to interpret quantitatively than those involving linear polymer because the polymers have not only a broad molar mass distribution but also a distribution of molecules with different extents of branching.

In this paper, we describe experiments on latex films consisting of a copolymer of vinyl acetate (VAc) and butyl acrylate (BA) with a weight ratio of 4:1. This copolymer latex is commonly used in North America for interior architectural coatings. In these experiments, we use 9-acryloxymethylphenanthrene (PheMA) as the comonomer to introduce the Phe group into the donor-labeled latex particles. We used 4'-(dimethylamino)-2-acryloxy-5-methyl benzophenone (NBenA) for labeling P(VAc-BA) latex particles with the acceptor dye.

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 $r_{\text{VAc}} \approx 0.02$ – 0.07 and $r_{\text{BA}} \approx 3.07$ – 8.00 , respectively.¹² 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 group¹³ has shown that domains of BA-rich copolymers form and become dispersed in a PVAc-rich continuous phase during batch emulsion polymerization. (A similar result is expected for miniemulsion polymerization.) This group also showed that semicontinuous emulsion copolymerization of these monomers under monomer-starved conditions gave homogeneous latex particles with little phase separation.



In this paper we investigate polymer diffusion in films based on P(VAc-BA) latex particles with VAc/BA = 4:1 by weight. 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 was prepared in the presence of 1 mol % of PheMA. The acceptor-labeled latex samples were prepared in the presence of NBenA at different concentrations ranging from 0.1 to 0.45 mol % of the second stage monomers. We show that we can follow interparticle polymer diffusion in films formed from a 1:1 mixture of D- and A-labeled particles. The diffusion rate increases with increasing temperature. We employ a simple diffusion model to estimate apparent diffusion coefficients for the polymer and use these values to calculate an effective activation energy E_a for the diffusion process. To test the method, we carry out extensive linear viscoelastic measurements over a similar temperature range as an alternative method for determining the temperature dependence of the polymer backbone motion.

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

ingredients (g)	seed stage	second stage
unlabeled seed ^a		27.1
VAc	60.0	16.3
BA	15.0	4.1
NBenA comonomer ^b		0.2
C ₁₂ -SH ^c		0.12 mL
SDS	0.45	0.14
NaHCO ₃ ^d	3.0	0.80
KPS	1.15	0.15
water	918.5	111.0

^a The seed latex particle (diameter 98 nm) 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 corresponds to 0.3 mol % based on total monomers of the second stage. ^c 1-Dodecanethiol was used as a chain transfer agent at 0.5 wt % of total monomers of the second stage. ^d Sodium bicarbonate as a pH buffer.

Experimental Section

Materials. Potassium persulfate (KPS), sodium dodecyl sulfate (SDS), sodium bicarbonate (NaHCO₃), and 1-dodecanethiol (C₁₂-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.^{14,15}

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. In these reactions, an unlabeled dispersion of seed particles was prepared on a large scale by batch emulsion polymerization with only base monomers, and the same seed was used for the preparation of the all latex particles. In the second stage, water and unlabeled seed latex were placed in the reaction flask and heated to 80 °C. Then, an initiator solution was added, and subsequently a preemulsion of monomers, surfactant, pH buffer, and water was fed into the flask.

As an example, the recipe for the synthesis of P(VAc-BA)-NBen(0.3) is summarized in Table 1, and the specific procedure is described below. Seed polymerization was carried out in a 2 L three-necked round-bottom flask equipped with a stirrer, a thermometer, and an N₂ inlet. The flask was immersed into an oil bath. Water (618.5 g) and SDS (0.45 g) were placed in the flask with stirring. After the SDS dissolved, the mixture of monomers (VAc 60 g, BA 15 g) was added. The system was thoroughly purged with nitrogen while the reaction mixture was heated to 80 °C. After the reactor temperature stabilized at 80 °C, the KPS solution (1.15 g in water 50 g) as an initiator was added. After the addition of the initiator solution was complete, the system was maintained at 80 °C for 1 h. The reaction was cooled to room temperature, and then the sodium bicarbonate solution (3 g in water 250 g) was added. The dispersion of particles ($d = 98$ nm, 7.5 wt % solids content) obtained was used as seeds for subsequent reactions.

In the second-stage polymerization, water (33.9 g) and an aliquot of the unlabeled seed latex (27.1 g) described above were placed in a 250 mL three-necked round-bottom flask provided with a stirrer, a thermometer, and an N₂ inlet. The system was purged with nitrogen while the reaction mixture was heated to 80 °C. The SDS (0.14 g) and NaHCO₃ (0.17 g) were dissolved in water (12.1 g), and then the monomer mixture (VAc 16.3 g, BA 4.1 g) including NBenA (0.2 g, 0.3 mol % of the second stage monomers) and 1-dodecanethiol (0.12 mL, 0.5 wt % of the second stage monomers) was

Table 2. Characteristics of the Latex Particles

latex ^a	dye [mol %] ^b	solids [%]	<i>d</i> [nm] ^c	<i>M_w</i> [kg/mol]	<i>M_w</i> / <i>M_n</i>	dye incorporation [%] ^d	<i>T_g</i> [°C]	gel content [%]
P(VAc-BA)	0.0	12.7		75	4.8	NO	14.0	0
P(VAc-BA)-Phe(1.0)	1.0	12.7	183	77	5.1	95	10.7	0
P(VAc-BA)-NBen(0.1)	0.1	13.0	224	71	4.4	93		
P(VAc-BA)-NBen(0.2)	0.2	13.5	211	73	4.0	95		
P(VAc-BA)-NBen(0.3)	0.3	13.8	205	73	4.0	97	11.8	0
P(VAc-BA)-NBen(0.45)	0.45	13.2	211	63	3.5	96		

^a Prepared by semicontinuous emulsion polymerization in the presence of unlabeled seed particles (diameter 98 nm). In these reactions, 0.85 wt % of C₁₂-SH on the second stage monomers is used for unlabeled P(VAc-BA) and P(VAc-BA)-Phe(1.0) and 0.5 wt % of C₁₂-SH is used for the all P(VAc-BA)-NBen latex samples. ^b Based on the second stage monomers. ^c 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. ^d In the calculation of the dye incorporation, we employed extinction coefficient values of 11 500 L/(mol cm) at 300 nm for PheMA and 25 400 L/(mol cm) at 350 nm for NBenA in chloroform.

added to the aqueous solution under stirring to form the preemulsion. After the reactor temperature stabilized at 80 °C, the initiator solution (KPS 0.15 g in water 5 g) was added into the reactor at the rate of 1 mL/min (10 min), and then preemulsion was subsequently added into the reactor at the rate of 0.13 mL/min (4.5 h). After the addition was complete, the system was maintained for 1.5 h. The reaction was cooled to room temperature, and then the sodium bicarbonate solution (0.63 g in water 60 g) was added. This reaction produced a dispersion with 13.8 wt % solids content with a particle diameter about 205 nm with a narrow size distribution.

In a similar fashion, we synthesized an unlabeled latex P(VAc-BA), a donor-labeled latex containing 1 mol % Phe groups P(VAc-BA)-Phe(1.0), and acceptor-labeled latex with four different levels of dye content. The characteristics of these materials and our notation for naming the samples are presented in Table 2.

For the Phe-labeled particles, it does not matter if the initiator is added simultaneously with the second stage monomer pre-emulsion or if the monomer emulsion is added slowly to the reaction containing the initiator. In contrast, for the synthesis of the NBen-labeled latex, it is necessary to add the monomer pre-emulsion after adding the second-stage initiator to the reaction mixture. When the two are added simultaneously, the second-stage monomer conversion reaches only 70%.

Characterization of Latex Particles. The sizes 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 latex dispersion were determined by gravimetry. The molar mass distribution was measured by gel permeation chromatography (GPC) using polystyrene as molar mass standards. Gel permeation chromatography (GPC) was 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, 10⁴/10, and 10⁵/10 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. An aliquot of latex particles without further purification were dissolved in THF to form a solution, which was passed through a 0.2 μm filter prior to injection in the GPC.

The degree of dye incorporation into copolymer was characterized by UV absorption measurements on solutions in chloroform, using the Beer-Lambert equation. Extinction coefficients of the dye derivatives at the absorption maxima were obtained from measurements on the dye monomers as model compounds. Polymer samples for UV analysis were prepared as follows: An aliquot of latex particles was purified to a conductivity of around 15 μS/cm by treating it with an ion-exchange resin (prepurified AG 501-X8 mixed-bed resin, Bio-Rad). The particles were then precipitated in MeOH. The resulting mixture was centrifuged at 15 000 rpm for 15 min at ca. 5 °C. The solids at the bottom of the tube were then collected with several washes with water, dried in a vacuum

oven at 30 °C overnight, and then dissolved in chloroform. UV spectra were recorded on a Perkin-Elmer Lambda 6 UV spectrophotometer.

The glass transition temperature (*T_g*) of 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. 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 until their water content was less than about 1 wt % and then further dried at 30 °C in a vacuum oven for 2 days. The gel content of polymers was defined as the ratio of the weight of insoluble polymers to the weight of initial polymers. The sol polymers were continuously extracted in 1,4-dioxane under reflux conditions. About 0.35–0.40 g of above dried latex polymers (*W_i*) was taken into a sample tube and then placed in 1,4-dioxane (150 mL) refluxed for 24 h. After cooling, the remaining gel polymer was dried to a constant weight (*W_g*) at 110 °C for 5 h. The gel content (%) is calculated from eq 1.

$$\text{gel content (\%)} = (W_g/W_i) \times 100 \quad (1)$$

Film Formation and Fluorescence Measurements.

Latex films for energy-transfer experiments were prepared from a 1:1 particle mixture of the donor- and acceptor-labeled dispersions. Prior to film formation, salts and surfactants were removed from the dispersion by treatment with previously purified¹⁶ ion-exchange beads (AG-501-X8 mixed-bed resin, Bio-Rad). Aliquots of the mixture were placed on quartz plates (1 × 2.5 cm) and allowed to dry for 12 h at 4 °C. The dry films were transparent but partially cracked.

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 by the single photon timing technique.¹⁷ Each film was placed in a quartz tube and deoxygenated with N₂ 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 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. Because the NBen chromophore is nonfluorescent, we can collect data over a wider range of wavelengths than in the case of anthracene, where acceptor fluorescence can distort the measured *I_{DA}(t)* signal. 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.¹⁷

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*.^{18,19}

$$w(r) = \frac{\alpha}{r^6} \quad (2a)$$

$$\alpha = \frac{3R_0^6 \kappa^2}{2\tau_D} \quad (2b)$$

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.^{20–22} As predicted by eqs 3 and 4, the donor decay in the absence of acceptor is exponential. For films prepared from P(VAc-BA)-Phe(1.0) alone, we obtained an unquenched lifetime $\tau_D = 43.3$ ns. 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.²³

$$I_D(t) = A \exp\left[-\frac{t}{\tau_D} - P\left(\frac{t}{\tau_D}\right)^{0.5}\right] \quad (3)$$

where

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

Here, P is proportional to the acceptor (quencher) concentration $[Q]$. R_0 is the critical Förster radius for energy transfer, and $[Q]$ is the concentration of quencher [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.²²

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

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

where t is the annealing time after sample preparation, t' is the fluorescence decay time, and $\text{area}(t)$ 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.

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

Rheological Measurements. The viscoelastic response of P(VAc-BA) was studied at several temperatures above T_g with a Rheometrics AA instrument in the oscillatory shear mode. We employed a cone-and-plate geometry (25 mm diameter, 0.04 rad cone angle, 0.048 mm gap height). Frequency was scanned between 0.01 and 80 Hz at a constant temperature. The highest frequency used was 80 Hz (due to limitations in the dynamic motor), and the lowest frequency used was set to prevent acquisition times longer than 20–30 min for each run. After testing linear viscoelastic response at all frequencies, small strains between 0.02 and 0.05 were imposed. The range of temperature studied was selected to be as close as possible to the range of temperature used in the diffusion experiments performed on these materials. However, the lower temperatures used are limited by the high relaxation times of the samples at temperatures close to T_g .

The following procedure was used to prepare the samples for the measurements of viscoelastic properties. First, the samples were dried under vacuum at 60 °C for 12 h to eliminate any trace of volatiles. Then, the samples were molded in a two-step procedure. In the first step a weighed amount of sample was pressed between metal plates in a Carver press at 90 °C to eliminate bubbles of air. Cleaned poly(ethylene terephthalate) (PET) sheets were used to prevent the contact between the sample and the plates. In the second step, the material free of air bubbles was remolded at the same temperature, but now controlling the thickness of the samples by using separators between the plates of the press. In this way, samples free of bubbles, approximately 25 mm in diameter and 0.5 mm thick, were obtained.

Some precautions were taken to ensure that the instrumental conditions were the same during the entire experiment. Before and after running each material, the instrument response was checked running standard samples at selected temperatures. The standard commonly used for checking the calibration of this instrument is PDMS at 35 °C, but we also check the instrument response at higher temperature (100 °C) by using a PVAc sample as a standard.

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.²⁴ Dye-labeled P(VAc-BA) latex samples were prepared by seeded semicontinuous emulsion polymerization. The seed particles themselves (98 nm diameter) were prepared without adding dodecyl mercaptan (C_{12} -SH) as a chain-transfer agent. The seed consists of a similar copolymer and represents 9.1 wt % of the final particles prepared by two-stage emulsion polymerization. The most important feature of our semicontinuous emulsion polymerization reaction is that, in the second stage, the monomers including dye comonomer must be fed into the reaction as a preemulsion along with the KPS solution as the initiator. Only in this way do we obtain high monomer conversion and good dye incorporation. In Figure 1 we plot the evolution of conversion and particle diameter as a function of polymerization time in the presence of 0.3 mol % of NBenA at 80 °C. In this reaction, the KPS solution is fed for 10 min, and then the preemulsion of monomers including NBenA is fed subsequently over 260 min. This reaction was run on a larger scale to facilitate taking 10 mL aliquots during the polymerization to measure instantaneous and global monomer conversions and particle diameter. We see in the figure that the instantaneous monomer conversion was always more than 80% over the whole polymerization reaction. The global conversion was consistent with the calculated conver-

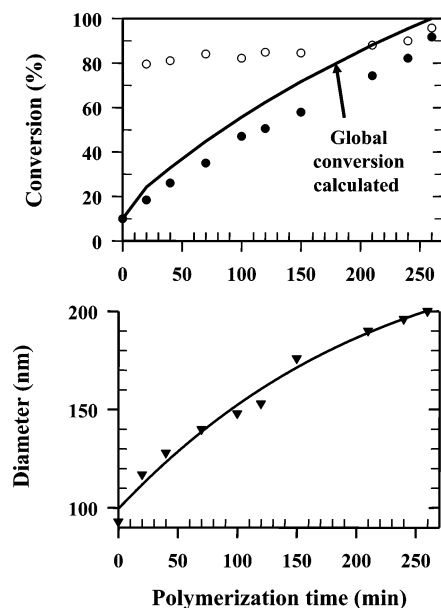


Figure 1. Plot of (a) the instantaneous monomer conversion (○) and global monomer conversion (●) and (b) the particle diameter (▼) as a function of polymerization time in VAc–BA semicontinuous emulsion polymerization, where monomers including 0.3 mol % of NBenA were fed into the reaction as a preemulsion along with the KPS solution as the initiator at 80 °C in the presence of unlabeled seed latex particle (diameter = 98 nm). The preemulsion was fed over 260 min.

sion. The particle diameter increased as predicted with monomer conversion. These results indicate that the semicontinuous emulsion polymerization reaction at 80 °C in the presence of 0.3 mol % of NBenA takes place under monomer-starved, or nearly monomer-starved, conditions.

To form dye-labeled copolymers, we introduced the dye comonomers in the second stage of the reaction. We synthesized D-labeled P(VAc–BA)–Phe with 1 mol % of PheMA based on second-stage monomers. For acceptor-labeled particles, we synthesized a series of NBen-labeled P(VAc–BA) latex samples in which various amounts of NBenA, ranging from 0.1 to 0.45 mol %, were introduced in the second stage. In each of these reactions, C_{12} -SH was employed in the second stage as a chain-transfer agent to control molar mass of the polymers. Somewhat different amounts of C_{12} -SH were added to the reaction with PheMA than to the reaction with NBenA (see Table 1) to obtain polymers with $M_w \approx 70\,000$ g/mol based on GPC standards. All of the reactions produced particles with a narrow size distribution with mean diameters of ca. 200 nm.

Dye incorporation was characterized by UV absorption measurements. These rely on the respective monomers as model compounds for determining molar extinction coefficients and indicate a dye incorporation efficiency greater than 93%. GPC measurements with tandem UV and RI detectors provide further information about dye distribution in the copolymer.²⁵ In Figure 2, we show the results for P(VAc–BA)–NBen(0.3) as an example. The trace for the polymer, as monitored by the RI signal, and for the dye, as monitored by the UV signal, have similar shapes and elute 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 is no detectable dyes in the samples not bound to the polymer.

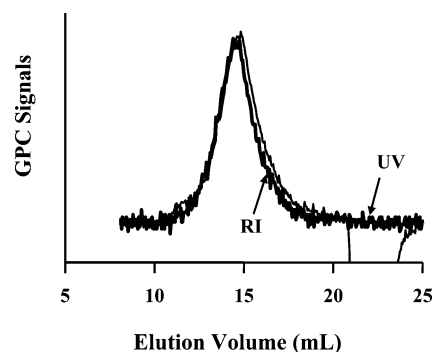


Figure 2. Apparent molar mass distributions from the UV and RI signals of NBen-labeled P(VAc–BA) latex prepared by semicontinuous emulsion polymerization in the presence of 0.3 mol % NBenA. For measurements of the UV signals, we employed $\lambda_{ex} = 350$ nm.

We examined the samples for gel content of copolymers with refluxing 1,4-dioxane using the method described by Asua et al.²⁶ We found that there is no detectable gel in any of the P(VAc–BA) latex samples.⁴² This is a consequence of the chain-transfer agent used to lower the molar mass during the polymerization reactions. The T_g values determined by DSC (Table 2) were 11.8 °C for the NBen-labeled latex polymers, 10.7 °C for the Phe-labeled polymer, and 14.0 °C for the unlabeled P(VAc–BA) sample. In each of the samples, we observe only one T_g . This result is consistent with the findings of Misra et al.,²⁷ 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 conditions gives homogeneous latex particles with little phase separation.

ET Studies of Polymer Diffusion. The chromophore (NBen) has a strong charge-transfer transition with a maximum absorption at 350 nm. The extinction coefficient ($\epsilon = 25\,400\text{ M}^{-1}\text{ cm}^{-1}$ in chloroform) compares favorably with the anthracene derivatives we employed previously ($\lambda_{max} = 359\text{ nm}$, $\epsilon = 8000\text{ M}^{-1}\text{ cm}^{-1}$) as an energy-transfer acceptor from Phe. In fact, the NBen chromophore provides two distinct advantages over An and one small disadvantage. The higher value of ϵ leads to a somewhat larger characteristic ET distance R_0 (ca. 2.7 nm²⁸) than that (2.3 nm²⁹) for ET from Phe to An. In addition, NBen is nonemissive. This means that we could monitor the donor fluorescence decay signal over the entire 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.³⁰ As a consequence, we could use smaller levels of acceptor dye labeling (0.3 mol % NBen vs 1 mol % An) in our experiments. In addition, we can monitor donor emission over a wider range of wavelengths without concern for unwanted contributions from acceptor dye fluorescence. Both features make our ET measurements more effective. The small disadvantage is related to the charge-transfer nature of the NBen excited state. Changes in the polarity of its environment lead to small shifts in its absorption spectrum. These shifts make it more difficult to determine the exact value of R_0 in a given experiment and make it more difficult for us to employ our most sophisticated methods of data analysis.

Latex films were prepared by casting a 1:1 mixture of D- and A-labeled latex onto a quartz plate and then

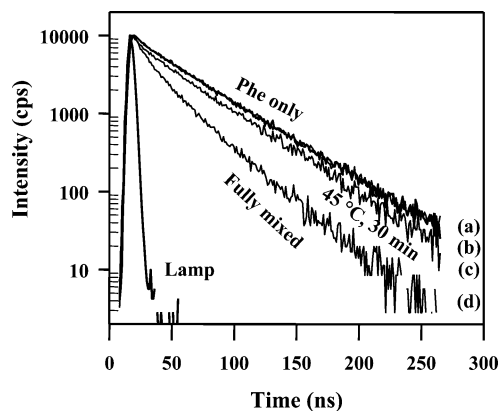


Figure 3. Phenanthrene (donor) fluorescence decay curves ($I_D(t)$) measured at 45 °C for P(VAc-BA) latex films. (a) The pure Phe-labeled latex, (b) the newly formed film dried at 4 °C, consisting of a 1:1 ratio of P(VAc-BA)-Phe(1.0) and P(VAc-BA)-NBen(0.3), (c) the same film shown in (b) annealed for 30 min at 45 °C, and (d) the solvent-cast fully mixed 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. Note that curves a and b overlap.

allowing the film to dry over 12 h in a cold room at 4 °C. The films formed were transparent but showed small cracks. Representative donor fluorescence decays for a film consisting of P(VAc-BA)-Phe(1.0) + P(VAc-BA)-NBen(0.3) annealed for various periods of time at 45 °C are shown in Figure 3. The uppermost curve, containing only donor, is exponential. From the newly formed film of the D- + A-labeled latex we find an $\text{area}(0)$ of 40.5 ns, corresponding to $\Phi_{\text{ET}}(0)$ of 0.05. Since little or no polymer diffusion takes place at the temperature in our samples, we attribute this difference to transboundary energy transfer prior to the onset of polymer diffusion. After the film was annealed for 30 min at 45 °C, the area under the decay curve decreased, an indication of a large increase in ET due to polymer diffusion. In the case of a similar latex mixture dried at 22 °C, we find $\Phi_{\text{ET}}(0) = 0.25$, illustrating that significant polymer diffusion occurs during drying at that temperature.

To evaluate the extent of mixing f_m , defined by eq 7, we need a value for $\Phi_{\text{ET}}(\infty)$, which corresponds to full mixing of the donor- and acceptor-labeled latex polymers. There are two ways to obtain a sample to serve as a model for $\Phi_{\text{ET}}(\infty)$. On one hand, one can take a latex film and anneal it for a sufficient time at high temperature that mixing becomes complete. This type of mixing requires the polymers to diffuse a distance comparable to the radius of the initial latex particles. Because the polymer diffusion rate is strongly accelerated by increasing temperature, Φ_{ET} will normally increase to its maximum value. Alternatively, one can dissolve the dry polymers in an organic solvent. In solution, one expects full mixing of the polymer molecules. A film cast from the solution is then a good model for the determination of $\Phi_{\text{ET}}(\infty)$.

Here we use the solvent-cast film method to obtain $\Phi_{\text{ET}}(\infty)$. A latex blend containing a 1:1 mixture of donor- and acceptor-labeled dried particles was purified by treating it with ion-exchange resin and then freeze-dried. The powder was dissolved in dichloromethane. This solution was cast onto a quartz plate and allowed to dry at room temperature for 12 h. For the case of a film of P(VAc-BA)-Phe(1.0) + P(VAc-BA)-NBen(0.3), we obtained $\Phi_{\text{ET}} = 0.48$. We found, unexpectedly, that

Table 3. Characteristics of Fully Mixed Solvent-Cast Films from 1:1 Mixtures of P(VAc-BA)-Phe(1.0) and P(VAc-BA)-NBen at the Different Concentrations of NBen

NBen-labeled latex samples	[NBen] [mM] ^a	before annealing		after annealing	
		$\text{area}(\infty)^b$	$\Phi_{\text{ET}}(\infty)$	$\text{area}(\infty)^b$	$\Phi_{\text{ET}}(\infty)$
P(VAc-BA)-NBen(0.1)	6	29.5	0.30	25.7	0.40
P(VAc-BA)-NBen(0.2)	12	25.3	0.40	22.7	0.47
P(VAc-BA)-NBen(0.3)	18	21.9	0.48	18.3	0.58
P(VAc-BA)-NBen(0.45)	27	17.4	0.59	12.9	0.7

^a Based on films cast from 1:1 mixtures of Phe-labeled latex and NBen-labeled latex. ^b In the calculations, $\tau_D = 43.3$ ns.

when this film was annealed at 110 °C and cooled to room temperature, Φ_{ET} increased to 0.58. In the past, for simple linear methacrylate polymers,³¹ as well as for MMA copolymers with simple acrylates,⁷ we found the value of Φ_{ET} for the solvent-cast films remained unchanged after annealing and chose this value for $\Phi_{\text{ET}}(\infty)$. Here we imagine that there is some local microphase separation that occurs in the solvent-cast film that is overcome upon annealing at higher temperature. We choose the higher value (0.58) as that of $\Phi_{\text{ET}}(\infty)$. We note that when we take a latex film with this composition and anneal it for 5 h at 110 °C, we find an $\text{area}(5 \text{ h})$ value of 19.6 ns, corresponding to $\Phi_{\text{ET}} = 0.54$. This result supports our choice of 0.58 as the appropriate value for $\Phi_{\text{ET}}(\infty)$.

To support this decision, we found that the fluorescence decay curves for each of the annealed solvent-cast films fit well ($\chi^2 < 1.1$) to eq 3. We use these fits (see below) to estimate a value for R_0 in our experiments. In Table 3 we present the values of “ $\text{area}(\infty)$ ” and Φ_{ET} obtained for solvent-cast films prepared from 1:1 mixtures of P(VAc-BA)-Phe(1.0) with each of the different NBen-labeled latex, before and after annealing at 110 °C. One can see that the magnitude of $\text{area}(\infty)$ decreases and $\Phi_{\text{ET}}(\infty)$ increases with increasing NBen concentration in those films.

In Figure 4, we plot values of Φ_{ET} and f_m as a function of annealing time for four latex films containing the different concentrations of NBen annealed at 45 °C. In the calculation of f_m values for the films with different amounts of NBen, we used the $\text{area}(\infty)$ values (Table 3), corresponding to solvent-cast films annealed at 110 °C. While the values of Φ_{ET} for a given annealing time are sensitive to the concentration of NBen in the film, these differences disappear when one considers f_m . We learn that the calculation of f_m effectively normalizes the results for differences in the extent of labeling and that NBen levels have no significant effect on the rate of polymer diffusion.

Estimation of R_0 . The annealed solvent-cast films described above represent a series of film samples with a common concentration of donor chromophore (60 mM) and NBen concentrations ranging from 6 to 27 mM. The fluorescence decay profiles were fitted to eq 3, and the P parameters calculated from these fits are plotted against acceptor concentration in Figure 5. The plot is linear and passes through the origin as expected for a well-behaved system characterized by a random distribution of NBen in films. From the slope of the plot and using eq 4, we calculate $R_0 = 2.44$ nm, assuming a random distribution of immobile Phe* and NBen groups ($\kappa^2 = 0.476$). We note that this value is somewhat smaller than the value of $R_0 = 2.72$ nm from analysis of the fluorescence decay curves in films of P(VAc-BA)

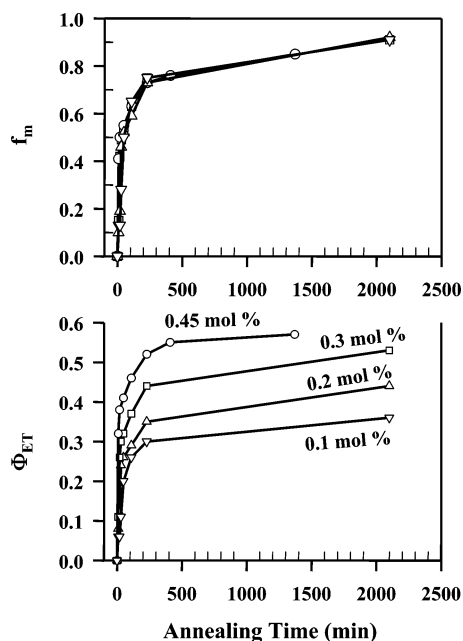


Figure 4. Plots of energy transfer Φ_{ET} (lower figure) and f_m (upper figure) vs annealing time of the P(VAc-BA) latex films containing the different concentrations of NBen annealed at 45 °C. The concentration of NBenA (mol %) is based on NBen-labeled latex particles.

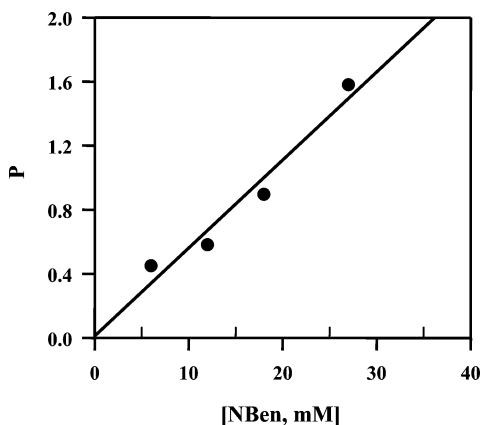


Figure 5. Plot of P , where P values are obtained by fitting the decay curves for phenanthrene to eq 3 with τ_D fitted at 43.3 ns, vs [NBen, mM] in fully mixed solvent-cast films, yielding $R_0 = 2.44$ nm.

containing 120 mM PheMA and a range of concentrations of the monomer NBenA. We are currently examining the origin of this difference.²⁸

Polymer Diffusion in P(VAc-BA) Films at Various Temperatures. A series of P(VAc-BA)-Phe(1.0) + P(VAc-BA)-NBen(0.3) latex films were prepared at 4 °C. After the films were dried for 12 h in the cold room, their fluorescence decay curves were measured. The initial quantum yield for energy transfer for these films was found to be $\Phi_{ET}(0) = 0.04$ – 0.05 . To obtain a value for the fully mixed film ($M_w \approx 75\,000$ g/mol) containing 0.3 mol % NBenA, film samples were dissolved in dichloromethane and then cast as a film. After annealing the solvent-cast film at 110 °C for 1 h, we obtained $\Phi_{ET}(\infty) = 0.58$ (which corresponds to $\text{area}(\infty) = 18$ ns) (Table 3).

In Figure 6a, we plot f_m values as a function of annealing time for the films annealed at various temperatures ranging from 35 to 75 °C. These data indicate

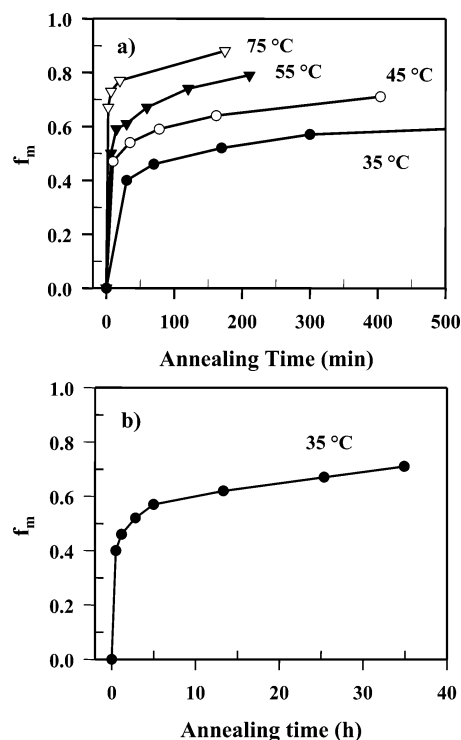


Figure 6. Plots of f_m vs annealing time for P(VAc-BA)-Phe-(1.0) + P(VAc-BA)-NBen(0.3) latex films annealed at 35, 45, 55, and 75 °C.

that f_m increases with annealing time, reflecting the interdiffusion between Phe-labeled polymers and NBen-labeled polymer chains. We also see that temperature has an important effect on the rate of polymer diffusion. For example, for an annealing time of 100 min, the f_m value attained by a film is 0.46 at 35 °C, 0.59 at 45 °C, 0.71 at 55 °C, and 0.83 at 75 °C. In Figure 6b, we also show the long time behavior of f_m for the film annealed at the lowest annealing temperature (35 °C). We can see that at this temperature f_m increases rapidly during the first 40–60 min, followed by a slower increase at longer annealing times. This variation in diffusion rate can be attributed to the broad molar mass distributions of the latex copolymer ($M_w/M_n = \text{ca. } 4.5$). The copolymers of lowest molar mass contribute to the early rapid diffusion. The larger molar mass copolymers, which diffuse more slowly, make their contribution to the growth in ET over a longer time scale.

To quantify the temperature dependence of the diffusion process in a meaningful way and to explore the distribution of diffusion rates in our system, it is necessary to analyze the data obtained in terms of an appropriate diffusion model. If, for example, we had an appropriate theoretical model, we could calculate the magnitude of the diffusion coefficients (D) for the polymers in these films. Unfortunately, there is no such model for a system consisting of branched polymers with a distribution of branching and chain length. To proceed with this analysis, we estimate apparent diffusion coefficients (D_{app}) for the polymers in the films by fitting the f_m data to a spherical diffusion model that satisfies Fick's second law of diffusion.³² In simpler systems consisting of unentangled linear polymer, simulations have shown that values of f_m (the fractional growth in energy-transfer efficiency due to polymer diffusion) are proportional to the fractional mass f_s , transferred across the intercellular boundary for f_m values up to about 0.7.³³ Under these circumstances, D_{app} values are pro-

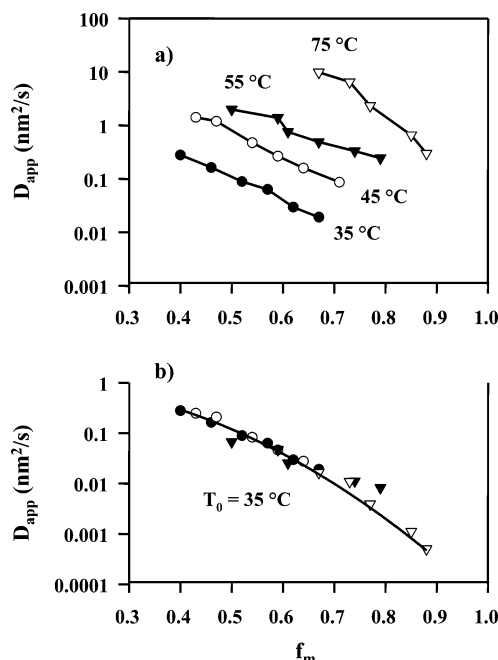


Figure 7. (a) Plots of the apparent diffusion coefficient (D_{app}) as a function of f_m for P(VAc-BA)-Phe(1.0) + P(VAc-BA)-NBen(0.3) latex films annealed at various temperatures. (b) The master curve of D_{app} values at 35 °C was calculated using $E_a = 34$ kcal/mol (142 kJ/mol) as a shift factor.

portional to the true D values and averaged over all the chains of broad molar mass distribution and the history aging. We have in the past used this approach to quantify the influence of changes in temperature^{34,35} or the influence of plasticizing additives³⁶ 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 .

In Figure 7a, 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 45 °C gave a value of $D_{app} = 1.20$ nm²/s after 10 min, 0.27 nm²/s after 80 min, and 0.09 nm²/s after 400 min. 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. A quantitative analysis of the temperature dependence of the diffusion process for our copolymer is developed in the following paragraphs.

Temperature Dependence of Polymer Diffusion in P(VAc-BA) Films. The temperature dependence of polymer diffusion can be described in terms of the Williams-Landel-Ferry (WLF) equation³⁷ with parameters close to those obtained from viscoelastic relaxation measurement.³⁸ Over a sufficient broad range of temperatures, for polymer diffusion, the WLF equation takes the form

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

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

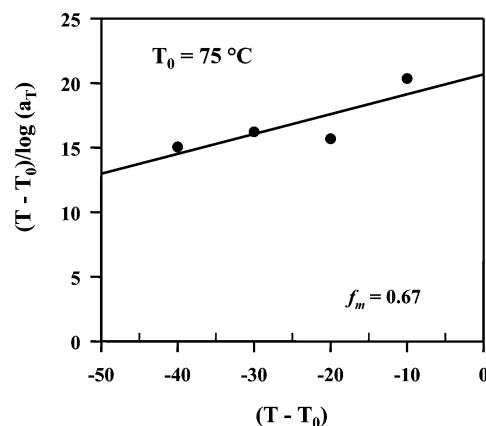


Figure 8. Plot of the $(T - T_0)/\log(a_T)$ against $(T - T_0)$ with $T_0 = 348$ K (75 °C) in P(VAc-BA)-Phe(1.0) + P(VAc-BA)-NBen(0.3) latex films at the extent of mixing f_m of 0.67. From the curve, we obtained $C_1 = 5.86$ and $C_2 = 149.5$ K at 90 °C.

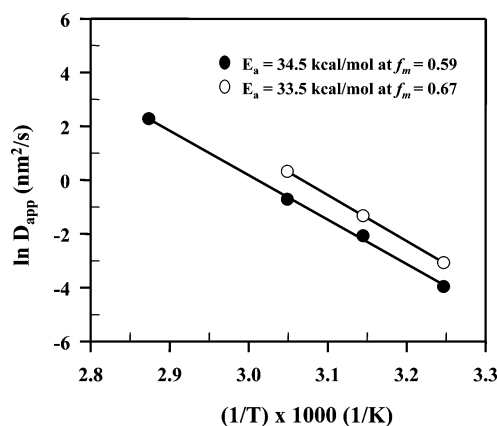


Figure 9. Plots of $\ln D_{app}$ vs $1/T$ over the temperature range from 35 to 75 °C at f_m values of 0.59 and 0.67.

on the choice of T_0 , but these values are easily transferred 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.

To estimate values of C_1 and C_2 from diffusion data, one can fit the experimental values of D to eq 8. From the linear plot of $(T - T_0)/\log(a_T)$ against $(T - T_0)$, C_1 can be calculated from the slope and C_2 can be calculated from the ratio of the intercept to the slope. In Figure 8, we plot $(T - T_0)/\log(a_T)$ against $(T - T_0)$. For D_{app} values at $f_m = 0.67$, a linear plot is obtained with $T_0 = 348$ K (75 °C), yielding values of $C_1 = 6.51$ and $C_2 = 134.5$ K. For comparison with rheological measurements, we convert these values to a reference temperature of 363 K (90 °C) and find $C_1 = 5.86$ and $C_2 = 149.5$ K.

Over a limited temperature range, plots of $\ln D$ vs $1/T$ appear linear, and one can calculate the apparent activation energy for polymer diffusion ($E_{a/D}$) from the slopes of these plots. In Figure 9, we show Arrhenius-type plots of $\ln D_{app}$ vs $1/T$ at both $f_m = 0.59$ and 0.67. We obtained an average value of $E_{a/D} = 34 \pm 0.5$ kcal/mol over the temperature range 35–75 °C. Since temperature affects the rate of diffusion through a change in the monomeric friction coefficient, the magnitude of the $E_{a/D}$ should be independent of f_m . Therefore, we used this value of $E_{a/D}$ as a shift factor to create a master

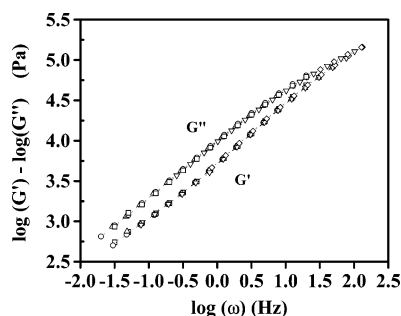


Figure 10. Plot of master curves of G' and G'' values for P(VAc-BA) latex films at $T_0 = 100\text{ }^{\circ}\text{C}$.

curve of D_{app} values at $35\text{ }^{\circ}\text{C}$. The shifted values calculated in this way are shown in Figure 7b. We take the success in generating the master curve as strong support for the validity of our analysis to obtain D_{app} values.

Temperature Dependence of the Viscoelastic Properties of P(VAc-BA) Films. While there is data in the literature about the viscoelastic relaxation of PVAc itself, we found no corresponding data about its copolymers with BA. To test the meaningfulness of the data analysis described above, we carried out oscillatory shear measurements as a function of frequency over a range of temperatures from 50 to $100\text{ }^{\circ}\text{C}$, approximating that of the diffusion experiments. These experiments employed the unlabeled sample P(VAc-BA) (Table 2) with $T_g = 14\text{ }^{\circ}\text{C}$. The time-temperature superposition principle was used to superimpose log-log plots (not shown) of storage modulus (G') and loss modulus (G'') against frequency at several temperatures ranging from 50 to $100\text{ }^{\circ}\text{C}$ and to calculate the shift factor (a_T) at each temperature relative to the reference temperature. Only shifts in the horizontal scale were applied. It was found that the shift factors corresponding to G' and G'' were practically the same. In Figure 10, we plot master curves of G' and G'' for P(VAc-BA) latex films at $T_0 = 100\text{ }^{\circ}\text{C}$ (373 K). We note that G' is smaller than G'' over the entire range of frequencies. The absence of a crossover suggests that few if any entanglements are present in this polymer sample and supports the validity of a simple Fickian diffusion model in the analysis of the energy-transfer experiments described above.

The slopes of G' and G'' curves in the terminal zone depart from the expected $+2$ and $+1$ slopes. This deviation can be associated with a population of polymer molecules of higher molecular weights (and higher relaxation times) that dominates the terminal zone, probably due to the seed used in the semibatch polymerization. The shift factors obtained at various temperatures can be fitted to eq 8 to obtain the WLF parameters C_1 and C_2 . In Figure 11, we plot $\log(a_T)$ against temperature. From the curve, we obtained $C_1 = 6.67$ and $C_2 = 143.0\text{ K}$ at $T_0 = 363\text{ K}$ ($90\text{ }^{\circ}\text{C}$). As a test of our methodology, we carried out parallel experiments on two commercial samples chemically similar to our materials. We used poly(vinyl acetate) and a commercial latex based on a P(VAc-BA) copolymer from ICI Paints with a similar composition to our sample. For the PVAc ($T_g = 25\text{ }^{\circ}\text{C}$) we obtained $C_1 = 7.24$ and $C_2 = 140.0\text{ K}$, calculated at the same $T - T_g$. Calculations for the commercial latex ($T_g = 23\text{ }^{\circ}\text{C}$) yield $C_1 = 5.86$ and $C_2 = 133.7\text{ K}$. These values are very similar to the WLF parameters obtained from diffusion experiments and converted to the same $(T - T_g)$ ($C_1^{\circ} = 5.94$ and $C_2^{\circ} = 147.5\text{ K}$).

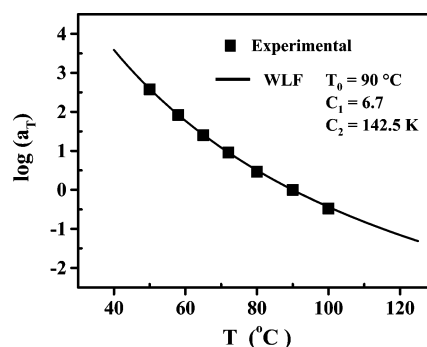


Figure 11. Plot of $\log(a_T)$ against temperatures ranging from 50 to $100\text{ }^{\circ}\text{C}$. From the curve, we obtained $C_1 = 6.67$ and $C_2 = 142.5\text{ K}$ at $T_0 = 90\text{ }^{\circ}\text{C}$.

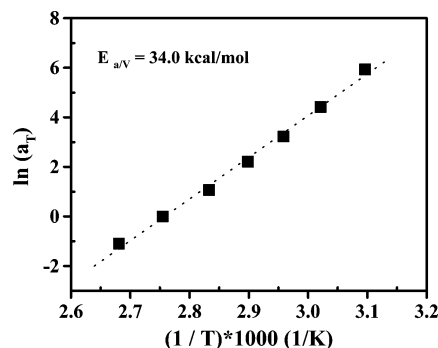


Figure 12. Plot of $\ln(a_T)$ against $1/T$ over temperature range from 50 to $100\text{ }^{\circ}\text{C}$. Assuming a linear plot we obtained $E_a = 34.0\text{ kcal/mol}$ from the slope.

Equation 8 indicates that a full description of the temperature dependence of $\log(a_T)$ requires two parameters C_1 and C_2 . As a consequence, a plot of $\log(a_T)$ against $1/T$ should be curved. Over a limited range of temperatures, this plot can appear linear. From the slope of this plot, one can calculate an apparent activation energy for viscoelastic relaxation ($E_{a/V}$), whose magnitude will increase as the measurement temperatures approach T_g . In Figure 12, we show this kind of plot for the rheological data obtained for the P(VAc-BA) sample. From the slope, we obtained $E_{a/V} = 34\text{ kcal/mol}$ over the temperature range of 50 – $100\text{ }^{\circ}\text{C}$, which is coincident with the value of $E_{a/D}$ obtained from the energy-transfer experiments. For the commercial samples, we measured $E_{a/V} = 37.3\text{ kcal/mol}$ for PVAc and 35.4 kcal/mol for the latex in a similar range of temperatures.

The value of $E_{a/D}$ obtained here for P(VAc-BA) can be compared with a value of 38 kcal/mol we obtained³⁹ for polymer diffusion in poly(butyl methacrylate) (PBMA, $T_g = 32\text{ }^{\circ}\text{C}$) latex films examined between 51 and $90\text{ }^{\circ}\text{C}$. This value is very close to that calculated from creep compliance studies by Ferry's group⁴⁰ on PBMA in that temperature range. More recently, we studied polymer diffusion in methyl methacrylate-butyl acrylate copolymer latex films (P(MMA-BA), $T_g = 12\text{ }^{\circ}\text{C}$) and obtained an effective $E_{a/D} = 43\text{ kcal/mol}$, determined between 50 and $80\text{ }^{\circ}\text{C}$.⁶ It is interesting to note that the T_g of this polymer is close to that of the P(VAc-BA) copolymer described above. Over a similar range of temperatures, the $E_{a/D}$ for the PVAc copolymer is significantly smaller.

Summary

We synthesized donor- and acceptor-labeled P(VAc-BA) copolymer latex particles by semicontinuous emulsion polymerization in the presence of unlabeled

seed latex particles. The base polymer was a copolymer with weight ratio of VAc/BA = 4/1. 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 varying amounts of NBenA from 0.1 to 0.45 mol %. The latex particles had diameters of ca. 200 nm, T_g values of ca. 12 °C, no gel content, and $M_w \approx 70\,000$ g/mol with broad molar mass distributions ($M_w/M_n \approx 4.5$).

We used fluorescence resonant energy-transfer measurements to analyze polymer diffusion across interfaces in these latex films. Films were cast from a 1:1 mixture of Phe- and NBen-labeled latex particles and dried at 4 °C over 12 h. From an examination of fully mixed solvent-cast films, the characteristic distance for energy transfer between Phe and NBen (the Förster radius R_0) was calculated to be 2.44 nm. Polymer diffusion in these latex films was monitored as a function of time at four different temperatures, from 35 to 75 °C. Analysis of the data in terms of an Arrhenius analysis of the cumulative apparent diffusion coefficients led to an effective activation energy $E_{a/D} = 34 \pm 0.5$ kcal/mol. Viscoelastic relaxation measurements on an unlabeled polymer of similar molar mass were analyzed in terms of the WLF model. From this analysis, we calculated an effective activation energy $E_{a/V} = 34$ kcal/mol for a temperature range 50–100 °C.

Theory predicts that $E_{a/D}$ and $E_{a/V}$ should be similar, but not exactly the same. Bartels et al.⁴¹ have derived an expression for the difference between these two values in terms of the thermal expansion coefficient for the bulk polymer and the temperature dependence the chain dimensions. The magnitude of $E_{a/D}$ is predicted to be somewhat smaller than $E_{a/V}$. We can now conclude that the activation energy $E_{a/D} = 34$ kcal/mol obtained for polymer diffusion in P(VAc-BA) latex film from the FRET measurements is in good agreement with the value ($E_{a/V} = 34$ kcal/mol) obtained from viscoelastic relaxation measurements.

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