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Synthesis and Microstructure Characterization of Dye-Labeled Poly(vinyl acetate-*co*-dibutyl maleate) Latex for Energy Transfer Experiments

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ABSTRACT: We examined the emulsion copolymerization of vinyl acetate (VAc) with dibutyl maleate (DBM) (VAc:DBM 4:1 w/w) in the presence of three dyes chosen for fluorescence resonance energy transfer (ET) experiments. The donor dyes were 9-acryloxymethylphenanthrene (PheMA) and 9-methacryloxymethylphenanthrene (PheMMA), and the nonfluorescent acceptor dye was 2′-acryloxy-4′-methyl-4-(*N*,*N*-dimethylamino)benzophenone (NBen). The presence of the DBM comonomer significantly retards the rate of polymerization, which makes it hard to obtain monomer-starved feeding conditions for semicontinuous VAc−DBM emulsion polymerization. Under batch emulsion conditions, the polymer produced from the 4:1 wt ratio of VAc:DBM shows a composition by ^{1}H NMR throughout the polymerization that is very close to the monomer feed ratio. Other evidence, however, shows that there is microphase separation in the latex polymer. It appears that the nature of this phase separation remains constant as a function of monomer conversion. This copolymerization behavior allowed us to obtain dye-labeled latex particles with uniform dye labeling. In this way we synthesized latex particles with a diameter of ca. 100 nm containing 1 mol % PheMA or PheMMA and similar particles containing 0.3 mol % NBen. We report preliminary nonradiative energy transfer experiments on these latex films and on their solvent-cast counterparts. These experiments provide further information about phase separation in the films and also about the rates of polymer diffusion in these P(VAc-*co*-DBM) latex films. We compare results obtained in films in which PheMA is the donor dye with those in which PheMMA is the donor dye.

Introduction

Poly(vinyl acetate) and its copolymers are widely used in industry due to their low cost, ready availability, and compatibility with other materials. The largest volume application is in the area of waterborne coatings. Because of their excellent adhesive characteristics, they are a key component of many types of adhesives.[1] In this paper, we are interested in the copolymer of vinyl acetate (VAc) with dibutyl maleate (DBM). This polymer has been used as the base latex for architectural paints as well as for waterborne adhesives. It has also been used in studies like ours as a model for ethylene−vinyl acetate (EVA) copolymer latex. In the experiments described here, we consider latex particles prepared from a 4:1 weight ratio of VAc:DBM. We are interested in developing a scientific understanding of how the coating and adhesive properties of this material evolve via coalescence of latex particles after a waterborne formulation dries. To carry out these experiments, we need to synthesize appropriate latex particles labeled with dyes for fluorescence resonance energy transfer (ET) experiments.

Since the early 1990s, we have studied polymer diffusion in latex films by fluorescence decay measurements of nonradiative energy transfer.[2] In these experiments, we chose phenanthrene (Phe) as the donor dye and anthracene (An) as the acceptor dye. We have used derivatives of these dyes to label a series of different methacrylate and acrylate polymers for fluorescence energy transfer study. For almost all of these experiments, we used 9-methacryloxymethylphenanthrene (PheMMA) as the donor dye. In some instances where reactivity ratios were unfavorable, or where the methacrylate retarded the rate of emulsion polymerization, we used the corresponding acrylate, 9-acryloxymethylphenanthrene (PheMA).[3] Experiments by Sosnowski et al.[4] demonstrated that, in semicontinuous emulsion polymerization under monomer-starved conditions, dye molecules were incorporated uniformly into the latex polymer. When the Phe groups are well separated in a polymer matrix, they undergo fluorescence decay with a characteristic exponential decay profile.

For the case of batch emulsion polymerization of butyl methacrylate, Sosnowski et al.[4] showed that the PheMMA was not incorporated uniformly. This dye remained preferentially in the monomer droplets until near the end of the reaction and formed a dye-rich low molar mass component when the reaction conversion approached completion. In films formed from these latex particles, the fluorescence decay of the Phe groups was not exponential. The more complex decay profile is likely an indication of Phe−Phe self-quenching due to the high

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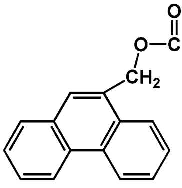
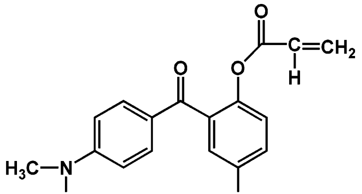
probability of finding neighboring Phe groups.

As we reported recently,[5] vinyl acetate polymerization and copolymerization are strongly inhibited by anthracene derivatives. As a consequence, we were unable to use an anthracene derivative as the acceptor chromophore for energy transfer (ET) from Phe. After an extensive search, we found that benzophenone derivatives are compatible with vinyl acetate polymerization and that 4-(*N*,*N*-dimethylamino)benzophenone derivatives (NBen) such as 2′-acryloxy-4′-methyl-4-(*N*,*N*-dimethylamino)benzophenone have suitable spectroscopic properties to serve as an ET acceptor from Phe.[6] We estimate the characteristic (Förster) energy transfer distance for the Phe−NBen pair in VAc copolymer films to be in the range 2.4−2.7 nm.

In this paper, we examine the synthesis of Phe- and NBen-labeled poly(vinyl acetate-*co*-dibutyl maleate) [P(VAc-*co*-DBM)] with a monomer weight ratio of 4:1. Unlike the polymerization of vinyl acetate itself, the copolymerization process is very slow in the presence of DBM.[7] As we show, even under very slow monomer addition, the second stage of seeded emulsion polymerization occurred under monomer-flooded conditions. We investigated batch emulsion polymerization and found that, for this monomer composition, the polymer produced had a composition similar to the monomer feed throughout the reaction. As a consequence, we were able to synthesize donor- and acceptor-labeled particles and use them to study polymer diffusion in P(VAc-*co*-DBM) latex films. The results we obtained are different from what one would expect for homogeneous copolymer films and point to the formation of phase-segregated domains within the particles during their synthesis.



R = CH_3 PheMMA
R = H PheMA



NBen

Experimental Section

Materials and Instrumentation. Vinyl acetate (VAc, Aldrich) and dibutyl maleate (DBM, Aldrich) were distilled prior to use in order to remove inhibitor traces. Potassium persulfate (KPS, Aldrich) and dodecyl mercaptan (DM, Aldrich) were used as received. Deionized water was collected from a Milli-Q water system. Molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) at 22 °C, using an instrument equipped with Styragel columns HR-1 and HR-5E, a Waters 480 tunable UV−vis absorbance detector, and a Waters R410 differential refractometer detector. Reagent grade THF was used as the eluent at a rate of 0.8 mL/min. Linear poly(methyl methacrylate) (PMMA) standards were used to calibrate the columns. UV absorption spectra were measured with an HP8452A diode array spectrometer. Steady-state fluorescence measurements were carried out with a SPEX Fluorolog 212 fluorescence spectrometer. Particle sizes and size distributions were measured by capillary hydrodynamic fractionation (CHDF) 2000 (MATEC). Differential scanning calorimetry (DSC) experiments were carried out with a Universal V2.6D TA Instruments under N_2 at a scanning rate of 10 °C/min. Samples of 5 ± 1 mg were used. ^1H NMR spectra were obtained on a Varian model HA-200 spectrometer using $CDCl_3$-*d* as the solvent.

Table 1. Recipe for Semibatch Emulsion Polymerization of VAc−DBM

ingredients	seeds (g)	second stage (g)
seeds		10.000
VAc	12.000	16.000
DBM	3.000	4.000
$NaHCO_3$	0.150	0.200
SDS	1.500	
KPS	0.150	0.200
H_2O	133.200	69.600

Table 2. Recipes for Batch Emulsion Polymerization of VAc−DBM

	ingredients	amount (g)
initial charge	VAc	16.000
	DBM	4.000
	C_{12}-SH	0, 0.203, 0.845[a,b]
	dye comonomer	0−1 mol %[c]
	$NaHCO_3$	0.200
	SDS	0.160
	H_2O	74.0
added	KPS	0.200
	H_2O	5.000

[a] Corresponds to 0, 0.24, and 1.0 mL respectively. [b] For the doubly labeled latex, no C_{12}-SH was used. [c] For NBen-labeled polymers, 0.3 mol %, for PheMA- and PheMMA-labeled polymers, 1.0 mol %, and for the doubly labeled latex, 0.15 mol % NBen-acrylate + 0.5 mol % PheMMA.

Semibatch Emulsion Polymerization of VAc with DBM. An unlabeled dispersion of seed particles was prepared on a large scale by batch emulsion polymerization with only base copolymer (Table 1). The same seed was used for the preparation of all latex particles prepared by semicontinuous emulsion polymerization. In these reactions, seeds represent 5 wt % of the final latex polymer. In the second-stage polymerization, an aliquot of the seed dispersion (10.0 g) described above was introduced into a 250 mL three-neck flask equipped with a condenser and a mechanical stirrer. The dispersion was purged with N_2 for 30 min and then heated to 80 °C under N_2. Two solutions were then fed into the flask at the same time and at constant feed rate (ranging from 0.018 to 0.078 mL/min). One solution contained KPS (0.200 g), $NaHCO_3$ (0.200 g), and water (variable). The other contained VAc (16.000 g) and DBM (4.000 g). Some of the reactions included a fluorescent comonomer (PheMMA, 0.267 g, 0.5 mol % of the total monomer). After the addition was complete, the reaction mixture was stirred and heated for another 3 h. Typical recipes are given in Table 1.

Batch Emulsion of Vinyl Acetate (VAc) with Dibutyl Maleate (DBM). In a typical reaction (cf. Table 2), a 250 mL three-neck flask equipped with a condenser and a mechanical stirrer was filled with water (74.0 g), VAc (16.000 g), DBM (4.000 g), SDS (0.160 g), and sodium bicarbonate (0.200 g). The mixture was purged with N_2 for 30 min and then heated to 80 °C. A solution of potassium persulfate (KPS, 0.200 g) in water (5.0 g) was injected. The reaction was kept at 80 °C for another 5 h and then cooled to room temperature. A dispersion of latex particles (d = 123 nm, 20 wt % solids content) was obtained with a narrow size distribution ($D_w/D_n = 1.1$). To follow the polymerization kinetics, aliquots (ca. 1.0 g) were withdrawn periodically during the reaction and placed into an ice−water bath to stop the polymerization. The latex dispersion was then precipitated in methanol and centrifuged to isolate the solids. The conversion was measured gravimetrically. The isolated solids were then dissolved in $CDCl_3$-*d* for ^1H NMR measurements. In some experiments, certain amounts of dye-*co*-monomers were dissolved in the monomer phase before it was introduced into the reaction mixture.

We prepared both high (high-*M*) and low (low-*M*) molecular weight P(VAc-*co*-DBM) particles, using *n*-dodecyl mercaptan (DM) as the chain transfer agent for the low-*M* latex. We also prepared a doubly labeled latex sample as described in Table 2. Characteristics of the P(VAc-*co*-DBM) latex particles are presented in Table 3. A sample of PVAc homopolymer was synthesized under batch emulsion polymerization conditions

Table 3. Characteristics of P(VAc-*co*-DBM) Latex Particles

	C_{12}-SH (mL)	M_w	PDI[a]	gel content (%)
P(VAc-*co*-DBM) (high-*M*)	0	$2.8 \times 10^{5\,b}$		≈50
PheMMA- P(VAc-*co*-DBM)	0	$2.6 \times 10^{5\,b}$		≈50
PheMA- P(VAc-*co*-DBM)	0	$2.7 \times 10^{5\,b}$		≈50
NBen-P(VAc-*co*-DBM)	0	$2.8 \times 10^{5\,b}$		≈50
doubly labeled P(VAc-*co*-DBM)[c]	0			
NBen-P(VAc-*co*-DBM) for GPC[d]	0.24	2.5×10^5	3.0	0
P(VAc-*co*-DBM) for DSC[e]	1.00	5.0×10^4	2.5	0
PVAc	0			≈30

[a] Polydispersity index (M_w/M_n). [b] M_w of the sol fraction. [c] This polymer was labeled with both PhMMA (0.5 mol %) and NBen (0.15 mol %). [d] Corresponds to Figure 3. [e] Corresponds to Figure 9B, curve (4).

using a recipe similar to that employed for synthesis of the seed particles described above (cf. Tables 1 and 3).

Film Preparation. A few drops (3−5 drops) of a latex dispersion (containing 1:1 wt ratio of mixed Phe- and NBen-labeled particles, 20 wt % solids) were spread on a small quartz plate (20 × 10 mm). The film was allowed to dry at 22 °C in the open air and was dry within 2 h. The films were then removed to a cold room (4 °C) to prevent further polymer interdiffusion.

The films on quartz plates were placed directly on a high mass (2 cm thick) aluminum plate in an oven preheated to the annealing temperature and then annealed for various periods of time. The annealed films were taken out of oven and placed directly on another high mass aluminum plate at room temperature. The films were then allowed to cool for 3−5 min before carrying out fluorescence decay measurements at 22 °C.

Solvent-cast films were prepared from the same dispersion [1:1 wt ratio of Phe- and NBen-labeled P(VAc-*co*-DBM)]. A latex film was allowed to dry, and the dry film was dissolved in tetrahydrofuran (THF). The solution was cast onto a quartz plate and allowed to dry at room temperature for 24 h.

Film Characterization. *DSC Measurements.* The glass transition temperature T_g of our VAc homopolymer and VAc−DBM copolymer samples were determined by differential scanning calorimetry (DSC) on 5 ± 1 mg samples under N_2 at scanning heating and cooling rate of 10 °C/min. For most samples three heat−cool cycles were run: heating from −20 to 60 °C, followed by cooling back to −20 °C. A complete measurement takes about 1 h. The T_g values were obtained as the inflection point on the second heating curves.

Gel Content Determination. A sample of latex (4.0 g) was dried to a constant weight W_0. The dried polymer was subsequently immersed in 1,4-dioxane (10 mL). The system was kept shaking at room temperature for 72 h, often yielding a semitransparent solution. The solution was then centrifuged at 20 000 rpm for 20 min, and the top transparent layer was poured off and saved. The precipitate was washed three more times with excess 1,4-dioxane to remove residual sols from the gel. All the dioxane solutions were collected and dried for GPC ($M_w = 2.8 \times 10^5$, PDI = 2.6) and DSC measurements ($T_g = 8$ °C). The remaining sample (the gel) was dried and weighed (W_1). The gel content (%) was calculated from the expression

$$\text{gel content (\%)} = (W_1/W_0) \times 100 \qquad (1)$$

Fractionation of P(VAc-co-DBM) Copolymers for ET Measurements. A separate experiment, similar to that described above, was used to separate a mixed latex dispersion (ca. 4.0 g) consisting of a 1:1 wt ratio of mixed Phe- and NBen-labeled particles into its sol and gel components. The separate fractions were characterized by ^{1}H NMR (in $CDCl_3$-*d*) to determine the polymer composition and by UV absorption spectroscopy for samples dissolved in $CHCl_3$ to determine the dye content. The UV analysis employed ϵ_{max}(NBen, 350 nm) = 2.3×10^4 M^{-1} cm^{-1} and ϵ_{max}(Phe, 295 nm) = 1.1×10^4 M^{-1} cm^{-1}, from which we found 3.04×10^{-5} mol of NBen/g of polymer and 1.04×10^{-4} mol of Phe/g of polymer in both the sol and gel fractions. The dye concentrations in the sol are identical with that in the original polymer before fractionation. The results showed that there is no preference for the dyes between sol and gel fractions.

Fluorescence Decay Measurements and Data Analysis. For fluorescence decay measurements, each labeled film, before and after annealing, was placed in a quartz tube and degassed with flowing N_2 gas for 3−5 min before each measurement. Fluorescence decay profiles were measured by the time-correlated single photon counting technique. The excitation wavelength was 300 nm, and emission from the sample was detected through a combination of a band-pass filter (310−400 nm) and a cutoff filter (335 nm) to minimize the amount of scattered sample excitation light (300 nm) from reaching the detector. In the absence of benzophenone as an energy transfer acceptor, for samples containing 1 mol % donor, the Phe decay profiles were exponential, with $\tau_0 = 44.6$ ns for both PheMMA- and PheMA-labeled P(VAc-*co*-DBM) latex film. Each measurement was continued until there were 5000 counts in the maximum channel. This requires 10 min for the newly formed films and 12−15 min for films annealed for longer times.

For a dipole−dipole coupling mechanism, the energy transfer rate $w(r)$ between a donor and an acceptor depends on the inverse sixth power of their separation distance r[8,9]

$$w(r) = \frac{\alpha}{r^6}; \quad \alpha = \frac{3{R_0}^6\kappa^2}{2\tau_0} \qquad (2)$$

Here R_0 is the characteristic (Förster) energy transfer distance, and τ_0 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.[10,11] In the absence of an acceptor, the donor decay is exponential. 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[12]

$$I_D(t) = A \exp\left[-\frac{t}{\tau_0} - P\left(\frac{t}{\tau_0}\right)^{0.5}\right] \qquad (3)$$

where

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

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.[13]

$$\Phi_{ET}(t_n) = 1 - \frac{\int_0^\infty I_{DA}(t)\,dt}{\int_0^\infty I_D(t)\,dt} \tag{5a}$$

$$\Phi_{ET}(t_n) = 1 - \frac{\text{area}(t_n)}{\text{area}(D)} = 1 - \frac{\langle \tau_d \rangle}{\tau_0} \tag{5b}$$

The quantum efficiency of energy transfer $\Phi_{ET}(t_n)$, defined in eq 5a, can be evaluated with eq 5b, where $\int I_D(t)\,dt$ is the area under the normalized donor decay profile of a film containing only donor. Since the unquenched donor decay profiles for the phenanthrene derivatives employed here are exponential, the value of the integral [area(D)] equals the unquenched donor lifetime τ_0. The term $\int I_{DA}(t)\,dt$ describes the area under the normalized donor decay profile of a film containing both donor and acceptor. These areas have the dimension of time. Each defines an average decay time [$\text{area}(t_n) = \langle \tau_d \rangle$], where t_n refers to the time that a given sample was annealed prior to the fluorescence decay measurement. To obtain an accurate area for each decay profile, we fit each decay curve to the empirical eq 6 (with $\tau_0 = 44.6$ ns fixed, A_1, A_2, and P adjustable) and then evaluated the integral analytically from the magnitude of the fitting parameters.

$$I_D(t) = A_1 \exp[-t/\tau_0 - P(t/\tau_0)^{1/2}] + A_2 \exp(-t/\tau_0) \tag{6}$$

Our measure of polymer diffusion in latex films is the "extent of mixing" parameter f_m

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

which represents the fractional growth in the quantum efficiency in the system. $\Phi_{ET}(0)$ represents the extent of ET across the interfaces in the newly formed film, whereas $\Phi_{ET}(\infty)$ refers to ET efficiency in a film in which the donors and acceptors have been fully randomized. Under these circumstances, the $I_D(t)$ profile should fit to eq 3 with a value of P consistent with the fully randomized acceptor concentration in the film.

Results and Discussion

Polymer Synthesis. In the past, to study polymer diffusion in latex films by energy transfer, we prepared donor and acceptor latex particles in which the dyes were uniformly distributed throughout the particle and randomly distributed along the polymer chains. To promote this type of dye distribution, we carried out particle syntheses by seeded semicontinuous emulsion polymerization under monomer-starved feeding conditions. In this way we have overcome problems associated with reactivity ratios or with differences in transport rates of the dye from the monomer droplets through the aqueous medium to the growing particles. A common test of starved-feed conditions is to measure the instantaneous monomer conversion. Values in excess of 90% are normally taken as evidence of monomer starved conditions.

The polymer we examine here is prepared from a 4:1 weight ratio of VAc and DBM (10.6/1 mole ratio). The reaction temperature was 80 °C. In Figure 1, we show time−conversion plots for batch emulsion polymerization of vinyl acetate (curve a) and for a 4:1 w/w mixture of VAc and DBM (curve b). One sees immediately that the presence of DBM slows down the conversion rate. When we monitored reactions run under the semicontinuous polymerization conditions described in Table 1, we observed monomer droplets in the reaction. It was particularly easy to see monomer droplets dripping from the reflux condenser. Under these conditions the instantaneous monomer conversion, even with the slowest monomer addition we attempted, was less than 90%. Indeed, when we tested the reaction at the end of the monomer feed stage, we found a conversion of only 70%. The monomer conversion reached 100% when we continued to heat the reaction for another 3 h. As a consequence, we decided to examine batch emulsion polymerization as a strategy for fluorescence labeling of VAc−DBM copolymers.

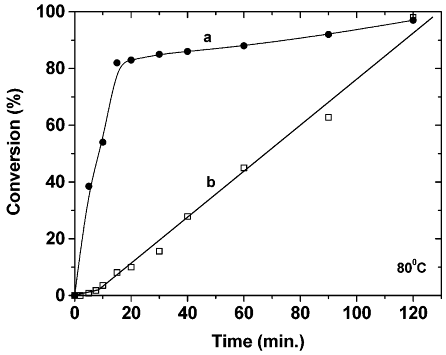


Figure 1. Monomer conversions for the batch emulsion polymerization of VAc with or without DBM: (a) monomer conversion curve of vinyl acetate homopomerization; (b) monomer conversion curve of the vinyl acetate polymerization in the presence of DBM (4:1 w/w).

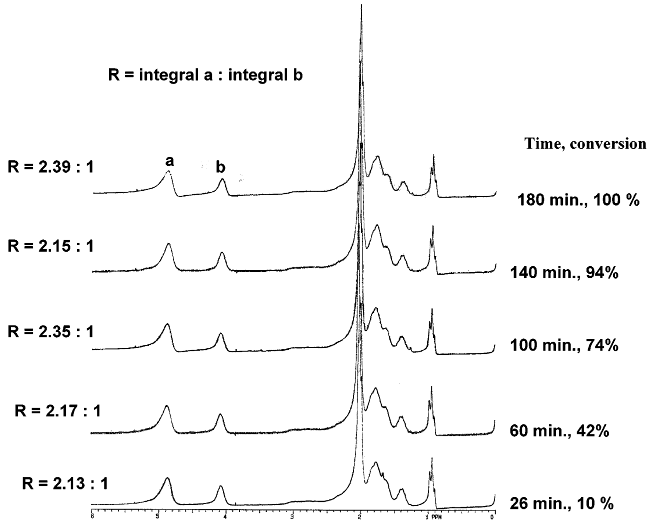


Figure 2. ^{1}H NMR spectra showing the evolution of the composition of P(VAc-*co*-DBM) during the VAc−DBM batch emulsion copolymerization. *R* values indicate the values of the ratio (area peak a)/(area peak b). At the right of each spectrum, we indicate the reaction time and the extent of conversion.

For simple solution polymerization, one anticipates that VAc and DBM will tend to form an alternating copolymer. While the reactivity ratios for this pair are not known, they are likely to be similar to those for VAc plus diethyl maleate (DEM) for which $r_1(\text{VAc}) = 0.171$ and $r_2(\text{DEM}) = 0.040$.[14] Maleate esters have a strong reluctance to homopolymerize. In Figure 2, we show ^{1}H NMR spectra of the copolymer isolated from a bulk copolymerization of VAc and DBM (4:1 w/w) at various extents of conversion (cf. Table 2). The signal at 4.9 ppm is due to the C*H*−OAc proton of the VAc group, whereas the signal at 4.1 ppm is due to the $-CO_2C\mathit{H}_2-C_3H_7$ ester proton of the DBM unit. The ratio of the integrals of the peak areas is constant throughout the polymerization reaction. This value of 2.25 ± 0.15 corresponds

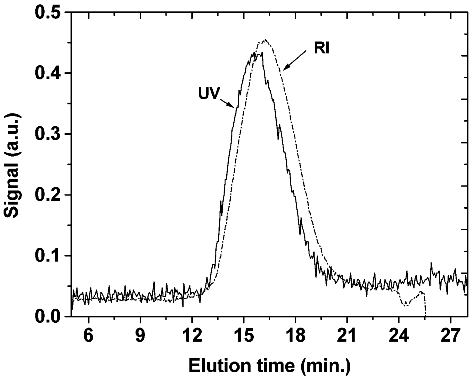


Figure 3. Representative GPC traces for donor PheMMA- and acceptor NBen-labeled P(VAc-*co*-DBM) synthesized by conventional batch emulsion polymerization. This is an NBen−P(VAc-*co*-DBM) polymer with $M_w = 250\,000$ (PDI = 3.0) synthesized in the presence of 0.24 mL of dodecyl mercaptan.

to a mole ratio of 9.2:1, which is close to the mole ratio (10.6:1) in the monomer feed. This result indicates that there is somewhat less VAc incorporated into the copolymer than is present in the feed but that the copolymer composition remains constant over a wide range of monomer conversion.

Incorporation of Donor and Acceptor Dyes via Batch Emulsion Copolymerization. Since the batch emulsion polymerization showed that the polymer composition remained constant throughout the polymerization reaction, we were interested to see whether this approach would yield useful dye-labeled polymer particles. In this analysis, we compare, in a gel permeation chromatography (GPC) run, the refractive index (RI) signal and the UV absorption signal. For this analysis, we need a sample with a negligible gel content, so that the entire sample is soluble in THF and will elute from the GPC columns. For these experiments we used the samples that had a nominal GPC molar mass of $M_w = 2.5 \times 10^5$ and PDI = 3.0, prepared in the presence of 0.24 mL of dodecyl mercaptan. In Figure 3, we plot both the refractive index (RI) signal and the UV absorption signal for the isolated NBen-labeled latex polymer at the end of the reaction. A signature of uniform dye incorporation is overlapping peaks from the two detectors. Since the UV−vis detector precedes the RI detector, there is a small time delay between the two signals. We take this overlap as a strong indication of random dye incorporation at this level (0.3 mol %) of NBen content.

Samples prepared in the absence of a chain transfer agent showed a significant gel content[15] (ca. 50%). As described in the Experimental Section, we fractionated samples of these polymers into their gel and sol fractions. These fractions were examined by UV absorption spectroscopy. We found a similar dye content in the sol and gel components of each polymer.

Similar experiments in the presence of chain transfer agent (dodecyl mercaptan) were carried out with the two different phenanthrene comonomers, PheMA and PheMMA. Here, from simple consideration of reactivity ratios, we expected better incorporation of the acrylate derivative PheMA than the methacrylate. The reactivity ratios for the dye derivatives with VAc are unknown, but values are available for other acrylate and methacrylate derivatives. For example, for VAc with methyl acrylate (MA), r_1(VAc) = 0.030, r_2(MA) = 6.7, and for VAc with methyl methacrylate (MMA), r_1(VAc) = 0.070, r_2(MMA) = 22.2.[14] Thus, both acrylates and methacrylates have a tendency to homopolymerize in the copolymerization with VAc, and the tendency is much more pronounced for methacrylates. For the terpolymerization reactions with dye comonomer with VAc plus DBM, we used tandem fluorescence and RI detectors to monitor the GPC response of the polymer at the end of the reaction. As that in the case of NBen, the two signals overlapped, for the case of both PheMA and PheMMA. We conclude that the donor dyes, at 1.0 mol %, are randomly incorporated into the latex polymer. We can rationalize this result in terms of a balance between the preference for a terminal methacrylate radical to add to another methacrylate monomer and the low concentration of acrylate or methacrylate monomer in the feed.

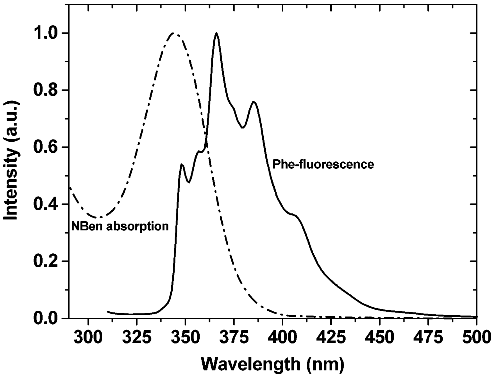


Figure 4. Donor fluorescence spectrum of a PheMMA−P(VAc-*co*-DBM) film and the acceptor absorption spectrum of an NBen−P(VAc-*co*-DBM) film.

Another test of random dye incorporation at low levels of dye content is the shape of the donor decay profile for Phe-labeled latex films. Any tendency for the Phe groups to aggregate leads to a nonexponential decay with a fast component in the decay profile. Here we find a somewhat different result. Films formed from Phe-labeled P(VAc-*co*-DBM) particles exhibited simple exponential decay profiles when the dye content was 1 mol %. We obtained the same result when either PheMA or PheMMA was used as the dye-*co*-monomer. The unquenched lifetimes for films of both PheMA and PheMMA labeled P(VAc-*co*-DBM) were 44.6 ns.

In some experiments, we reduced the amount of Phe-*co*-monomer in the reaction. Under these circumstances, we observed small deviations form a simple exponential decay. We fitted these decays to a sum of two exponential terms. For the PheMMA-labeled polymer with 0.5 mol % dye, we found a small (ca. 4%) contribution of a faster component in the decay. For a film with only 0.05 mol % PheMMA, we found 6% fast component with somewhat larger amplitude. While we have no unique explanation for this result, it is not due to competing background fluorescence from the polymer itself, nor is it likely to be due to dye aggregation. We conclude that only the latex particles with 1.0 mol % Phe are suitable for energy transfer studies of polymer diffusion in P(VAc-*co*-DBM) latex films.

ET Studies of Labeled P(VAc-*co*-DBM) Latex Films. In Figure 4, we show the emission spectrum of PheMMA−P(VAc-*co*-DBM) and the absorption spectrum of NBen−P(VAc-*co*-DBM). Between 340 and 380 nm there is significant overlap between the donor emission and the acceptor absorption. There are two advantages of NBen as an acceptor compared to the anthracene derivatives we employed in previous experiments. The

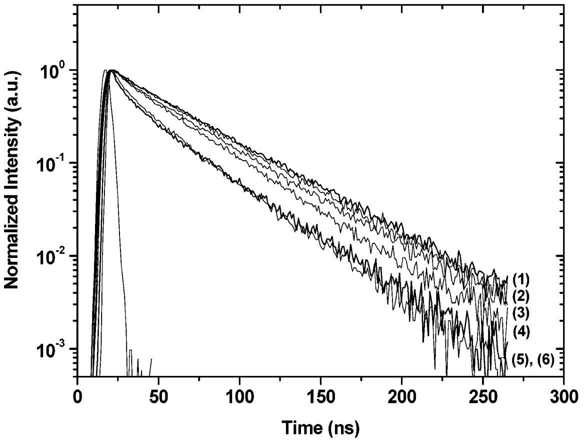


Figure 5. Donor fluorescence decay profiles of (1) a P(VAc-*co*-DBM) film labeled with donor PheMMA (1 mol %) only, (2) a nascent film formed at room temperature, prepared from a 1:1 ratio of PheMMA-labeled P(VAc-*co*-DBM) (PheMMA, 1 mol %) and NBen-labeled P(VAc-*co*-DBM) (NBen, 0.3 mol %) latex particles, (3) a similar film annealed at 100 °C for 30 min, (4) a film formed from a THF solution of a mixture with the same composition as the film in (2), and (5) a film formed the isolated sol fraction of the high-*M* polymers as described in the text and then cast from 1,4-dioxane solution. This film consists of a 1:1 ratio of donor-labeled and acceptor-labeled polymer. (6) A solvent-cast film formed from the doubly labeled latex containing 0.5 mol % Phe and 0.15 mol % NBen groups.

first is that NBen does not fluoresce. As a consequence, we can monitor donor fluorescence over the entire emission band. This leads to faster data acquisition. In the case of anthracene, acceptor emission at $\lambda > 360$ nm meant that donor decay profiles were monitored through a narrow band-pass filter. The second is that the charge transfer transition of NBen, with a maximum at 340 nm in P(VAc-*co*-DBM) has a higher molar extinction coefficient than the L_a band of the anthracene chromophore. [16] Thus, R_0 for nonradiative energy transfer from Phe to NBen (here, ca. 2.5 nm, see below)[16] is slightly higher than that from Phe to An (ca. 2.3 nm).[17] As a consequence, we can carry out ET experiments with a lower level of acceptor labeling with NBen as the acceptor dye than with An.

Films were prepared from a 1:1 mixture of donor- and acceptor-labeled particles. The two dispersions were mixed, spread on a quartz substrate, and allowed to dry in the open air at 22 °C over 2 h. The films formed were typically 100 ± 20 μm thick. The films were then transferred to a refrigerator at 4 °C to minimize polymer interdiffusion until the fluorescence decay curves were measured. Examples are presented in Figure 5, where we compare the evolution of the decay profiles for films in which the donor chromophore was derived from PheMMA. The film with donor only is exponential. There is a small curvature at early times in the decay curve labeled (2) from a newly formed film. When this film was annealed at 100 °C for 30 min, the curvature becomes more pronounced. Greater curvature is seen in a film formed by dissolving a dried sample of the mixed latex in tetrahydrofuran (THF) and casting a film. The lowermost curve in Figure 5 is from a solvent-cast film of the sol fraction isolated from the dry latex film. The behavior of the isolated sol and gel fractions will be discussed in more detail below.

To determine the extent of polymer diffusion in latex films by means of eq 7, we need to determine independently the value of the two parameters $\Phi_{ET}(0)$ and $\Phi_{ET}(\infty)$ (eq 7). In the newly formed films, we found values of $\Phi_{ET}(0)$ on the order of 0.1. In our experience, for films formed from 100 nm diameter latex particles, the presence of sharp interfaces with ET arising only from donor and acceptor groups on opposite side of this interface would lead to a $\Phi_{ET}(0)$ value on the order of 0.05−0.07.[18] Our result here is consistent with a small amount of polymer diffusion accompanying film drying, possibly as a result of the plasticizing effect of water on PVAc copolymers. In the following section, we describe experiments directed toward determing the best value for $\Phi_{ET}(\infty)$.

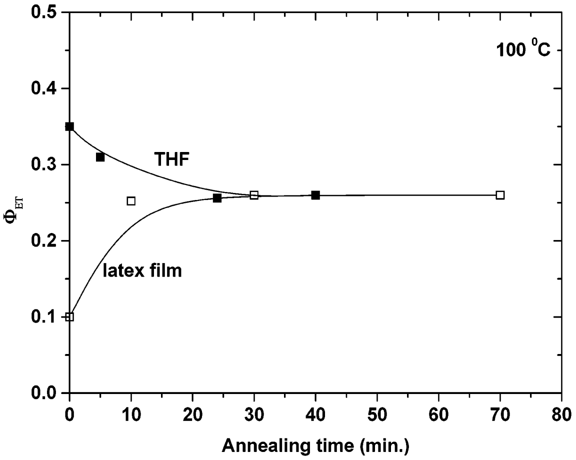


Figure 6. Evolution of the efficiency of energy transfer Φ_{ET} after annealing at 100 °C in P(VAc-*co*-DBM) films (high-*M* with gel) consisting of a 1:1 by weight mixture of donor- and acceptor-labeled polymer. Open squares: latex film. Filled squares: solvent (THF) cast film.

Phase Segregation in P(VAc-*co*-DBM) Copolymers. Our experiments to determine the best value for $\Phi_{ET}(\infty)$ led to unusual results that are best explained in terms of phase segregation in the P(VAc-*co*-DBM) polymer obtained by batch emulsion polymerization. A value for $\Phi_{ET}(\infty)$ is normally obtained in one of the two ways. One can take a film and anneal it for a long time at a sufficiently high temperature that full mixing of donor and acceptor dyes takes place. Because the polymer diffusion rate is strongly accelerated by increasing temperature, Φ_{ET} will normally increase to its maximum value. Alternatively, one can dissolve a dry film sample in an organic solvent. In solution, one expects full mixing of the polymer molecules. A film cast from this solution is then expected to be a good model for the determination of $\Phi_{ET}(\infty)$. This value should be stable to annealing at elevated temperatures.

The results in Figure 6 indicate that the results here are more complex. For a latex film, the initial value of Φ_{ET} is 0.1, as mentioned above. Upon annealing at 100 °C, this value grows in time and appears to level off at a value of 0.26, much lower than the value of ca. 0.6 expected from eqs 3−6. When a sample of this polymer is dissolved in tetrahydrofuran (THF) and a film is cast from this solvent, the film shows an Φ_{ET} value of 0.35. Upon annealing, this value decreases. This type of behavior is indicative of partial demixing of immiscible components upon solvent evaporation, followed by further demixing as the sample is heated. After about an hour at 100 °C, the energy transfer efficiency levels off at a value similar to that reached by the latex film.

To seek a deeper level of understating of this behavior, we separated the “sol” and “gel” components of a film

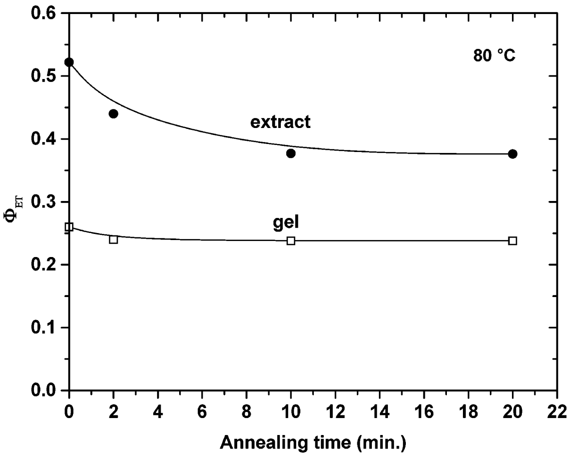


Figure 7. Evolution of the energy transfer efficiency Φ_{ET} upon annealing at 80 °C in solvent-cast films of the soluble extract and the gel fractions of the high-*M* P(VAc-*co*-DBM) polymers. The films consist of a 1:1 by weight mixture of donor- and acceptor-labeled polymer.

containing a 1:1 mixture of PheMMA-labeled polymer and NBen-labeled polymer. The sol fraction appeared to be soluble in THF and could be analyzed by GPC. When this sol fraction was dissolved in THF and cast as a film onto a quartz substrate, the newly dried film exhibited an Φ_{ET} value of 0.52. More important, the measured decay profile fit well to eq 3. Since the dye content of the sol fraction is representative of the sample as a whole, we can use the optimized *P* value from this analysis to calculate an effective ET radius for the dyes in this matrix. In this way we calculate $R_0 = 2.5$ nm, slightly smaller than our current best estimate (2.7–2.8 nm) for this dye pair in a matrix consisting of a 4:1 w/w copolymer of vinyl acetate and butyl acrylate.[16] To examine whether eq 3 provides the best fit to this donor fluorescence decay curve, the decay curve was also fitted to eq 6, with an additional fitting parameter. The best fit gave $A_2 = 0$, in other words, an expression identical to eq 3.

We emphasize this point because when this solvent-cast film was annealed (upper curve in Figure 7), demixing led to a decrease in Φ_{ET}. The $I_D(t)$ decay profiles of these films no longer gave reasonable fits to eq 3. Normalized decay profiles from the films annealed for 2, 10, and 20 min were fitted to eq 6 and gave A_2 values 0.06, 0.18, and 0.24, respectively (Figure 8).

Our choice as the best value of $\Phi_{ET}(\infty)$ is 0.52. To test the validity of this choice, we synthesized a sample of P(VAc-*co*-DBM) labeled with both PheMMA (0.5 mol %) and NBen (0.15 mol %) using the recipe given in Table 2. If the dyes are incorporated randomly into the polymer, we expect that this sample will be a good model representing full mixing of polymer-bound donor and acceptor chromophores. The $I_D(t)$ decay curve for a film of this latex gave a reasonable fit to eq 3, with a similar *P* parameter and a similar Φ_{ET} value (0.52) to those obtained from the sol fraction of the 1:1 latex film [Figure 5, curves (5) and (6)] described above. The fitting parameters for the film of the doubly labeled latex particles remained constant when the decay curves were remeasured after annealing the film at 100 °C. We conclude that the sol film before annealing has a nearly random mixture of donor and acceptor chromophores. In our studies of polymer diffusion in P(VAc-*co*-DBM) latex films, we will assume that $R_0 = 2.5$ nm and employ $\Phi_{ET}(\infty) = 0.52$ as a measure of full mixing.

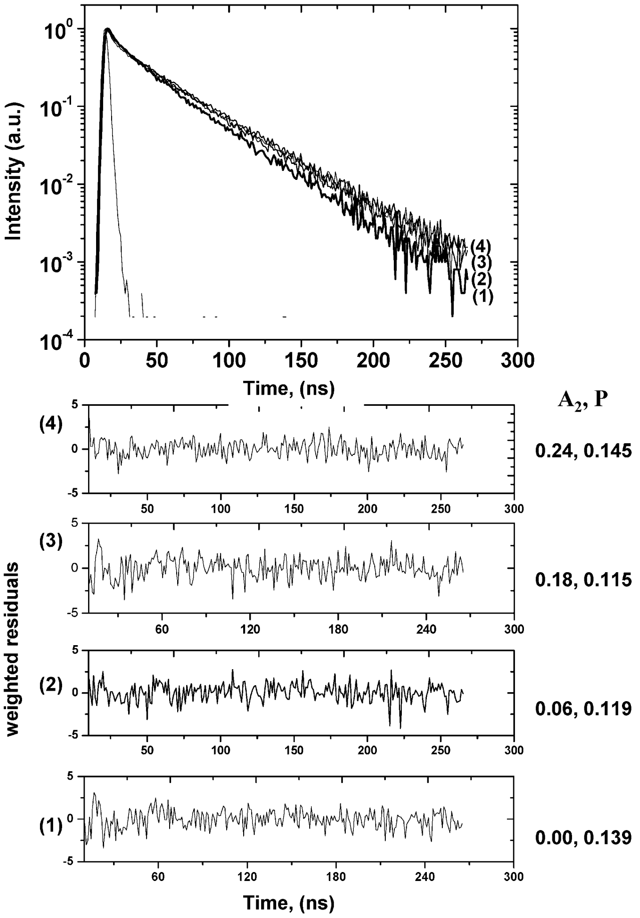


Figure 8. Donor fluorescence decay curves from a solvent-cast film, after annealing at 80 °C, consisting of a 1:1 by weight mixture of the soluble extract of the high-*M* PheMMA- and NBen-labeled P(VAc-*co*-DBM) polymers (PheMMA: 1 mol %, NBen: 0.3 mol %): (1) without annealing; (2) annealed for 2 min; (3) annealed for 10 min; (4) annealed for 20 min. The individual decays were fitted to eq 6, and the magnitude of each A_2 and *P* fitting parameters ($A_1 + A_2 = 1$) is indicated to the right of the corresponding weighted residual plot.

The gel component was suspended in THF and similarly cast as a film. Here the Φ_{ET} values are much smaller and do not vary as the films are annealed. In this sample, gelation occurred during the emulsion polymerization reaction. The gel phase consists of microgel components, in which each microgel is labeled with either Phe or NBen, but not both. The chromophores mix only via diffusion of the dangling ends of the microgel across the interface between adjacent microgel fragments. The microgel fragments themselves cannot diffuse. These results recall the experiments of Tamai et al.,[19] who studied energy transfer in latex films consisting of pre-cross-linked latex particles.

The copolymers we studied composed of VAc and DBM with a molar ratio of 10.6:1 and were synthesized under batch emulsion polymerization conditions. We were curious to see whether we could detect differences by DSC in the glass transition temperature T_g of the different components. One set of traces is shown in Figure 9A. The lowermost curve is that of PVAc homopolymer of high molar mass ($M_w \approx 4.0 \times 10^5$). It shows a single T_g at 41 °C. The three curves above it are those of the late latex polymer isolated from the batch copolymerization of VAc with DBM, at 10%, 42%, and 100% conversion, respectively. These curves have a series of inflections consistent with multiple glass

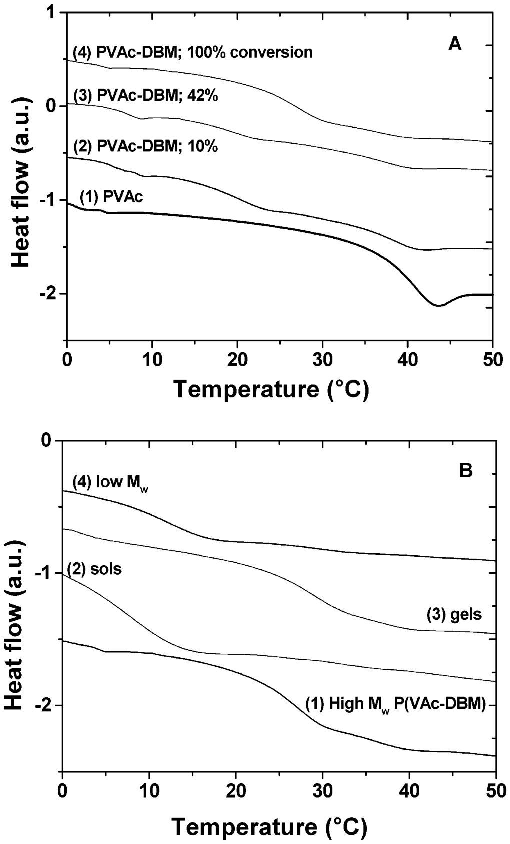


Figure 9. Differential scanning calorimetry traces: (A) for samples of a PVAc homopolymer and for P(VAc-*co*-DBM) isolated from the reaction at different extents of monomer conversions. (1) PVAc homopolymer; (2) P(VAc-*co*-DBM) at 10% conversion; (3) P(VAc-*co*-DBM) at 42% conversion; (4) P(VAc-*co*-DBM) at 100% conversion; (B) comparison of the lower-*M* ($M_w = 5.0 \times 10^4$) and high-*M* P(VAc-*co*-DBM) polymers with the behavior of the sol extract and gel fraction isolated from the high-*M* sample.

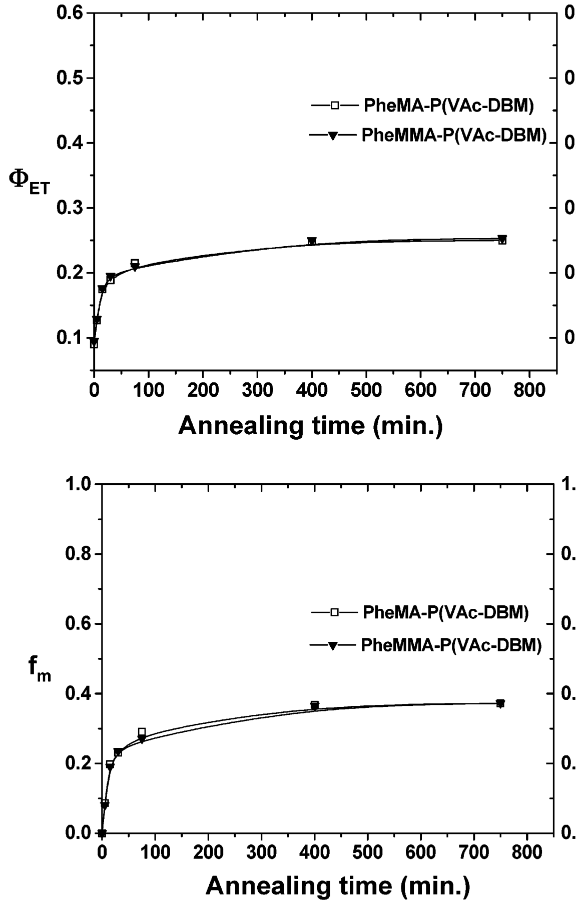


Figure 10. Evolution of the energy transfer efficiency Φ_{ET} (A), and the corresponding extent of mixing f_m (B), upon annealing at 55 °C for latex films consisting of a 1:1 mixture of donor- and NBen-labeled P(VAc-*co*-DBM) polymer (high-*M* with gel). The plots compare the behavior of films containing PheMA as the donor label with that of films containing PheMMA as the donor label.

transition temperatures. At full conversion, there appears to be a weak transition near 5 °C, a stronger transition at about 25 °C, and a hint of a weak transition near 35 °C.

In Figure 9B, we compare DSC traces of the P(VAc-*co*-DBM) sol component with that of the gel component. The gel component has a pronounced thermal transition with an inflection at 28 °C and a weaker transition at ca. 35 °C. These correspond to the major transitions seen in the high-*M* sample from which the gel and sol fractions were isolated. The sol fraction exhibits only one T_g at 8 °C. While one might ordinarily attribute this to a single component, the energy transfer experiments described above on solvent cast films of this component show clear evidence for demixing upon annealing at 100 °C. One may expect a difference in the compositions between the sols and gels. ^{1}H NMR measurements showed that they have identical compositions. The other difference between sols and gels in P(VAc-*co*-DBM) polymer is the degree of branching. In one experiment, we synthesized a copolymer in the presence of 1 mL of chain transfer agent DM (cf. Table 2) to suppress the degree of branching during polymerization. According to Lovell et al.,[15] branching in VAc polymerization is primarily an interpolymer process. For comparison, we show the DSC trace of this gel-free lower M P(VAc-*co*-DBM) sample ($M_w \approx 5 \times 10^4$). This sample shows a strong T_g at ca. 12 °C with a negligible shoulder at higher temperature. We conclude that differences in the degree of branching lead to branch-rich and branch-poor components during batch polymerization.

ET Studies of Polymer Diffusion in P(VAc-*co*-DBM) Latex Films. The fluorescence decay curves in Figure 5 can be interpreted in terms of polymer diffusion across the interparticle boundaries in P(VAc-*co*-DBM) latex films. In the top half of Figure 10, we plot the increase in Φ_{ET} as a function of sample annealing at 55 °C. These values grow from 0.1 in the newly formed film to 0.26 in the film annealed for 8 h. We see in this figure that the film prepared with the methacrylate donor dye PheMMA and the film prepared with the acrylate donor dye PheMA evolve at the same rate. The results are consistent with those in Figure 6, where Φ_{ET} for the latex film evolves until it reaches the limiting value of 0.26. In the bottom half of Figure 10, we transform these quantum efficiencies into f_m values, using the value (0.52) from the freshly cast sol-fraction film as our model for $\Phi_{ET}(\infty)$.

Summary

We examined emulsion copolymerization of vinyl acetate with dibutyl maleate (4:1 w/w VAc:DBM). The presence of the second monomer DBM retards the polymerization process. In the two-stage semicontinuous polymerization, we were unable to feed the monomer sufficiently slowly to achieve monomer-starved conditions. Under conventional batch emulsion polymerization conditions, we found that the polymer composition remained constant from 10% to 100% monomer conversion, with a composition containing slightly less VAc than in the monomer feed. Phase-separated copolymers form at even very low monomer conversion. Under these conditions, the dye derivatives also appeared to be incorporated randomly into the polymer.

In films prepared from the pure latex containing 1 mol % phenanthrene, the fluorescence decay profiles were simple exponential. In films prepared from 1:1 mixtures of donor and acceptor-labeled latex, the energy transfer efficiency in the newly formed film was 0.10, consistent with a small extent of polymer diffusion during drying step. Upon annealing at 55 °C for 100 min, the Φ_{ET} values (measured at room temperature) grew to 0.21. This growth in Φ_{ET} indicates that there is a slow diffusion of polymer molecules across the interparticle boundaries in these latex films and that the high degree of branching and the presence of gel limit the amount of polymer diffusion that can take place.

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