

Synthesis of Dye-Labeled Poly(vinyl acetate-*co*-ethylene) (EVA) Latex and Polymer Diffusion in their Latex Films

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ABSTRACT: We describe the synthesis of dye-labeled poly(vinyl acetate-*co*-ethylene) (EVA) latexes with the purpose of understanding the polymer diffusion behavior in their latex films. Polymer diffusion was followed with experiments based upon fluorescence resonance energy transfer (ET). Both the batch and semibatch emulsion polymerizations of vinyl acetate-ethylene (VAc-E) were examined. The ethylene content of these EVA samples was designed at ~20 wt % (50 mol %). Under batch emulsion polymerization conditions, the reaction is characterized by a rapid monomer conversion and an increment of E content with reaction time. VAc-E batch emulsion polymerization in the presence of the donor dye 9-phenanthryl methyl methacrylate produced EVA with non-random dye distribution, which makes these samples unsuitable for ET experiments. The semibatch emulsion polymerization of VAc-E was carried out under VAc-starved feeding conditions. The resulting EVA was characterized by constant chemical composition throughout the feed. In addition, our data suggest the presence of two components, distinct in molar mass and degree of branching, in these EVA samples. More importantly, these VAc-E polymerizations in the presence of dyes [9-phenanthryl methyl acrylate as the donor and 2'-acryloxy-4'-methyl-4-(*N,N*-dimethylamino)-benzophenone as the acceptor] produced EVA with random dye incorporation, making these samples effective for ET experiments. Unlike the typical polymer diffusion behavior in latex films, characterized by small extents of polymer diffusion in newly dried latex followed by an increase of the extent of diffusion upon annealing, our ET experiments showed that polymer diffusion in these EVA latex films was complete by the time the films were dry. We attribute this striking difference to the low glass transition temperature (T_g) of the EVA and to its low effective monomeric friction coefficient at the drying temperature. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 5581–5596, 2005

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INTRODUCTION

Waterborne adhesives based on latex dispersions prepared by emulsion polymerization have been available since the 1970s and currently repre-

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sent nearly 50% of the market.¹ Among these, adhesives based on vinyl acetate polymers are the most widely used because of their quickness in setting, high strength, and excellent adhesion to cellulose-containing substrates like wood and paper. These types of polymers are also cost-effective and have been used for a variety of applications other than as adhesives, such as paints, textile sizing, and binders for nonwoven fabrics.² For almost all of these applications, vinyl acetate copolymer latexes are internally flexibilized with a comonomer such as ethylene, a hydrophobic vinyl ester or an acrylate such as butyl acrylate. The increased polymer flexibility provides increased polymer mobility and, therefore, a better adhesion. As a result, waterborne adhesives based on vinyl acetate copolymers are able to join difficult-to-bond substrates such as plastic films and metal surfaces.

One class of latex that has been used in waterborne adhesives consists of a copolymer of vinyl acetate and dibutyl maleate [P(VAc-DBM)]. In these polymers, the comonomer DBM conveys its plasticizing effect via the flexibility of its bulky side chains that add free volume to the system. In contrast, ethylene plasticizes PVAc by increasing the flexibility of the polymer backbone.³ Both effects result in a lowering of the glass transition temperature (T_g) of the final copolymer. On a weight basis, ethylene is far more effective, a fact that is reflected in the low T_g of polyethylene homopolymer (below -75 °C).⁴ In addition, poly(vinyl acetate-co-ethylene) (EVA) copolymers possess enhanced toughness, flexibility, and serviceability. Therefore, over the years, there has been extensive research on the properties of EVA, much of it carried out in industry.⁵⁻¹²

In this paper, we describe our first experiments on polymer diffusion in EVA latex films studied by the energy transfer (ET) technique. A major portion of the paper is devoted to a description of the synthesis and characterization of the labeled latex, a non-trivial matter, given the reactivity of the propagating radicals in ethylene-vinyl acetate copolymerization. The EVA latexes were designed to have an ethylene content of ~ 20 wt %, which, on a weight basis, is the same as the DBM content in the P(VAc-DBM) latex polymers described in our previous publications.¹³⁻¹⁵ For this composition, one predicts that there should be no detectable crystalline polyethylene domains,¹⁶ and with the Fox equation,¹⁷⁻²¹ one predicts a T_g of 0 °C.

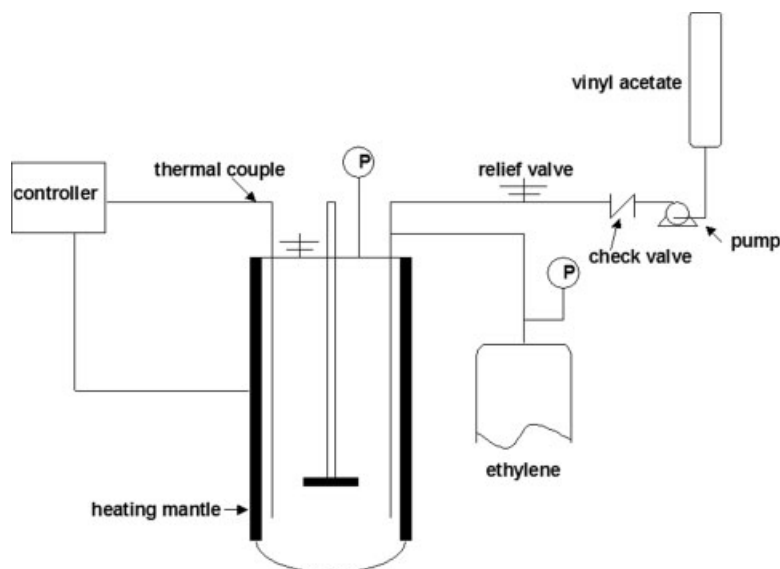
The molar content of ethylene (50 mol %) in these EVA samples is much higher than the molar content of DBM (8.6 mol %) in the P(VAc-DBM) samples. This difference has an important effect on the vinyl acetate-ethylene (VAc-E) emulsion copolymerization kinetics, which is very different from that of VAc-DBM copolymerization.

An important characteristic of VAc-E copolymerization is the extensive amount of chain transfer reaction that occurs from the propagating VAc and E radicals to preformed polymer chains. This chain transfer to polymer leads to the formation of short- and long-chain branches, and through coupling reactions to the formation of gel.²² We anticipated at the start of these experiments that, as in the case of P(VAc-DBM),¹³ the presence of long-chain branches might retard significantly the rate of polymer diffusion in these latex films. This turned out not to be the case. Polymer diffusion in EVA latex films was much more rapid than that determined previously for other VAc copolymers with bulky side groups, even though the experiments were carried out at similar values of $T - T_g$, and the polymers had similar molecular weights.

EXPERIMENTAL

Materials and Instrumentation

All chemicals were purchased from Aldrich and used as-received unless noted otherwise. Ethylene was purchased from BOC Gases. 9-Phenanthrylmethyl methacrylate (PheMMA) was purchased from Toronto Research Chemicals, Inc. 9-acyloxymethyl phenanthrene (PheMA), and 4'-dimethylamino-2-acryloxy-5-methyl benzophenone (NBen) were both synthesized in our group.^{23,24} Vinyl acetate (VAc) was distilled prior to use to remove inhibitor traces. Deionized water was collected from a Milli-Q water system. ¹H NMR spectra were obtained on a Varian Model HA-300 spectrometer. 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 PMMA standards



Scheme 1. Schematic of the EVA semibatch emulsion polymerization reactor.

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 with a Brookhaven BI-90 particle sizer. Differential scanning calorimetry (DSC) experiments were carried out with a Universal V2.6D TA Instruments under N_2 at a scanning rate of $10\text{ }^\circ\text{C}/\text{min}$. Samples of $5 \pm 1\text{ mg}$ were used.

Batch Emulsion of Vinyl Acetate (VAc) with Ethylene (E)

The emulsion copolymerization of VAc with E under pressure was carried out in a 300-mL 4561 Parr reactor equipped with a controller (Parr Instruments Co.; Model 4843) (Scheme 1), which is able to control both the reactor temperature and the rate of rotation. A three-way on/off solenoid valve controlled the delivery of cooling water to the cooling coils inside the reactor (not shown). Pressure was monitored with a PCM pressure transducer capable of detecting a pressure range of 1 psi. For semibatch emulsion polymerization, a Series II model A3389 HC metering pump, capable of delivering liquid at a rate between 0.01 and 9.99 mL/min against a positive pressure of 3000 psi, was employed for pumping the feed into the reactor. In addition to a rupture disc (3000 psi at $350\text{ }^\circ\text{C}$), check valves installed in the pump head and feed line prevent the backflow of the feed.

In a typical batch emulsion polymerization (Table 1), H_2O (80.000 g), VAc (16.000 g), sodium dodecyl sulfate (SDS, 0.160 g), sodium bicarbonate (0.200 g) and potassium persulfate (KPS, 0.200 g) were placed in the reaction vessel. The mixture was purged with N_2 for 30 min and ethylene was then introduced into the reactor until the pressure read 400 psi. The system was then heated to $80\text{ }^\circ\text{C}$. The reaction was kept at this temperature for another 5 h and then cooled to room temperature. A dispersion of latex particles ($d = 125\text{ nm}$, $\sim 20\text{ wt } \%$ solids content) was obtained with a narrow size distribution. The monomer conversion was measured gravimetrically. In some experiments, certain amounts of dye-co-monomers were dissolved in the monomer phase before it was introduced into the reaction mixture.

Semibatch Emulsion Polymerization of VAc with E

The seeds used here were P(VAc-DBM), synthesized according to the recipe presented in Table 2. For details of this synthesis, see ref 13.

Table 1. Recipe for Batch Emulsion Copolymerization of VAc with E

VAc	16.000 g
Ethylene	400 psi
SDS	0.160 g
KPS	0.200 g
H_2O	80.0 g

Temp., $80\text{ }^\circ\text{C}$; time, 5 h; stirring speed, 400 rpm.

Table 2. Recipe for Semibatch Emulsion Polymerization of VAc–E

Ingredients	Seeds (g)	Second stage (g)
Seeds		10.000
VAc	12.000	16.000
DBM	3.000	
C ₁₂ -SH	0.150	20 μ L
Ethylene		400 psi
NaHCO ₃	1.500	0.200
KPS	0.150	0.200
H ₂ O	133.200	70.0

The seeds represent 5 wt % of the final latex polymer. In the second-stage polymerization, an aliquot of the P(VAc-DBM) seed dispersion (10.0 g) was introduced into the reactor together with other ingredients [KPS (0.200 g), NaHCO₃ (0.200 g), and water (70.0 g)] listed in the Table 2, except for the monomers. The reactor was then sealed and degassed with N₂ for 30 min. Ethylene gas was introduced into the reactor until the pressure read 400 psi. The reactor was closed and heated to the reaction temperature (70 °C). The monomer VAc (16.000 g) [some of the reactions included a fluorescent comonomer (0.5 mol % PheMMA, PheMA or 0.15 mol % NBen based on VAc, and/or 20 μ L dodecyl mercaptan (C₁₂-SH)] was fed in with rates ranging from 0.01 to 1 mL/min. After the addition was complete, the reaction mixture was stirred and heated at 70 °C overnight. Typical recipes are given in Table 2. Table 3 summarizes the characteristics of these EVA latex particles.

Film Characterization

DSC Measurements

The glass transition temperatures T_g of the EVA samples were determined on 5 ± 1 mg samples under N₂ by using DSC. For all the samples, three heat-cool cycles were run from -40 to 60 °C at 10 °C/min. The T_g values were obtained as the inflection point on the second heating curve, since the 2nd and 3rd heating curves were identical.

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) in a centrifuge tube (15 mL). The tube was capped with a septum. The system was kept shaking, with a

Burrell Wrist Action Model 75 shaker, at room temperature for 72 h, yielding a transparent solution. The solution was then centrifuged at 20,000 rpm for 20 min, and the transparent layer was poured out and saved. The tube was washed three more times with excess 1,4-dioxane to remove residual sols from the insoluble solid. The remaining sample (presumed to be the gel) was dried and weighed (W_1). The gel content (%) was calculated from the following expression

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

Viscoelastic Properties

Measurements were made using a Rheometrics RAA instrument in the oscillatory shear mode (parallel plates, 25-mm diameter). The mechanical response was measured over a range of frequencies from 10^{-2} to 70 Hz at several temperatures ranging from 30 to 100 °C. Small strains (0.01–0.05) were applied in order to obtain response in the linear viscoelastic regime. When the same sample was used for measurements at different temperatures, corrections for the change in the distance between the plates with temperature were made.

Samples for these measurements were prepared by compression molding. First, the latex 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 known amount of sample was pressed between metal plates in a Carver Press at 70 °C for 2–4 min. Dust-free poly(ethylene terephthalate) sheets (3M, 100- μ m thick) were used to prevent direct contact between the sample and the plates. In the second step, the material free of air bubbles was remolded at the same temperature to its final dimensions (25 mm in diameter and \sim 0.8-mm thick).

Table 3. Summary of Particle and Latex Characteristics of EVA

Latex	d (nm)	Gel (%)	M_w (10^4) ^a	E Content (wt %)
Phe–EVA	114	0	6.3	21
NBen–EVA	113	0	6.7	20
Blank EVA	115	0	6.5	21

^a M_w of the main peak of the GPC traces, based upon polystyrene standards.

Fluorescence Decay Experiments

Film Preparation

A few drops (3–5 drops) of a latex dispersion (containing 1:1 wt ratio of mixed Phe- and NBen-labeled EVA particles, 20 wt % solids) were spread on a small quartz plate (20 × 10 mm²). The film was allowed to dry at 4 °C in a refrigerator and was dry within 24 h. Solvent-cast films were prepared from the same dispersion (1:1 wt ratio of Phe- and NBen-labeled EVA). The latex film was allowed to dry, and the dry film was dissolved in THF. The solution was cast onto a quartz plate and allowed to dry at room temperature for 24 h.

For ET experiments, 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 the 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.

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 N₂ 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. The emission from the samples 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. Each measurement was continued until there were 5000 counts in the maximum channel.

Fluorescence decay profiles for films containing only the donor chromophore were well fitted to a simple exponential expression. When both donor and acceptor groups were present, the donor decay profiles $I_D(t)$ were fitted to the stretched exponential expression

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

where τ_D is the unquenched donor lifetime, A_1 , A_2 , and P are adjustable fitting parameters. In the data analysis employed here, we do not

ascribe meaning to the fitting parameters, but rather use these parameters to evaluate the integrated area under each decay curve. These areas were then used to calculate the quantum efficiency of ET $\Phi_{ET}(t_n)$ for films that were aged or annealed for a time t_n prior to the fluorescence decay measurement. In eq 3, the integral of $I_D(t)$ is the area under the 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 equals the unquenched donor lifetime τ_D . The integral of $I_{DA}(t)$ describes the area under the donor decay profile of a film containing both donor and acceptor, annealed for a time t_n :

$$\Phi_{ET}(t_n) = 1 - \frac{\int_0^\infty I_{DA}(t)dt}{\int_0^\infty I_D(t)dt} = 1 - \frac{\text{area}(t_n)}{\tau_D} \quad (3)$$

Our measure of polymer diffusion in latex films is the “extent of mixing” parameter f_m ,

$$f_m(t_n) = \frac{\Phi_{ET}(t_n) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} = \frac{\text{area}(0) - \text{area}(t_n)}{\text{area}(0) - \text{area}(\infty)} \quad (4)$$

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.

RESULTS AND DISCUSSION

VAc–E Batch Emulsion Copolymerization

In this paper, we focus on the synthesis of dye-labeled EVA latexes with an ethylene content of ~20 wt % (50 mol %) for ET experiments. Both the batch and semibatch emulsion polymerizations of VAc with E were investigated. These reactions were carried out in a 4561 Parr reactor with a model 4843 temperature controller. Under batch emulsion polymerization conditions, all the ingredients, including H₂O, SDS, NaHCO₃, KPS, and VAc, were introduced into the reaction vessel. After degassing the reactor with N₂, ethylene was introduced until the pressure read 400 psi. The reactor was then sealed and heated to 80 °C. The reaction was deemed started (for timing purposes) when the system reached this temperature. The pressure inside the reactor increased to

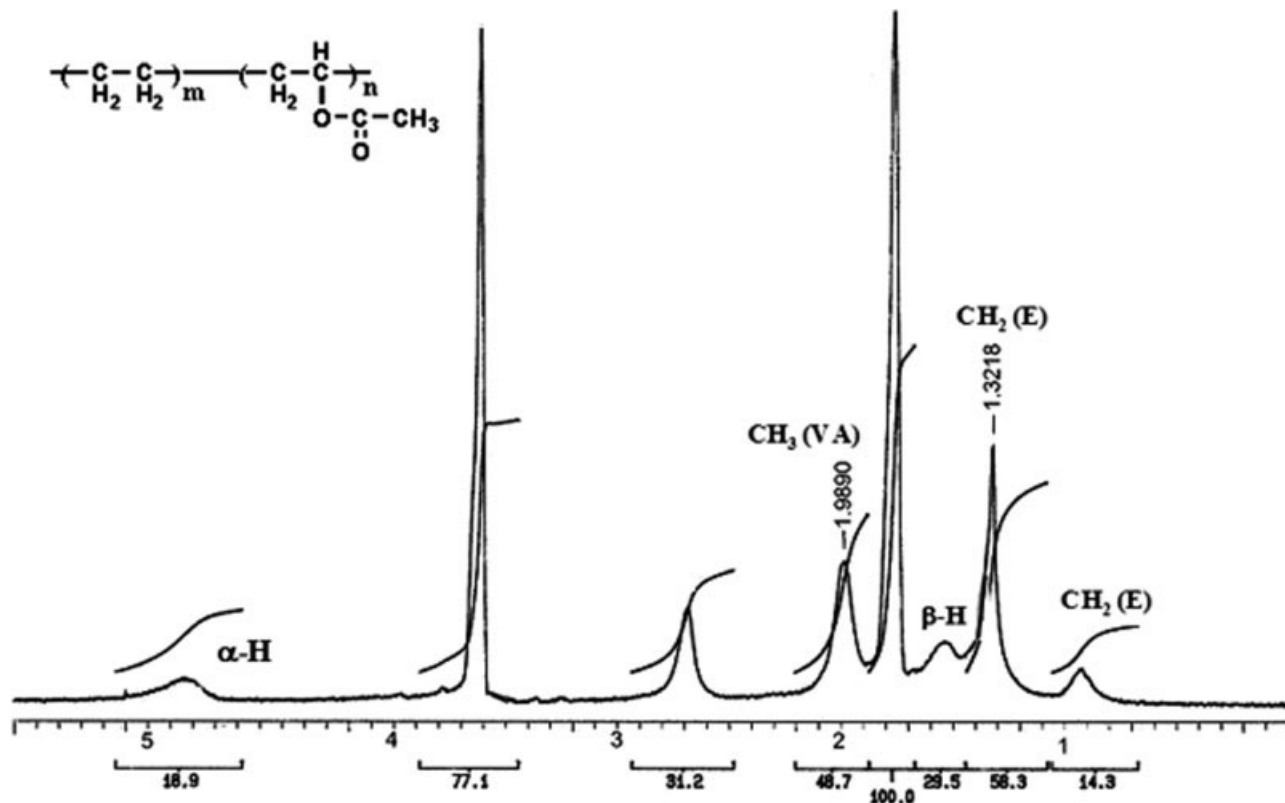


Figure 1. ^1H NMR spectrum of EVA synthesized via VAc–E batch emulsion copolymerization at 80°C , $\alpha\text{-H}$: CH of VAc, $\beta\text{-H}$: CH_2 of VAc. The spectrum was taken of a solution prepared by dissolving a dry EVA sample in $\text{THF-}d_8$.

~ 450 psi at 80°C . This temperature was maintained for 5 h, and over this time, the pressure decreased to ~ 350 psi. The reactor was cooled to room temperature, and the ethylene inside was released. To study the polymerization kinetics, aliquots were withdrawn from the reactor at certain time intervals after the reaction started.

The E and VAc content of the EVA copolymer was calculated from the ^1H NMR spectrum of the polymer. Figure 1 is a representative spectrum of an EVA sample synthesized under the conditions described here. The latex aliquot was dried before it was further treated under vacuum at 50°C for 24 h. The dry sample was then dissolved in $\text{THF-}d_8$, for ^1H NMR measurement. We used $\text{THF-}d_8$ instead of CDCl_3 as the solvent because the peak due to residual water in CDCl_3 appeared at 1.6 ppm and interfered with our analysis. The moisture peak in $\text{THF-}d_8$ was at 2.7 ppm, which caused less interference with our analyses of the NMR spectra.

In Figure 1, the peak at 4.9 ppm corresponds to the CH of the vinyl acetate segment. This integral was deemed as one H in calculating the

molar ratio of ethylene to VAc. The CH_3 group of VAc appears as a singlet peak at 2.0 ppm. The broad peak between 1.4 and 1.6 ppm corresponds to the CH_2 of the VAc. The ethylene CH_2 peak appears at 1.3 ppm. The peak at 0.9 ppm corresponds to the CH_3 group derived from H-abstraction by the ethylene CH_2 radical. The residual H's of the THF in the sample complicate the analysis of the NMR spectrum. The $\text{THF-}d_8$ itself has two signals of equal area at 1.8 and 3.6 ppm due to hydrogen impurities. We could use the integral of the peak at 3.6 ppm to correct for the THF contribution to the signal in the 0.5–2.8 ppm region. The molar ratio of ethylene to vinyl acetate was calculated based on eq 5, where I represent the integral of a peak in the ^1H NMR spectra.

$$\text{E:VAc} = \frac{I_{0.5-2.3 \text{ ppm}} - I_{3.6 \text{ ppm}} - 5I_{4.9 \text{ ppm}}}{4I_{1.3 \text{ ppm}}} \quad (5)$$

The lower curve in Figure 2 shows the evolution of the polymer composition (molar ratio of E:VAc) with reaction time. The E:VAc mole ratio of the polymer, 10 min after the polymerization began,

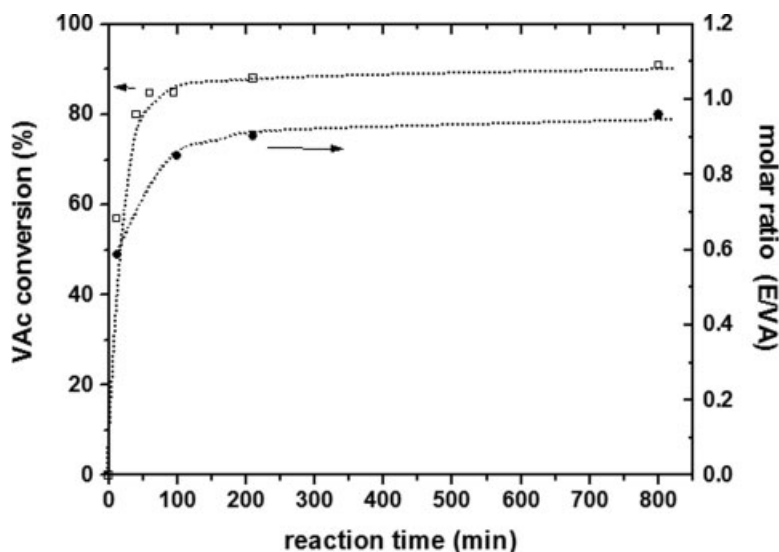


Figure 2. VAc conversion and polymer composition vs. reaction time for batch emulsion polymerization of VAc with ethylene at 80 °C: (□) the E:VAc mole ratio was determined by ^1H NMR in $\text{THF-}d_8$; (●) VAc conversion vs. reaction time calculated based on gravimetry and the E:VAc mole ratio.

is 0.6. This ratio increased to 0.9 at 100 min and eventually leveled off at ~ 1 . This result indicates that the E content of the EVA formed at the early stage of the reaction was lower than that of the EVA formed later. The extent of VAc conversion, monitored gravimetrically during the polymerization, is shown in the upper curve of Figure 2. We see a rapid VAc conversion at the beginning of this polymerization. The VAc conversion reached 80% within 30 min, and eventually leveled off at $\sim 90\%$.

VAc–E polymerized very quickly under batch emulsion polymerization conditions, at a rate comparable to that of VAc itself. This behavior is very different from that of VAc–DBM batch emulsion copolymerization,¹³ where the presence of DBM retards the polymerization rate substantially. For solution polymerization of VAc with maleate ester, $r_{\text{VAc}} = 0.171$ and $r_{\text{maleate}} = 0.040$.²⁵ The presence of maleate ester inhibits the rate of VAc polymerization due to the formation of more stable maleate radicals. For the VAc–E copolymerization, both propagating radicals are very reactive, and there is no retardation of VAc conversion by E.

The evolution of the polymer composition with reaction time during VAc–E batch emulsion polymerization is different from that observed during VAc–DBM batch emulsion polymerization described in ref 13, where the copolymer composition remained constant throughout

the polymerization. Although some authors believe that the reactivity ratios for VAc/E are similar over a wide range of pressures,²⁶ other authors reported that the reactivity ratios varied with the ethylene pressure and reaction temperature. For example, Van Der Meer et al. reported, for solution polymerization of VAc–E in isopropanol at 500 psi, 62 °C, values of $r_{\text{VAc}} = 1.49$ and $r_{\text{E}} = 0.77$.²⁷ Gospodinova et al. studied EVA copolymer synthesized under batch emulsion polymerization at low and medium pressures (1–6 MPa). They fractionated the EVA samples based on selective solubilization in different solvents and measured the composition of these fractions by ^1H and ^{13}C NMR. They found that the ethylene units in one fraction showed a tendency to alternate with VAc, while the ethylene units in the other fraction showed a tendency to form blocks.²⁸ A later study on these fractions revealed different T_g and T_m (melting point) values, supporting the existence of polymers that differed in composition.¹⁶ Our results here are similar to those reported in ref 28. The EVA formed at the early stage of reaction shows a lower E:VAc molar ratio than at later stages. We imagine that this variation in composition is a consequence of VAc polymerization in H_2O , particularly during the early stages of the reaction (E has very low solubility in H_2O), as well as a possible mismatch in the VAc/E reactivity ratios.

Our goal in the work described here was to synthesize dye-labeled EVA for ET experiments. This requires polymers randomly labeled with fluorescent dyes. Under batch emulsion polymerization of VAc-DBM, despite the mismatch between reactivity ratios ($r_{\text{VAc}} = 0.070$ and $r_{\text{MMA}} = 22.2$),²⁵ we were able to synthesize PheMMA and NBen-labeled P(VAc-DBM) latexes to meet this goal (see ref 13). These P(VAc-DBM) copolymers were characterized by random dye incorporation. In addition, the PheMMA-P(VAc-DBM) (Phe: 1 mol %) exhibited a single exponential fluorescence decay profile. Since dye incorporation is a function of monomer reactivity ratios and differences in transport rates of the dyes from the monomer droplets through the aqueous phase to the growing particles, we rationalized 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 methacrylate monomer in the polymerization locus. VAc-E batch emulsion polymerization kinetics is rather different from that of VAc-DBM. To satisfy our curiosity, we tried to incorporate PheMMA into EVA under batch emulsion polymerization conditions described here.

PheMMA (0.5 or 1 mol % based on VAc) was dissolved in the VAc before it was introduced into the reaction vessel. Other operational procedures were the same as those described in this section. At the end of the reaction, we examined the dye incorporation by using GPC with UV and RI detectors. The GPC traces indicated the presence of polymers with Phe dye, preferentially distributed in the low molar mass species. The donor-only fluorescence decay profiles from the Phe-EVA latex films deviated from exponential. We conclude that the VAc-E batch emulsion polymerization conditions described here produce Phe-labeled EVA with a nonhomogeneous donor distribution, and these polymers are not suitable for ET experiments.

VAc-E Semibatch Emulsion Copolymerization

To control the EVA polymer composition and instantaneous VAc conversion, semibatch emulsion polymerizations of VAc-E were carried out. The seed particles were prepared by VAc polymerization with DBM, as described in ref 13. The seed particles had a diameter of 48 nm and a solids content of ~10 wt %. In the synthesis of EVA latexes by semibatch emulsion polymeriza-

tion, the seeds represent 5 wt % of the final latex polymers.

For this reaction, all the ingredients, including the P(VAc-DBM) seeds, NaHCO₃, KPS, and H₂O, were placed in the reaction vessel. After degassing the reactor with N₂, ethylene was introduced until the pressure read 400 psi. The reactor was then sealed and heated to 70 °C. The pressure inside the reactor increased to ~450 psi. The system was maintained at 70 °C, and then the phase containing vinyl acetate and C₁₂-SH was fed into the reactor at a rate of 0.01 mL/min (i.e., over 1717 min, cf. Table 2). Then, the reaction was post heated at 70 °C overnight. The pressure of the reactor dropped slowly from 450 to 350 psi during the monomer feed and remained unchanged with post-reaction heating. The reactor was cooled to room temperature, and the ethylene inside was released. To follow the polymerization kinetics, aliquots of the reaction mixture were taken at different time intervals after the monomer feed started. The aliquots were placed into an ice/water bath to stop the polymerization. The polymers in these aliquots were used to obtain the data presented in Figures 3-6.

Figure 3 shows the evolution of the polymer composition (determined by ¹H NMR) vs. polymerization time. We see that despite the decrease of ethylene pressure during the feed stage (from 450 to 350 psi), the polymer composition (E:VAc = 1:1 mol) remained constant throughout the reaction and post-reaction heating. This result indicates that the EVA composition is insensitive to the pressure drop from 450 to 350 psi.

VAc conversion was monitored gravimetrically, and particle diameters were measured by dynamic light scattering. In Figure 4, the lower curve shows the cube of the diameter (D^3) of particles present in aliquots of the dispersions at different reaction times. The particle size increased from 58 nm at 200 min to 114 nm at 1717 min. The linear dependence of D^3 on reaction time indicates that during the feed stage, there was negligible secondary nucleation, taking into account the constant polymer composition throughout the reaction.

The upper curve in Figure 4 shows a linear increment of the solids content vs. reaction time. The solids content increased from 2.5% at 200 min to 19.0% at 1717 min, at which point the monomer feed was complete. This result provides strong support for the idea that there was

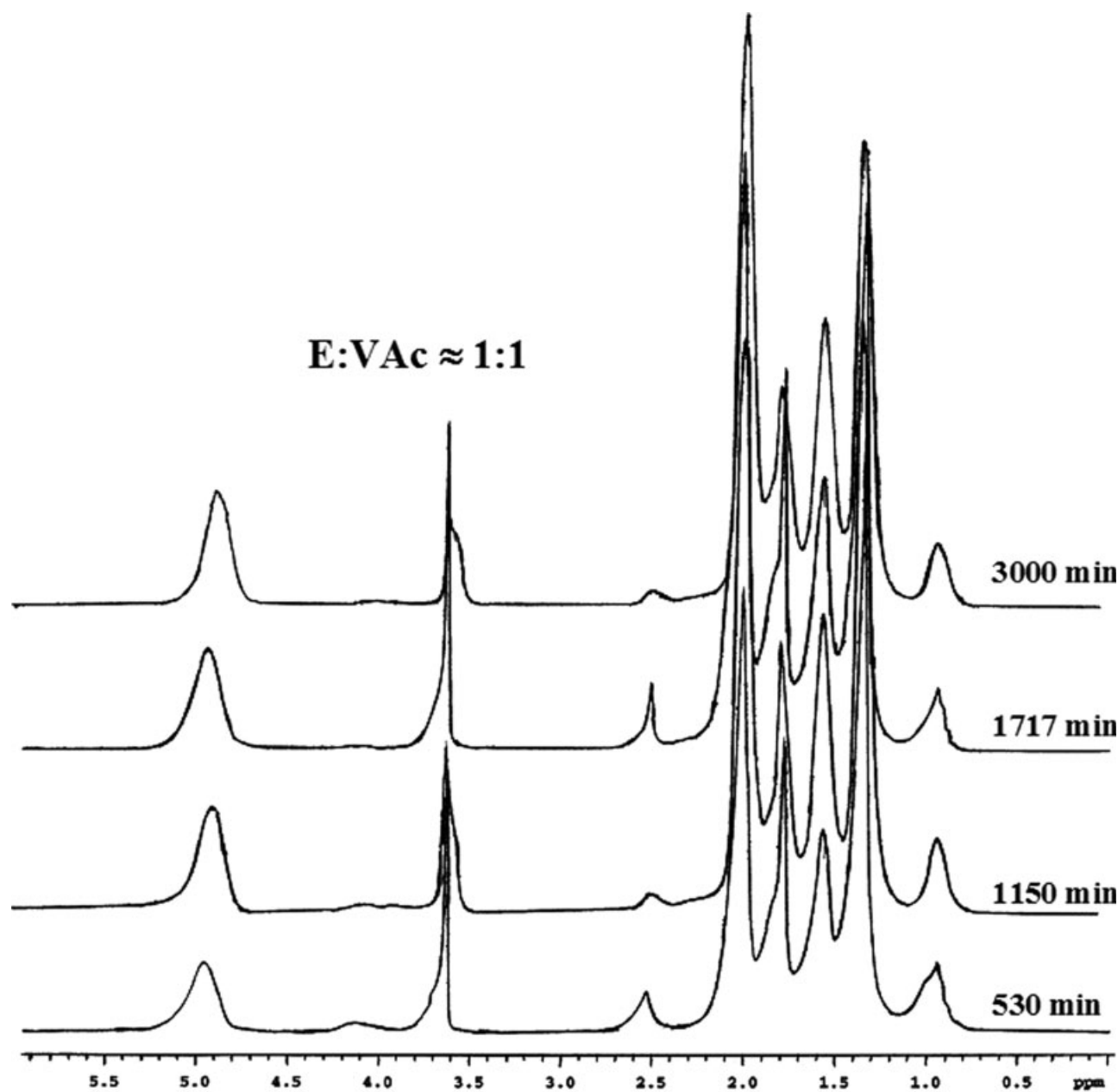


Figure 3. ^1H NMR spectra ($\text{THF-}d_8$) showing the evolution of the composition of EVA during semibatch emulsion copolymerization at $70\text{ }^\circ\text{C}$. The numbers on the right side of each spectrum indicate the reaction time. At 1717 min, the monomer feed to the reactor was complete; the 3000 min spectrum is from a sample post-heated overnight after the feed stage was complete.

a complete instantaneous VAc conversion as VAc was added to the reactor and that the E–VAc semibatch emulsion copolymerization at $70\text{ }^\circ\text{C}$ described here was under VAc-starved feeding conditions.

Figure 5 shows the evolution of the GPC trace of the EVA with reaction time. At 530 min, the GPC trace showed two peaks, a major one with

a weight average molar mass of $\sim 66,000$ ($\text{PDI} = 6$) and a minor one with an average molar mass exceeding the GPC column cutoff ($\sim 500,000$). Gel content measurements, using the protocol described in the Experimental section, indicated the absence of gel in the EVA aliquot at 530 min and thereafter. Thus, the GPC traces shown in Figure 5 are close representations of the molar

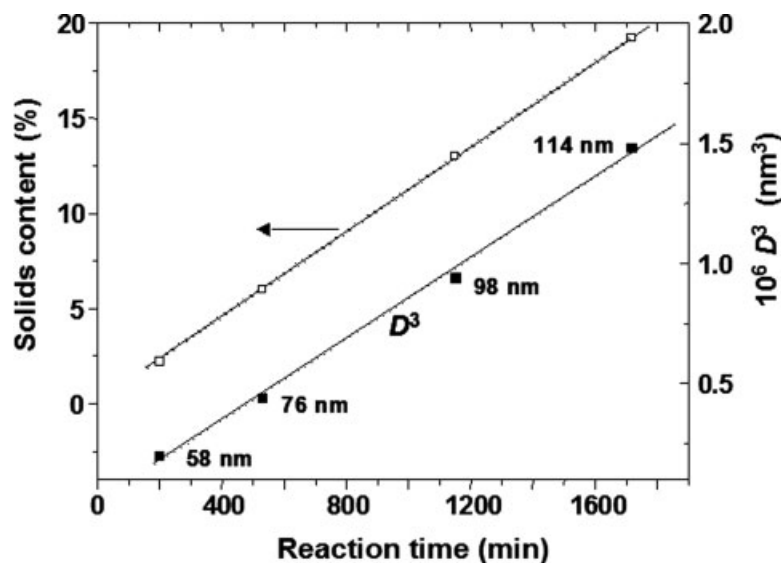


Figure 4. Growth of the cube of the particle diameter (D^3) and the solids content for VAc–E semibatch emulsion copolymerization at 70 °C.

mass distributions of the polymers in the corresponding aliquots. The presence of seeds in these aliquots may complicate the GPC traces. At 530 min, the seed polymer represents less than 10 wt % of the polymer in this aliquot. Since the seeds have a gel content of ~50%, the actual contribution from seeds to the polymers in this GPC sample is less than 5% (the gel is insoluble in THF). Thus the seed polymer makes little contribution to the GPC traces shown in Figure 5. With reaction time, the lower molar mass peak shown in the GPC trace at 530 min shifted to a higher molar mass (GPC trace at 1717 min; $M_w = 70,000$, PDI = 6). There was no change in the GPC trace following post-reaction heating. We conclude that the reaction reached completion when the monomer feed was complete.

Figure 6 shows the DSC traces of the EVA aliquots taken at different times. At 530 min, the EVA copolymer has only one T_g at ~-16 °C with negligible transitions at higher temperatures. At 1150 min, the main transition appeared at -10 °C and a weak transition appeared at 15 °C. When the feed was over at 1717 min, the EVA had a main transition at -6 °C with a minor inflection at 19 °C, with no subsequent change after post-reaction heating.

For a linear polymer, the T_g is independent of its molar mass when the contribution from the chain ends is negligible. Since the E:VAc ratio in the polymer remained constant throughout the

EVA polymerization, the increase of the main glass transition temperature from -16 to -6 °C (from time 530 to 1717 min) is not due to compositional heterogeneity. This increase of the main T_g of the aliquots at different times must indicate some difference in architecture between these EVA samples, most likely the extent of branching. The glass transition of the seed poly-

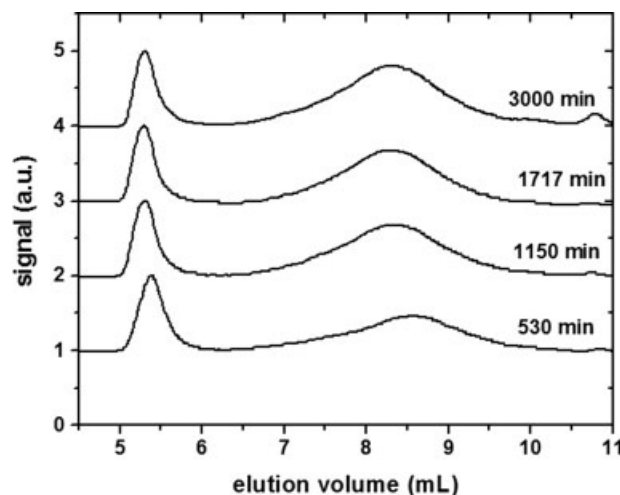


Figure 5. Elution profiles [refractive index (RI) detector signal] from the GPC of EVA latex prepared by semibatch emulsion polymerization at 70 °C in the presence of 0.02 mL C_{12} -SH. The traces are shown as a function of polymer conversion. The numbers on the right of each trace are the reaction time. At 1717 min, the feed stage was complete. The trace at 3000 min represents the latex sample post heated overnight.

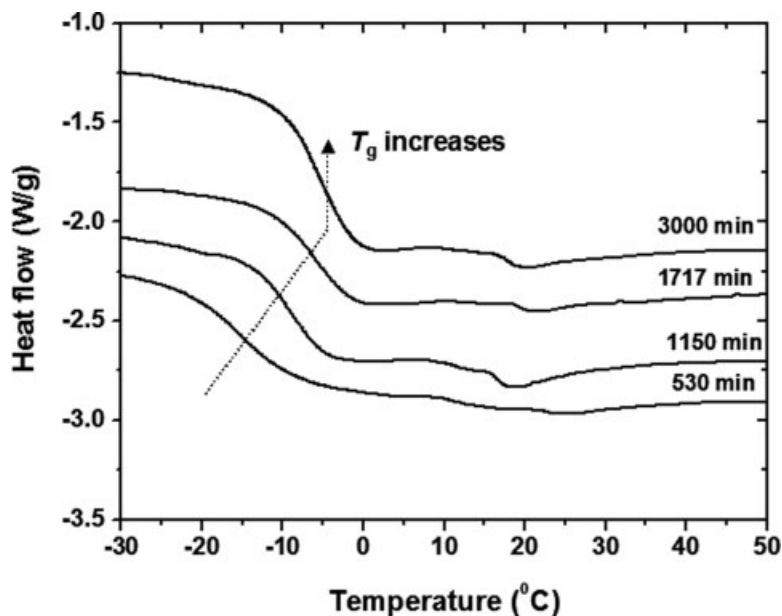


Figure 6. DSC traces for samples of EVA isolated from the VAc–E semibatch emulsion polymerization at different time. From the bottom to the top: 530 min, 1100 min, 1717 min (feeding over), and 3000 min (post heated overnight).

mer at 24 °C was not seen in any of the DSC traces. At 530 min, even when the seeds represented ~10 wt % of the total EVA polymer, its glass transition did not appear in the DSC trace.

Synthesis of Dye-Labeled EVA Latex Particles

The semibatch emulsion polymerization conditions described earlier were used to synthesize dye-labeled EVA latexes for ET experiments. The dyes were introduced during the feed stage. EVA latexes labeled with 0.5 mol % PheMA, 0.5 mol % PheMMA, and 0.15 mol % NBen (based on the feed stage VAc) were synthesized, respectively (see Table 2). Figure 7 shows the GPC traces of the PheMA–EVA, NBen–EVA, and the unlabeled EVA. Although the Phe–EVA has a molar mass distribution similar to that of the unlabeled EVA, NBen–EVA has a much smaller peak exceeding the GPC column cutoff. It is possible that this dye comonomer can also act as a chain transfer agent in the reaction. The main peaks in these GPC traces correspond to similar M_w (~70,000 g/mol). All of these reactions produced EVA latex particles with mean diameters of ~110 nm, narrow size distribution, solids content of ~20 wt %. The T_g values of these polymers are similar (~–6 °C).

Dye incorporation in Phe- and NBen-labeled EVA was characterized by GPC measurements

with UV and RI detectors.²⁹ The traces for the polymer, as monitored by the RI signal, and that for the dye, as monitored by the UV signal, have similar shapes (Fig. 8) for both the PheMA- and NBen-labeled EVA. We conclude that the dyes are uniformly incorporated into the second stage polymer and that there is no detectable dye not bound to the polymer.

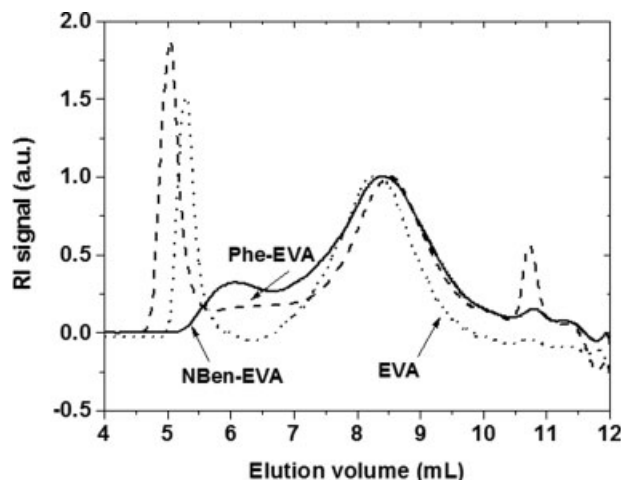


Figure 7. Elution profiles (RI detector signal) of EVA latex samples prepared by semibatch emulsion polymerization at 70 °C in the presence of 0.02 mL C_{12} -SH, with and without added dye-comonomer: (---) Phe–EVA; (.....) unlabeled EVA; (—) NBen–EVA.

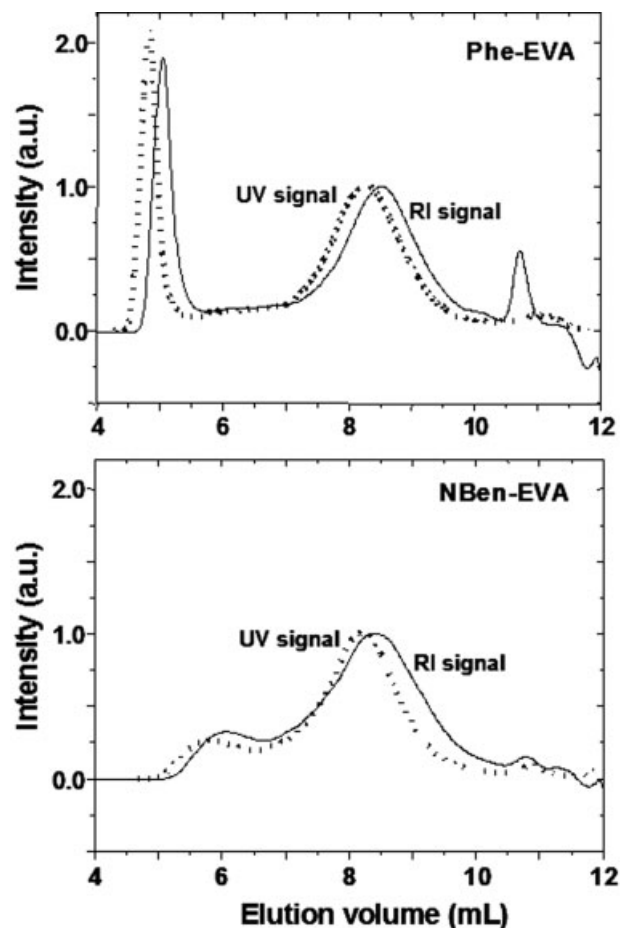


Figure 8. Elution profiles of dye-labeled EVA latex samples monitored by tandem UV and RI detectors: PheMA-EVA and NBen-EVA. These latex samples were prepared by semibatch emulsion polymerization at 70 °C in the presence of 0.02 mL C_{12} -SH. (---) UV signal; (—) RI signal.

The PheMMA-EVA sample showed a donor-only decay profile that deviated from an exponential profile. A nonexponential profile for Phe is often an indication that the dye groups are incorporated nonrandomly into the polymer. In contrast, the polymer labeled with Phe-MA exhibited an exponential fluorescence decay profile with a lifetime of 43.5 ns. Thus we chose PheMA-EVA for ET experiments. Figure 9 shows the emission spectrum of PheMA-EVA and the absorption spectrum of NBen-EVA. The significant overlap between the donor emission and the acceptor absorption at wavelengths between 340 and 380 nm validates this pair of polymers for ET experiments. As mentioned in ref 13, we can carry out ET experiments with a low level of acceptor labeling with NBen as the

acceptor because it is not fluorescent.^{13–15,30} In this report, we used an NBen concentration of 0.15 mol %, based on second-stage monomer.

Latex films were prepared by casting a 1:1 mixture of Phe- and NBen-labeled latex onto a quartz plate. The films were then allowed to dry over 24 h at 4 °C. The films formed were transparent and crack-free. Representative donor fluorescence decays for a film consisting of Phe-EVA EVA + NBen-EVA (1:1 wt) are shown in Figure 10. The curve labeled (1) is the exponential $I_D(t)$ decay of a film containing only donor chromophore with a lifetime of 43.5 ns. There is a significant decrease of the area under the $I_{DA}(t)$ decay curve labeled (2) from a newly formed film. When a similar film was dissolved in THF and recast a film, the shape of the fluorescence decay curve did not change noticeably (3).

ET Studies of Polymer Diffusion

As we have discussed in previous publications, a useful parameter for monitoring polymer diffusion in latex films is the extent of mixing, f_m . This term represents the fractional growth in the ET efficiency $\Phi_{ET}(t_n)$ from an initial value $\Phi_{ET}(0)$, the quantum efficiency of ET in the film at time $t = 0$, which should represent the case of a sharp interface between adjacent cells in a latex film, prior to the onset of diffusion. The third term employed in the calculation of f_m (eq 4) is $\Phi_{ET}(\infty)$. This term refers to the limiting situation where the polymers have fully intermixed and the dyes have become completely randomized in the matrix. For highly branched latex polymers and for polymers containing a significant gel fraction, the limiting value of $\Phi_{ET}(t_n)$ [$\Phi_{ET}(\text{lim})$], for samples annealed for long times or at elevated temperatures, can be less than the hypothetical value of $\Phi_{ET}(\infty)$. When $\Phi_{ET}(\text{lim})$ is less than $\Phi_{ET}(\infty)$, and thus the limiting value of $f_m < 1.0$, one can infer that some feature of the polymer architecture, such as correlation effects or the presence of an immobile gel component, prevents complete mixing of polymer in adjacent cells in a latex film.

In many examples that we have studied in the past, we have found values of $\Phi_{ET}(0)$ on the order of 0.05 to 0.07.³¹ These values correspond to what one would expect for a sharp interface in cells formed from latex particles with diameters on the order of 100 nm. Here we find the surprising result of $\Phi_{ET}(0) = 0.35[\Phi_{ET}(0) = 1 - (\text{area}(2)/\text{area}(1))]$, indicating that a large amount of poly-

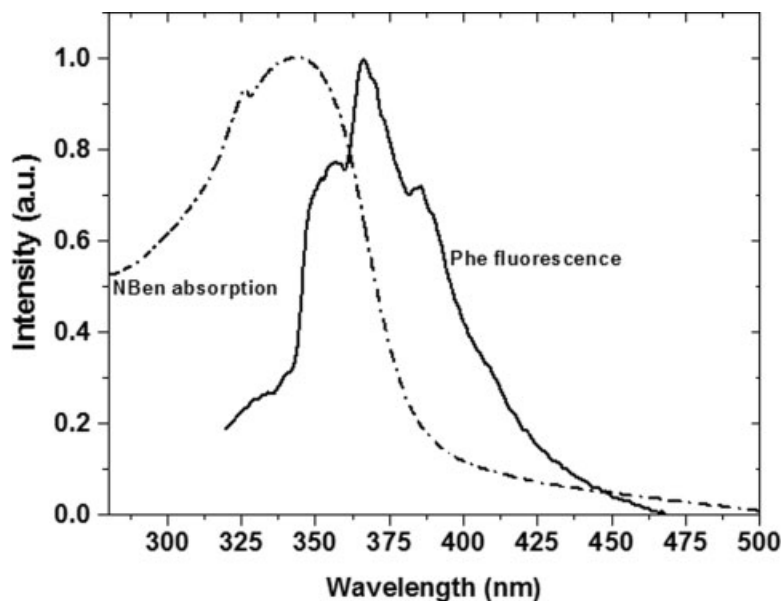


Figure 9. Donor fluorescence spectrum of a PheMA–EVA film and the acceptor absorption spectrum of an NBen–EVA film.

mer diffusion had taken place by the time of the measurement (film exposure to 22 °C for 10 min before measurement). Even more surprising is that we find the same value of Φ_{ET} in a film of the same composition prepared by casting from tetrahydrofuran, a good solvent for the polymer. In solution the donor and acceptor labeled polymers mix and the value of Φ_{ET} obtained for these films is normally close to or equal to $\Phi_{\text{ET}}(\infty)$. This result suggests that the polymers in the EVA latex film undergo full diffusive mixing during drying or after 10 min at room temperature.

To confirm that the decay profiles (2) and (3) represent fully randomized donor- and acceptor-labeled EVA polymers, we fitted the decay curves (2) and (3) to the Förster equation (eq 6), the model describing a random donor and acceptor distribution in three dimensions:

$$I_{\text{D}}(t) = A \exp \left[-\frac{t}{\tau_{\text{D}}} - P \left(\frac{t}{\tau_{\text{D}}} \right)^{0.5} \right] \quad (6)$$

$$P = \frac{4}{3} \pi^{3/2} \left(\frac{3}{2} \langle \kappa^2 \rangle \right)^{1/2} N_{\text{A}} R_0^3 [\text{Q}] \quad (7)$$

In these expressions, A is proportional to the intensity at zero time, and P is given by eq 7. N_{A} is Avogadro's number. R_0 is the characteris-

tic ET (Förster) radius, whose magnitude was determined to be 2.5 nm in P(VAc-DBM). $[\text{Q}]$ is the molar concentration of acceptor groups, and $\langle \kappa^2 \rangle$ is an orientation parameter, which takes the value 0.476 for randomly oriented dyes that are immobile on the time scale of the donor excited state lifetime.

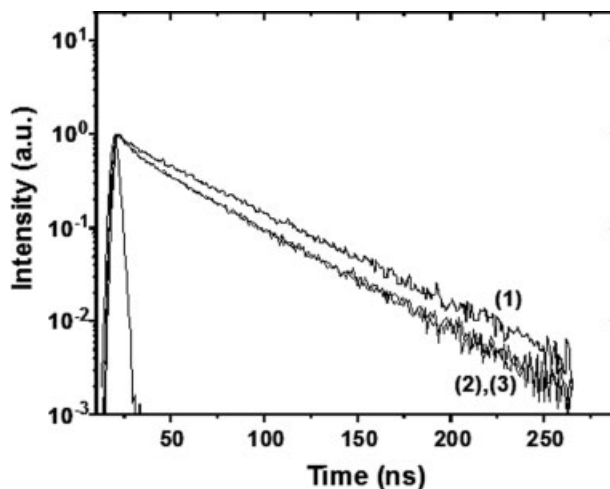


Figure 10. Phenanthrene (donor) fluorescence decay curves $[I_{\text{D}}(t)]$ for EVA latex films. (1) Film of the pure Phe-labeled latex, (2) a newly formed film dried at 4 °C (exposure to room temperature for 10 min before the measurement), consisting of a 1:1 ratio of EVA–Phe (0.5 mol %) and EVA–NBen (0.15 mol %), (3) the same film shown in (2) recast from a THF solution.

We found that the fluorescence decay curve in either case fit well to eq 6 ($\chi^2 < 1.2$). From the best-fit P value, we calculate a value for $[Q]$ that corresponds to randomization of the NBen acceptor dyes in the film. We infer from this result that the polymer diffusion was complete in the EVA latex film exposed to room temperature (22 °C) for ~ 10 min.

To see whether there would be any variation in the extent of polymer mixing at elevated temperatures, we annealed the EVA latex film corresponding to decay profile (2) at 55 °C. To calculate the f_m values, we set a hypothetical $\Phi_{ET}(0)$ value as 0.07 and set $\Phi_{ET}(\infty) = 0.35$, calculated from decays (2) and (3). In Figure 12 (left plots), we plotted the evolution of the Φ_{ET} and f_m vs. annealing time. Here the initial values at time 0 are: $\Phi_{ET} = 0.35$ and $f_m = 1$ [using the hypothetical $\Phi_{ET}(0)$ of 0.07, the f_m value at $t_n = 0$ was calculated to be 1, since the experimental Φ_{ET} from the freshly dried film is equal to that representing a full mixing of the dye-labeled polymers]. These values did not change upon annealing at 55 °C, indicating a lack of any further mixing or demixing.

Comparison with P(VAc-BA) Latex Films

The diffusion behavior observed in the EVA latex films was different than the diffusion behavior we found previously for P(VAc-DBM) and P(VAc-BA) latex films.^{30,32} In those latex films, $\Phi_{ET}(0)$ values were initially small, and then the $\Phi_{ET}(t_n)$ values increased as the samples were annealed. To understand the origin of the rapid diffusion described above the EVA latex films, we have chosen a poly(vinyl acetate-*co*-butyl acrylate) P(VAc-BA) sample studied by Oh et al.³² as a reference. These donor- and acceptor-labeled samples of 200 nm diameter particles, with a VAc:BA weight ratio of 4:1, $T_g = 12$ °C, and $M_w \approx 70,000$, have apparent molar masses similar to that of main peak of the EVA samples described here. We begin by comparing the viscoelastic properties of the two polymers.

In Figure 11, we present a master curves of the storage (G') and loss (G'') shear moduli, measured as a function of frequency (ω), for the EVA sample studied here. These curves were obtained through the time-temperature superposition principle. G' and G'' were measured as a function of frequency for several temperatures above T_g , and the curves horizontally shifted in

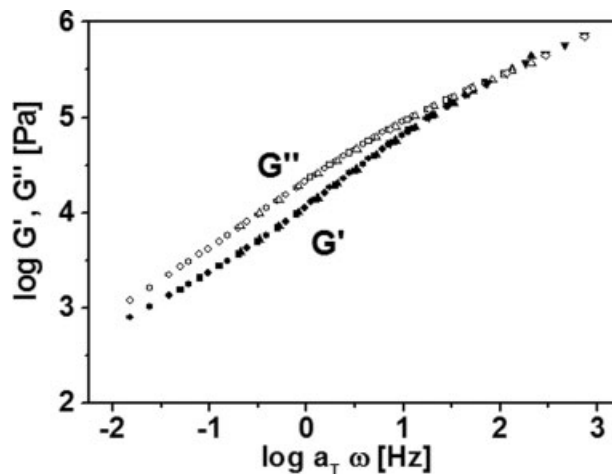


Figure 11. Master curves at 50 °C of the dynamic mechanical properties of the unlabeled EVA latex polymer constructed from measurements of G' and G'' as a function of frequency (ω) at a series of temperatures above T_g .

a log-log scale plot with respect to a reference temperature (50 °C).

The mechanical spectrum is featureless because of the polydispersity in molecular weights and/or branching of the EVA sample. One can see that G'' is larger than G' over almost the entire range of frequencies, showing some incipient overlapping at higher frequency values, a signature of the onset of entanglement coupling. We conclude that the high molecular weight components detected in the GPC analysis of this spectrum are not present in sufficient amount to impart a substantial entanglement contribution to the mechanical spectrum. The influence of these high molecular weight species can be seen in the accessible range of the terminal zone of the mechanical spectrum, since the limiting slopes at low frequency are different from the theoretical values (-1 for G'' , -2 for G') expected for polymers free to flow. These features of the mechanical spectrum described above are similar to those observed in the P(VAc-BA) sample we chose for comparison (see Figure 10 in ref 32).

In Figure 12, we compare the evolution of f_m for the two latex films. For polymer diffusion in P(VAc-BA) latex films, little polymer diffusion occurred as the films were dried at 4 °C. When the film was heated at 45 °C ($T - T_g = 33$ °C) for 6 h, the extent of polymer mixing f_m increased to 0.6. In contrast, the EVA film reached its full extent of mixing as the film dried at 4 °C and aged briefly at room tempera-

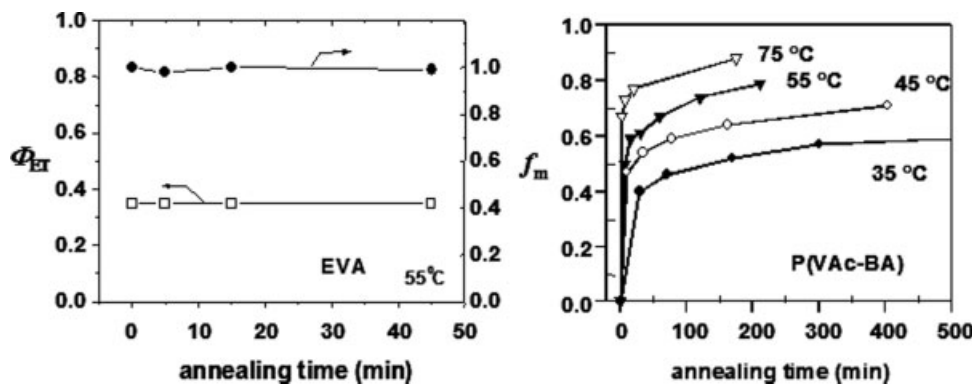


Figure 12. Left: Φ_{ET} and f_m vs. annealing time for EVA-Phe (0.5 mol%) + EVA-N-Ben (0.15 mol %) latex films annealed at 55 °C. Right: Results taken from ref 32 for P(VAc-BA) diffusion.

ture. This result indicates that despite the similar molecular weights, similar viscoelastic response and experiments at similar values of $T - T_g$, the diffusion rate in the P(VAc-BA) system is much slower than in EVA.

The fast diffusion observed for the EVA polymers at or below room temperature is striking and indicates a higher diffusion coefficient for EVA at a temperature ~ 30 °C higher than its T_g (-6 °C) compared with that of P(VAc-BA). Theories of polymer diffusion in melts express the translational motion of the polymer chain as a function of the curvilinear diffusion coefficient, inversely proportional to the monomeric friction coefficient ζ_0 and to the chain length. This coefficient ζ_0 represents the average drag force that the surroundings exert on each monomer unit when the polymer chain is diffusing. For random copolymers and using a mean-field approximation,³³ we can describe the dynamics of the whole chain in terms of an “effective” monomeric friction coefficient. In this case, the ζ_0^{eff} might be expressed as some type of average between the monomeric friction coefficients of the pure components. On the other hand, Ferry has pointed out that the presence of substituent groups attached to the monomer unit increases the value of ζ_0 when compared at corresponding temperatures.³⁴

On the basis of Ferry’s ideas, we might expect lower ζ_0 values for ethylene units, with no substituent groups on the main chain, than in monosubstituted monomers as BA or VAc. Comparison of ζ_0 data obtained from the literature confirms this idea. For example, for PVAc itself, $\log \zeta_0$ [dyne sec/cm] at $T - T_g = 31$ °C is -1.8 , which was calculated by using WLF coefficients and experimental values of ζ_0 taken from ref 34.

ζ_0 for ethylene units can be obtained from diffusion experiments on hydrogenated polybutadienes (structurally equivalent to PE with ~ 4 % of 1-butene as comonomer) carried out by Bartels et al.³⁵ The $\log \zeta_0$ [dynes sec/cm] value for PE obtained from these studies at $T - T_g = 31$ °C is -2.7 . This value for PE is similar to that very recently reported by Klopffer et al.,³⁶ also on hydrogenated polybutadiene samples ($\log \zeta_0$ [dynes sec/cm] ~ -3.0 at $T - T_g = 30$ °C, see Figure 7 in ref 36). Clearly, ζ_0 for PE is almost one order of magnitude lower than that for PVAc.

Summary

We prepared and characterized EVA latex labeled with donor and acceptor groups, with a composition of 4:1 by weight VAc:E. In samples prepared by batch polymerization, dye incorporation was not uniform. Better results were obtained when the polymer was prepared by semicontinuous polymerization in which VAc was added under starve-feed conditions. In ET experiments carried out with latex labeled with phenanthrene as the donor dye and an *N,N*-dimethylaminobenzophenone derivative as the acceptor dye, we found that polymer diffusion occurred extremely rapidly at room temperature. Polymer diffusion led to complete mixing of donor and acceptor groups on the time scale of film drying.

This result contrasts strongly with the behavior of a P(VAc-BA) latex sample of similar molecular weight. Here, at similar values of $T - T_g$, polymer diffusion was slow and easily measured

through an increase in ET over time. Although the EVA sample had a high molecular weight component as seen by GPC analysis, the amount of this component was not sufficient to lead to a significant entanglement contribution to the dynamic mechanical spectrum. In fact the G' and G'' master curves for the EVA sample resembled that of the P(VAc-BA) sample. One has to look for a factor other than entanglements, or the smaller particle diameter of the EVA sample (which contributes to a faster increase in Φ_{ET} values) as being responsible for the difference in diffusion rate of these two polymers. We have suggested, by reference to results described in the literature, that the "effective" monomeric friction coefficient of the EVA polymer may be as much as an order of magnitude smaller than that of the P(VAc-BA) polymer. This lower value of the monomeric friction coefficient leads to more rapid diffusion under otherwise similar circumstances for the EVA polymer.

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