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Effect of Hyperbranched Poly(butyl methacrylate) on Polymer Diffusion in Poly(butyl acrylate-*co*-methyl methacrylate) Latex Films

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ABSTRACT: Latex paint formulations normally contain volatile organic compounds (VOCs) to lower the modulus of the latex polymer and to enhance the rate of its diffusion in latex films. Here we show that hyperbranched poly(butyl methacrylate) (HB-PBMA) not only is miscible with poly(butyl acrylate-*co*-methyl methacrylate) [P(BA-MMA)] copolymers over a range of BA/MMA compositions but also acts as a diffusion promoter. At similar volume fractions (≤ 0.1), it is as effective at promoting P(BA-MMA) polymer diffusion as 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol, TPM), a classic coalescing aid. Unlike TPM, it does not cause a large decrease in the glass transition temperature of the polymer, and it has relatively little effect on the modulus of the polymer. Small molecule additives commonly lead to a reduction of useful mechanical properties of a polymer, such as tensile strength and toughness. Tensile tests show that P(BA-MMA) latex films containing HB-PBMA have better mechanical properties than the corresponding films containing TPM. Thus, this hyperbranched polymer represents a new kind of nonvolatile additive for latex that can promote the rate of polymer diffusion in latex films without significantly disrupting the desirable mechanical properties of the film.

Introduction

Organic solvents are often added as plasticizers to latex paint formulations. Their role is to aid in coalescence of the latex polymer particles. By plasticizing this polymer, they lower its glass transition temperature (T_g) and decrease its modulus. In this way, the forces associated with water evaporation are sufficient to deform the spherical polymer nanoparticles into densely packed polyhedral cells that form a transparent film upon drying.[1] The newly formed film is mechanically weak, but the film grows in strength over time as polymer molecules diffuse across the boundaries between adjacent cells.[2−4] Also over time, the added solvent evaporates. The T_g and modulus of the film increase, so that the binder film that supports the pigment on the substrate is no longer tacky to the touch. This technology has the unfortunate consequence of releasing volatile organic compounds (VOCs) to the air. Thus, there is an ongoing effort to create new technologies to provide latex films with comparable mechanical properties that are more friendly to the environment.

A variety of different strategies have been proposed for developing environmentally compliant latex coatings.[5−8] One approach is to build reactive functionality into the latex polymer so that it cross-links after it dries on a substrate.[9] In this way soft latex polymer is transformed into a tack-free tough rubbery film. Another approach considers reactive coalescing agents that become covalently incorporated into the polymer, with its T_g increasing as the additives become part of the polymer structure. For example, Rissanen synthesized five glycidyl compounds, some of which had better performance than a commercial nonreactive coalescing agent, Nexcoat 795.[10] Previous work in our research group showed that β-hexamethoxymethylmelamine was an effective reactive coalescing agent in a model automotive base coat formulation.[11] Until now, however, there are still no effective substitutes to replace VOCs as coalescing agents in latex formulations.

Several years ago, our laboratory showed that typical solvents used as coalescing aids in latex formulations, such as 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol, TPM) and ethylene glycol monobutyl ether (EB) not only lower the T_g of the latex polymer but also enhance the rate of polymer diffusion in the films.[12−14] The diffusion of polymer molecules across the interparticle boundaries in the film creates entanglements that provide mechanical strength to the films. Substances that increase the rate of polymer diffusion in latex films accelerate the buildup of useful mechanical properties. Theoretical models that explain this increase in diffusion rate are developed in terms of the contribution of the plasticizer to the free volume in the polymer−plasticizer mixture. By increasing the free volume in the film, the additive decreases the monomeric friction coefficient of the polymer, and this in turn leads to an increase in the magnitude of the diffusion coefficient for the polymer chains. Small molecules that increase the diffusion rate of polymer molecules in polymer films should also lower the T_g of the polymer.

In this paper, we report an unexpected phenomenon, a high molecular weight hyperbranched polymer added in small amounts to a latex formulation, that provides a striking enhancement to latex polymer diffusion rate with a minimal influence on the polymer T_g. This hyperbranched polymer was synthesized in the

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form of latex particles by semicontinuous emulsion polymerization, using a mixture of monomer, cross-linking agent, and a chain transfer agent to obtain the branched gel-free polymer.[15] This hyperbranched polymer has a different chemical composition [poly(*n*-butyl methacrylate), HB-PBMA] and a somewhat lower T_g (2 °C) than those (6, 13, 21 °C) of the poly(butyl acrylate-*co*-methyl methacrylate) [P(BA-MMA)] latex polymers we examined. For these polymer mixtures, the T_g values are intermediate between those of the components, but nowhere near as depressed as one would obtain by adding comparable volume fractions of traditional plasticizers such as Texanol. Thus, this polymeric additive is in effect a diffusion promoter rather than a coalescing aid. It is nonvolatile, and its presence in the film seems to have few deleterious effects on the ultimate mechanical properties of the film.

In the sections below, we consider three different strategies for combining HB-PBMA with the P(BA-MMA) latex: blending the two types of latex and then casting a film, dissolving the HB-PBMA in the BA-MMA monomer followed by miniemulsion polymerization, and using the HB-PBMA latex as seeds for synthesizing P(BA-MMA) by semicontinuous emulsion polymerization. We compare the influence of HB-PBMA on these latex films with that of comparable volume fractions of Texanol as a traditional plasticizer.

Experimental Section

Materials. Potassium persulfate (KPS), bisphenol A dimethacrylate (BPDM), sodium carbonate (Na_2CO_3), sodium dodecyl sulfate (SDS), 1-dodecanethiol (C_{12}-SH), hexadecane (HD), methacrylic acid (MAA), 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TPM) and 2,2′-azobis(2-methylpropionitrile) (AIBN) were used as received from Aldrich. Methyl-β-cyclodextrin (Me-β-CD) was kindly supplied by Rohm and Haas Co. and used as received. Methyl methacrylate (MMA, Aldrich), *n*-butyl acrylate (BA, Aldrich), and *n*-butyl methacrylate (BMA, Aldrich) were distilled at reduced pressure, and the purified monomers were stored at 4 °C until use. Water was purified by a Milli-Q ion-exchange filtration system. Phenanthrylmethyl methacrylate (PheMMA) was used as received from Toronto Research Chemicals Inc. 4′-Dimethylamino-2-methacryloxy-5-methylbenzophenone (NBenMA) was synthesized as described elsewhere.[16,17]

Latex Synthesis. To synthesize all donor (D)- and acceptor (A)-labeled particles described in this paper, 1 mol % (2.4 wt %) PheMMA (based on total monomer) and 0.3 mol % (0.8 wt %) NBenMA (based on total monomer) were included in the respective reaction mixtures and added into the monomer pre-emulsion, respectively. Poly(*n*-butyl acrylate-*co*-methyl methacrylate) (P(BA-MMA)) synthesized by semicontinuous emulsion polymerization was synthesized as described in ref 18. The labeled and unlabeled hyperbranched poly(*n*-butyl methacrylate) (HB-PBMA) samples are the same samples described in ref 15 (Table S1, Supporting Information).

Some P(BA-MMA) latex samples (denoted P(BA-MMA)$_{ME}$) were synthesized by miniemulsion polymerization. For many of these samples, the monomer mixture contained varying amounts of HB-PBMA. A typical recipe for the miniemulsion polymerization reaction is shown in Table 1. A monomer emulsion was prepared by sonicating a mixture of all of the ingredients in an ice bath for 20 min using a Branson model 450 digital sonifier (400 W, microtip 40% maximum power, pulse: 1.0 s on/1.0 s off). The monomer emulsion was then transferred into a reactor. The system was thoroughly purged with nitrogen before the reactor was immersed in an oil bath which was preheated to 80 °C. The system was maintained at 80 °C for 5 h. The reaction was then cooled to room temperature.

Table 1. Typical Miniemulsion Polymerization Recipe for the Synthesis of D-Labeled P(BA-MMA) Latex Containing 1 wt % HB-PBMA

ingredients (g)	
H_2O	13.0
SDS	0.06
HD	0.36/1.6 mmol
BA	5.5/43 mmol/55 wt %
MMA	4.4/44 mmol/44 wt %
MAA	0.1/1 mmol/1 wt %
C_{12}-SH	0.025/0.25 wt %
PheMMA	0.246/1 mol %/2.4 wt %
HB-PBMA	0.10
AIBN	0.062

Table 2. Typical Seeded Emulsion Polymerization Recipe for the Synthesis of A-Labeled P(BA-MMA) Latex Containing 5 wt % HB-PBMA Seed Particles

ingredients (g)		first stage	second stage
H_2O		3.0	
HB-PBMA latex		2.87	
methyl-β-cyclodextrin		0.12	
Na_2CO_3		0.12	
KPS		0.14	0.01
monomer			39.30
pre-emulsion			
H_2O	20.0		
SDS	0.084		
BA	10.45/82 mmol/55 wt %		
MMA	8.36/83 mmol/44 wt %		
MAA	0.19/2 mmol/1 wt %		
C_{12}-SH [a]	0.047/0.25 wt %		
NBenMA	0.168/0.3 mol %		

[a] 1-Dodecanethiol, chain transfer agent, used at 0.25 wt % of total monomers.

Another set of P(BA-MMA) latex samples was synthesized by semicontinuous emulsion polymerization using HB-PBMA latex as seeds. These samples are denoted P(BA-MMA)$_S$. The feed ratio of BA:MMA:MAA was 55:44:1. By varying the ratio of seeds to monomer, we synthesized two pairs of D- and A-labeled latex particles with HB-PBMA weight fractions of 5 and 10 wt % (based on total polymer). A typical recipe for the seeded polymerization reaction is shown in Table 2. In the first stage, the HB-PBMA latex dispersion (2.87 g, containing 1.0 g of polymer), water (3.0 g), and methyl-β-cyclodextrin (0.12 g) were added in a 100 mL three-neck flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. The flask was immersed in an oil bath. The system was thoroughly purged with nitrogen while the reaction mixture was heated to 80 °C. The KPS solution (0.14 g in water 1.0 g) as an initiator and the Na_2CO_3 solution (0.12 g in water 1.0 g) as a pH buffer were added into the reactor. In the second stage of polymerization, a pre-emulsion (39.3 g) of monomers, surfactant, chain transfer agent, and water was fed into the seed latex dispersion together with an initiator aqueous solution (0.01 g in water 2.0 g). The monomer feeding rate was kept identical (0.1 mL/min), controlled by Fluid Metering QG50 pumps, with a total feeding time of 5 h. After the addition was completed, the system was maintained at 80 °C for 0.5 h. Then the reaction was cooled to room temperature.

Preparation of P(BA-MMA)/HB-PBMA Latex Blends. P(BA-MMA)/HB-PBMA latex blends were prepared by mixing unlabeled HB-PBMA latex (Table S1, Supporting Information) with 1:1 mixtures of D- and A-labeled P(BA-MMA) latex. The HB-PBMA content of these samples was in the range of 0−10 wt % (based on total P(BA-MMA) polymer).

Preparation of P(BA-MMA) Latex Dispersions Containing TPM. P(BA-MMA) latices containing TPM were prepared by adding 0−10 wt % TPM (based on total P(BA-MMA) polymer) into the mixtures of D- and A-labeled P(BA-MMA) latices. The mixtures were stirred for 48 h at ambient condition before use. Previous experiments in our laboratory established that these conditions were sufficient for complete partitioning of the TPM into the latex particles.

Characterization of the Latex Particles. The solids content of each latex dispersion was determined by gravimetry. Particle diameters were measured by dynamic light scattering at a fixed scattering angle of 90° at 23 °C with a Brookhaven Instruments model BI-90 particle sizer equipped with a 10 mW He−Ne laser.

Characterization of the Latex Polymers. Polymer molecular weights and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using a Viscotek liquid chromatograph equipped with a Viscotek model 2501 UV detector and a Viscotek TDA302 triple detector. Two Viscotek GMHHR Mixed Bed columns were used with tetrahydrofuran (THF) as the elution solvent at a flow rate of 0.6 mL/min. Polystyrene standards were used for calibration. Copolymer compositions in P(BA-MMA) and HB-PBMA latex polymers were determined by ^{1}H NMR spectroscopy. ^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer using CD_2Cl_2 or $CDCl_3$ as the solvent in 5 mm NMR tubes. The residual ^{1}H signal of the solvent was used as a reference in all the spectra (CD_2Cl_2 δ 5.32, $CDCl_3$ δ 7.24). The glass transition temperatures (T_g) of the copolymers were measured with a TA Instruments DSC Q100 differential scanning calorimeter over a temperature range of −50 to 150 °C at a heating rate of 10 °C/min. Each sample was taken through two runs. T_g values were calculated from the second heating run.

Tensile Testing. Tensile tests were performed at a strain rate of 50 mm/min with an Instron 5543 tensile tester at ambient temperature. The averaged values of tensile strength, elongation, and Young modulus were obtained from at least five specimens for each sample. The following procedure was used to prepare the specimen for the stress−strain measurements. Latex film samples containing different concentrations of HB-PBMA or TPM were dried in PTFE dishes at room temperature to form films with a thickness of ca. 0.7 mm. After aging several days at room temperature, these films were then cut into strips (35.0 mm × 7.0 mm) for tensile tests.

Film Preparation. Latex films for fluorescence decay measurements were prepared from 1:1 particle mixtures of the D- and A-labeled dispersions. Several drops of a latex dispersion (about 20 wt % solids content) were spread on a small quartz plate (20 × 8 mm). The film was allowed to dry uncovered at 4 °C until visually transparent. It took about 2 h for a film to dry. The films prepared in this way have a thickness of ca. 60 μm. Solvent-cast films were prepared from the same latex mixture. A latex film was allowed to dry at 23 °C overnight, and the dry film was dissolved in a minimum amount of THF. The solution was recast onto a small quartz plate and allowed to dry at room temperature for 24 h.

Film Annealing. Some latex films were aged at ambient temperature (23 °C). Other films were annealed at 45 °C to enhance the polymer diffusion rate. For these samples, latex 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. Under these conditions, we estimate that it takes less than 1 min for the film to reach the preset oven temperature. The annealed films were taken out of the oven and placed directly on another high-mass aluminum plate at 4 °C for 2 min before carrying out fluorescence decay measurements.

Fluorescence Decay Measurements and Data Analysis. Fluorescence decay profiles of the films at 23 °C were recorded using a nanosecond time-correlated single photon counting system from IBH.[19] Each film was placed in a quartz tube and excited with a NanoLED (λ_{ex} = 296 nm). An emission monochromator (350 ± 16 nm) was used to minimize the amount of scattered light from the sample entering the detector. Data were collected until 5000 counts were accumulated in the maximum channel. The instrumental response function was obtained by using a degassed *p*-terphenyl solution (0.96 ns lifetime) as a mimic standard.[20]

For all the latex polymers examined in this work, the donor (Phe) decay profile in films free of acceptors was exponential with a lifetime τ_D = 44.3 ns. For films containing both donor and acceptor chromophores, the fluorescence-decay profiles became nonexponential. The shape of the curve depends upon the details of the donor−acceptor pair distribution. In a system containing uniformly distributed donor and acceptors in three dimensions, the donor fluorescence intensity decay $I_D(t')$ following instantaneous excitation is described by the Förster equation[12−14]

$$I_{\mathrm{D}}(t') = A\exp[-t'/\tau_{\mathrm{D}} - P(t'/\tau_{\mathrm{D}})^{1/2}] \tag{1}$$

where

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

Here, P is proportional to the acceptor (quencher) concentration [A]. R_0 is the critical Förster radius for energy transfer, which for the Phe/NBen pair takes a value of 2.51 ± 0.04 nm.[18] N_A is Avogadro's number. The orientation factor $\langle\kappa^2\rangle$ describes the average orientation of dipoles of donor and acceptor molecules. For a random distribution of immobile chromophores in three dimensions, $\langle\kappa^2\rangle$ is replaced by $\langle\kappa^2\rangle = 0.476$, a situation typical of dyes in polymer matrices.[20,21] Because the unquenched donor decay profile was exponential in each sample, its integral is equal to the unquenched donor lifetime τ_D. As diffusion takes place in a film cast from a mixture of donor- and acceptor-labeled polymer, more donors are quenched by the acceptors. Thus, the donor fluorescence decay becomes nonexponential. To obtain the area under these decay profiles, we fitted each decay curve to the empirical eq 3 and then evaluated the integral analytically from the magnitude of the fitting parameters, A_1, A_2, and P.[15−17] Here t is the annealing time after film preparation, t' is the fluorescence decay time, and area(t) refers to the normalized area under the fluorescence decay curve of a film annealed for time t.

$$I_{\mathrm{D}}(t', t) = A_1\exp[-t'/\tau_{\mathrm{D}} - P(t'/\tau_{\mathrm{D}})^{1/2}] + A_2\exp(-t'/\tau_{\mathrm{D}}) \tag{3}$$

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

$$\Phi_{\mathrm{ET}}(t) = 1 - \frac{\int_0^\infty I_{\mathrm{D}}(t', t)\,\mathrm{d}t'}{\int_0^\infty I_{\mathrm{D}}^0(t')\,\mathrm{d}t'} = 1 - \frac{\mathrm{area}(t)}{\tau_{\mathrm{D}}} \tag{4}$$

where $I_{\mathrm{D}}^0 t'$ is the decay profile of donor fluorescence intensity in the donor-only film.

The fraction of mixing f_m is an important parameter measuring the extent of growth of Φ_{ET} due to polymer diffusion and is defined in such a way that it corrects for the energy transfer efficiency in the nascent films. Values of f_m are calculated from fluorescence decay data using the equation

$$f_{\mathrm{m}}(t) = \frac{\Phi_{\mathrm{ET}}(t) - \Phi_{\mathrm{ET}}(0)}{\Phi_{\mathrm{ET}}(\infty) - \Phi_{\mathrm{ET}}(0)} \tag{5}$$

where, in principle, the numerator represents the change in energy transfer efficiency between the freshly prepared film and that annealed for time t and the denominator describes the difference in energy transfer efficiency between the initial and the fully mixed films. In a freshly prepared film, if particle deformation and contact at the cell boundaries happens on a different time scale than the onset of polymer diffusion, there is still some energy transfer from donors on one side of the sharp boundary to acceptors on the other side of the boundary. This contribution to energy transfer leads to $\Phi_{ET}(0) = 0.07$ for films formed from particles of the size examined here.[22] We have tested this idea using simulations that allow us to calculate values of Φ_{ET} for energy transfer across interparticle boundaries in the absence of diffusion.[23] Moreover, latex films commonly dry from edges to the center. We have shown that mixing between adjacent cells starts shortly after passage of the drying front. This result is consistent with ideas developed by Wool[24,25] that polymer diffusion across an interface can take place only after the two sides come into intimate contact. If this diffusion is significant enough, the initial value of Φ_{ET} would be greater than that expected for energy transfer across sharp interparticle boundaries.[26] Because some polymer diffusion can occur during sample drying, we calculated the magnitude of f_m with eq 5 using the value $\Phi_{ET}(0) = 0.07$.

$\Phi_{ET}(\infty)$ is a theoretical value which presumes that the donor and acceptor are uniformly but randomly distributed in the polymer at an acceptor concentration determined by the extent to which A-labeled polymer is diluted by D-labeled polymer upon complete mixing. Values of $\Phi_{ET}(\infty)$ were determined in a series of model experiments in which samples of each of the D-labeled polymers were mixed with different amounts of NBenMA as a low molar mass acceptor. Films were prepared by solvent casting, and $I_D(t)$ decay profiles were measured. Individual decays were fitted to eq 1, and values of the fitting parameter P were plotted against [NBenMA] (eq 2). The plots were linear and for each polymer led to a value of $R_0 = 2.5$ nm, consistent with the value reported previously.[18] From this value and the composition of the Phe/NBen latex films, we can calculate values of $\Phi_{ET}(\infty)$.

To compare polymer diffusion rates in different samples, it is convenient to assume a Fickian diffusion model and calculate an apparent diffusion coefficient D_{app} from the f_m values as described previously.[27] D_{app} values are cumulative mean diffusion coefficients, meaning that they integrate diffusion up to each extent of mixing. The advantages and short comings of this approach have been discussed in detail elsewhere.[15,26] Simulations have shown that while this approach overestimates the absolute magnitude of the diffusion coefficient for the polymer by a factor of 2−3, D_{app} are proportional to the true diffusion coefficients for values of $f_m \leq 0.7$.[15] D_{app} values are most useful for comparing the influence of temperature or the presence of additives on the rate of diffusion of a particular polymer sample.

Fujita−Doolittle Model. The Fujita−Doolittle equation, as expressed in eq 6, describes the influence of the volume fraction of additive ϕ_a on the rate at which polymer molecules diffuse in terms of the influence of the additive on the free volume of the mixture.[14,28−31] D_p represents the polymer diffusion coefficient, for which we insert apparent diffusion coefficients $D_{app}(T,\phi_a)$ obtained at temperature T in the presence of additive and corresponding values $D_{app}(T,0)$ obtained in the absence of additive.

$$\left(\ln \frac{D_p(T,\phi_a)}{D_p(T,0)}\right)^{-1} = f_p(T,0) + \frac{f_p^{\,2}(T,0)}{\phi_a \beta(T)} \qquad (6)$$

Here $f_p(T,0)$ is the fractional free volume of the polymer at temperature T with no additive present, and $\beta(T)$ is the difference in fractional free volume between the additive and the polymer at this temperature. Values of $\{\ln[D_p(T,\Phi_a)/D_p(T,0)]\}^{-1}$ were plotted against $1/\phi_a$, and from the intercept and the slope we calculated $f_p(T,0)$ and $\beta(T)$.

Results and Discussion

We recently reported that a strategy developed by Shearington for the synthesis of hyperbranched polymers by free radical polymerization could be used in semicontinuous emulsion polymerization to prepare latex particles consisting of high molecular weight PBMA polymers with a controlled extent of branching.[15] This approach uses a mixture of a cross-linking agent to introduce branches and a chain transfer agent to suppress gel formation. We used bisphenol A dimethacrylate (BPDM) as the cross-linking agent and *n*-dodecyl mercaptan (C_{12}-SH) as the chain transfer agent. We also synthesized similar polymers, with different levels of branching, labeled with donor and acceptor dyes, and used these polymers to study the rates at which the branched polymers themselves would diffuse in latex films.[32] One of the most striking results from this work was that the most highly branched polymer (HB-PBMA), with only 3 BMA units on average between branch points and a T_g of 2 °C exhibited extremely fast self-diffusion compared to linear PBMA, even after correction for the difference in T_g values. This is the observation that prompted us to examine the effect of this polymer as an additive on the diffusion rate of P(BA-MMA) copolymer latex films. Except in the miscibility experiments (see below), all the experiments reported here employed an unlabeled sample of HB-PBMA with $M_n = 40\,000$ g/mol and $M_w/M_n = 1.9$ (Table S1, Supporting Information).

Promoting Polymer Diffusion in Latex Blends. In latex blend experiments, one mixes two different types of latex particles in a common aqueous dispersion and dries the mixture to form a film. As the film dries, the two types of polymers are confined to separate particles, which deform as they pack into polyhedral cells. If the two types of polymers are miscible, they can begin to interdiffuse only after the film is dry and the two types of polymer are in contact at the cell boundaries. This concept applies not only to blends of HB-PBMA with P(BA-MMA) but also to blends of donor (D)- and acceptor (A)-labeled P(BA-MMA) latex. Thus, in the experiments described here, mixing of HB-PBMA with P(BA-MMA) will begin at the same time as the diffusive mixing of D- and A-labeled P(BA-MMA) polymer. In the paragraphs that follow, we will show not only that HB-PBMA is molecularly miscible with the three compositions of P(BA-MMA) that we examine but also that the presence of small amounts of HB-PBMA latex in the blend is very effective at promoting the rate at which D- and A-labeled P(BA-MMA) polymer molecules interdiffuse.

P(BA-MMA) Samples for Latex Blend Experiments. Latex blend experiments carried out to examine the diffusion rate of P(BA-MMA) polymer molecules in latex blend films employed samples of P(BA-MMA) latex prepared by semicontinuous polymerization under monomer-starved conditions. These reaction conditions ensure that the compositions of the latex polymer are uniform throughout the polymerization reaction. Three pairs of D- and A-labeled P(BA-MMA) latex were synthesized as described in ref 18, and all reaction mixtures included 1 wt % of methacrylic acid (MAA). D-labeled latex contains 1 mol % phenanthrene, whereas the A-labeled latex contain 0.3 mol % of a dimethylaminobenzophenone methacrylate derivative (NBen). The three pairs of samples have monomer weight ratios of BA:MMA:MAA of 55:44:1, 50:49:1, and 45:54:1. They are named according to their BA:MMA compositions as P(BA_{55}-MMA_{44}), P(BA_{50}-MMA_{49}), and P(BA_{45}-MMA_{54}) without specifically indicating the MAA content. The glass transition temperatures (T_g) of the copolymers were measured by DSC, giving $T_g \approx 6$ °C for P(BA_{55}-MMA_{44}), 13 °C for P(BA_{50}-MMA_{49}), and 21 °C for P(BA_{45}-MMA_{54}). All values are similar to those estimated values from the Fox equation using T_g(PBA) = −47 °C and T_g(PMMA) = 105 °C. The characteristics of all the latex particles synthesized are summarized in Table 3. The M_n values were in the range of 81 000−86 000 g/mol with a PDI between 1.8 and 2.2. As shown in Table 3, all samples have particle diameters of ca. 110 nm with narrow particle size distributions.

Table 3. Characteristics of the P(BA-MMA) Latex Polymers and Particles

	molecular weight[b] (g/mol)			particle size[c]		
latex sample[a]	M_n	M_w	M_w/M_n	d (nm)	poly[d]	solids content (%)
$P(BA_{55}\text{-}MMA_{44})^D$	83 000	161 000	1.9	112	0.034	47
$P(BA_{55}\text{-}MMA_{44})^A$	81 000	158 000	2.0	113	0.069	47
$P(BA_{50}\text{-}MMA_{49})^D$	86 000	155 000	1.8	104	0.026	46
$P(BA_{50}\text{-}MMA_{49})^A$	84 000	156 000	1.9	105	0.022	46
$P(BA_{45}\text{-}MMA_{54})^D$	85 000	188 000	2.2	115	0.057	47
$P(BA_{45}\text{-}MMA_{54})^A$	83 000	167 000	2.0	114	0.052	45

[a] Superscripts "D" and "A" refer to D- and A-labeled latices, respectively. Subscripts refer to copolymer weight compositions. [b] Absolute molecular weights were measured by GPC using a Viscotek TDA302 triple detector array in conjunction with independently determined values of d*n*/d*c*.[18] [c] Particle size and size distribution were measured by a BI-90 particle sizer. [d] Polydispersity (poly) is a measure of the width of the particle size distribution, taking values close to zero (0.000−0.020) for nearly monodisperse samples and small (0.020−0.080) for narrow size distributions.

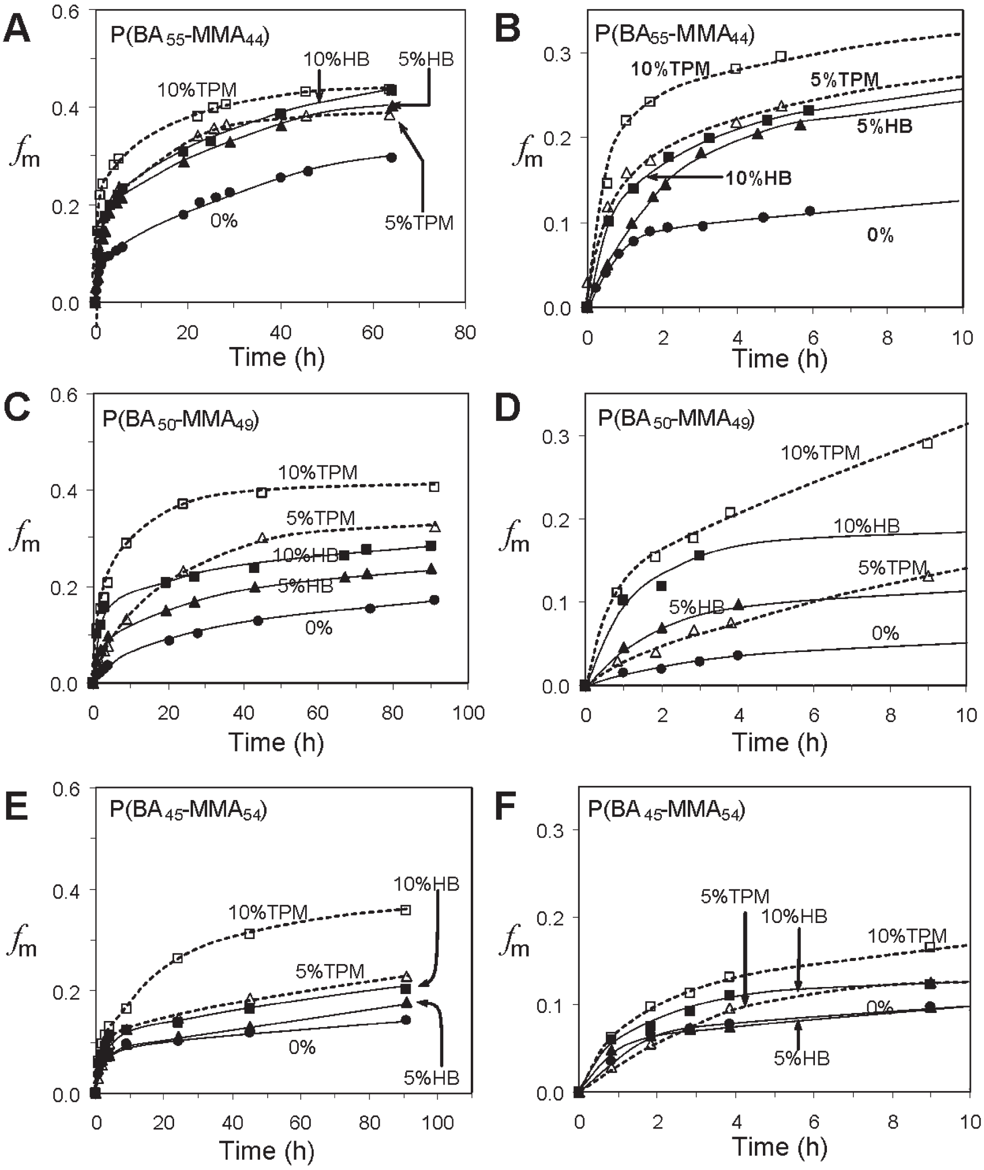

Figure 1. Comparison of the plots of the f_m versus annealing time for (A, B) $P(BA_{55}\text{-}MMA_{44})$, (C, D) $P(BA_{50}\text{-}MMA_{49})$, and (E, F) $P(BA_{45}\text{-}MMA_{54})$ latex films containing HB-PBMA and TPM at 23 °C: (●) 0 wt % additives, (▲) 5 wt % blended HB-PBMA particles, (■) 10 wt % blended HB-PBMA particles, (△) 5 wt % TPM, (□) 10 wt % TPM.

To monitor the influence of HB-PBMA on the diffusion of P(BA-MMA) in latex films, blends were prepared by mixing unlabeled HB-PBMA latex (Table S1, Supporting Information) with 1:1 mixtures of D- and A-labeled P(BA-MMA) latex dispersions. For each BA:MMA composition, HB-PBMA/P(BA-MMA) latex blends were prepared with three different weight fractions of HB-PBMA (0, 5, and 10 wt % based upon polymer solids). DSC results (Table S2, Supporting Information) show that the addition of 5 wt % HB-PBMA to each of the three P(BA-MMA) compositions lowers the T_g of the mixture by 2−3 °C. In contrast, addition of 5 wt % TPM lowers their T_g values by ca. 10 °C. While the variation in T_g is small, it suggests at least partial miscibility of the blend components.

Miscibility of HB-PBMA with P(BA-MMA). To examine in more detail the miscibility of HB-PBMA with P(BA-MMA), we carried out experiments with samples of D- and A-labeled of HB-PBMA reported in a recent publication.[32] We examined mixtures of HB-PBMA^D with P(BA-MMA)^A as well as mixtures of HB-PBMA^A with P(BA-MMA)^D. After these films were dry, they were dissolved in tetrahydrofuran to ensure mixing in the dissolved state and then allowed to dry. We measured donor fluorescence decay profiles on these films and assumed that they represent the limiting extent of mixing consistent with the miscibility of the two types of polymers. From the decay profiles, we calculated the quantum yields of energy transfer Φ_{ET} and refer to these values as the limiting values $\Phi_{ET}(\text{lim})$. These values were then compared to theoretical values of the energy transfer efficiency $\Phi_{ET}(\infty)$ assuming that the donor and acceptor dyes are randomly and uniformly distributed in the polymer film. Experimental values of $\Phi_{ET}(\text{lim})$ are indistinguishable from the $\Phi_{ET}(\infty)$ values appropriate for complete mixing (Table S3, Supporting Information). This statement holds true for the miscibility of HB-PBMA with all three different compositions of P(BA-MMA). We obtain this result for the cases in which the highly branched polymer is D-labeled (HB-PBMA^D), for which $\Phi_{ET}(\infty) \approx 0.5$, and for the examples employing A-labeled HB-PBMA^A. In this case, $\Phi_{ET}(\infty)$ is smaller ($\approx$0.12) because the acceptor concentration in the film is smaller (eq 2) than in the former set of examples. From these data, we conclude that HB-PBMA is miscible at the molecular level with the three different compositions of P(BA-MMA).

Comparing the Effectiveness of HB-PBMA and TPM on Polymer Diffusion Rates. To illustrate the effectiveness of unlabeled HB-PBMA latex in enhancing polymer diffusion rates for P(BA-MMA) polymers in P(BA-MMA) latex films, we compare its influence with that of TPM, a commonly used coalescing agent for latex paint formulations. TPM is a relatively high boiling organic solvent (bp 248 °C) with very low water solubility. When added to latex dispersions, it partitions essentially exclusively into the polymer phase. To incorporate TPM into latex particles, we added various amounts of TPM into dispersions containing three pairs of D- and A-labeled P(BA-MMA) latices. The mixtures were then stirred for 24 h to ensure that TPM had completely mixed with the latex particles. Latex films were cast, and ET experiments were carried out under the same conditions as those used for the HB-PBMA/P(BA-MMA) blend samples.

From analysis of the donor fluorescence decays, values of f_m were calculated. The three pairs of panels in Figure 1 present the time evolution of f_m at 23 °C on two different time scales: panels A and B for P(BA$_{55}$-MMA$_{44}$), panels C and D for P(BA$_{50}$-MMA$_{49}$), and panels E and F for P(BA$_{45}$-MMA$_{54}$). For comparison, f_m plots for the HB-PBMA/P(BA-MMA) blend samples are combined with corresponding plots for TPM/P(BA-MMA). The presence of both additives increased polymer diffusion rates, with similar overall trends. Figure 1B shows that in the early stages of film aging, the film containing 10 wt % TPM has higher f_m values than the film blended with 10 wt % HB-PBMA particles. The difference between the two f_m curves decreased as annealing time increased and eventually disappeared after the film was aged at 23 °C for 64 h. These results indicate that 10 wt % blended HB-PBMA particles and 5 wt % TPM have similar effects on polymer diffusion rates on the time scale of days. For the P(BA$_{50}$-MMA$_{49}$) and the P(BA$_{45}$-MMA$_{54}$) samples, the films containing TPM have significantly greater values of f_m than the films blended with the HB-PBMA particles (Figure 1C,E).

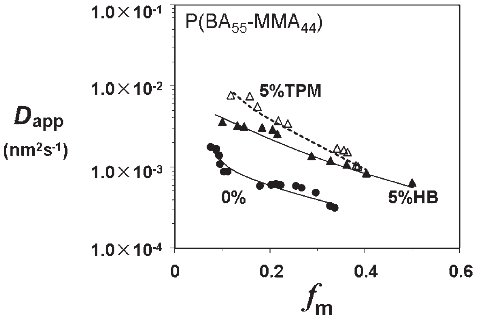

Figure 2. Comparison of the plots of the D_{app} versus f_m for P(BA$_{55}$-MMA$_{44}$) latex films containing (●) 0 wt % additives, (▲) 5 wt % blended HB-PBMA particles, and (△) 5 wt % TPM at 23 °C.

For a more quantitative comparison of the influence of these additives on polymer diffusion rates in P(BA$_{55}$-MMA$_{44}$) films, we fitted the f_m values to a Fickian diffusion model and calculated apparent diffusion coefficients, D_{app}. Latex films are commonly formed from polymers with a broad molecular weight distribution as well as a mixture of linear and branched polymer. The system has a distribution of diffusing species. Calculated values of D_{app} decline as the mixing process proceeds because, as time passes, more slowly diffusing species contribute to the increase in Φ_{ET}. Figure 2 compares plots of the D_{app} vs f_m for P(BA$_{55}$-MMA$_{44}$) films containing 5 wt % HB-PBMA particles, 5 wt % TPM, and without additives. Both HB-PBMA and TPM enhance the values of D_{app} by an order of magnitude over a broad range of f_m values. In the early stage (f_m < 0.25), the TPM-containing film had higher D_{app} values than the HB-PBMA blend film. But the difference of D_{app} between the two films appeared to decrease as f_m approached a value of 0.40.

Miniemulsion Polymerization Approach. The experiments employing latex blends described above demonstrated that HB-PBMA particles, as an additive, enhanced the interdiffusion rate of P(BA-MMA) latex films, having the largest effect on P(BA$_{55}$-MMA$_{44}$) films. In order to develop a quantitative model of this effect, we need to carry out a different kind of experiment in which we can reasonably assume that the additive polymer and base polymer are homogenously mixed in the latex particles prior to film formation. One way to promote mixing of the two polymers within the latex particles is via miniemulsion polymerization, in which the additive polymer is dissolved in droplets of the main monomers and persists throughout the polymerization reaction. Thus, we synthesized a series of P(BA$_{55}$-MMA$_{44}$)^D and P(BA$_{55}$-MMA$_{44}$)^A latex by miniemulsion polymerization in the presence of different amounts of HB-PBMA. Details are provided in the Experimental Section. In our notation, the superscript D or A indicates whether the P(BA-MMA) is labeled with a donor or acceptor dye, the subscript % indicates the wt % HB-PBMA added to the monomer for the polymerization reaction, and the subscript ME emphasizes that these latex particles were synthesized by miniemulsion polymerization.

The polymer obtained by miniemulsion polymerization is expected to have a different composition distribution than the polymer described above synthesized by semicontinuous emulsion polymerization under monomer-starved conditions. As a type of bulk polymerization, miniemulsion polymerization is sensitive to the reactivity ratio differences between MMA and BA, leading to the formation of MMA-rich and BA-rich polymer within each particle. While we

Table 4. Characteristics of the P(BA-MMA) Latex Polymers and Particles

	molecular weight[b] (g/mol)				particle size			
latex samples[a]	M_n	M_w	M_w/M_n	solids content (%)	d (nm)	poly[c]	T_g[d] (°C)	weight ratio by ^{1}H NMR BA/MMA
$P(BA\text{-}MMA)^D_{0\%ME}$	32 000	61 000	1.9	30	136	0.034		58/41
$P(BA\text{-}MMA)^A_{0\%ME}$	45 000	91 000	2.0	30	128	0.028	11	56/43
$P(BA\text{-}MMA)^D_{1\%ME}$	32 000	60 000	1.9	32	126	0.023		56/43
$P(BA\text{-}MMA)^A_{1\%ME}$	46 000	91 000	2.0	30	127	0.053	9	55/44
$P(BA\text{-}MMA)^D_{3\%ME}$	33 000	61 000	1.9	29	117	0.018	9	53/46
$P(BA\text{-}MMA)^A_{3\%ME}$	46 000	92 000	2.0	32	133	0.045		56/43
$P(BA\text{-}MMA)^D_{5\%ME}$	35 000	65 000	1.9	32	133	0.050	6	53/46
$P(BA\text{-}MMA)^A_{5\%ME}$	36 000	75 000	2.1	34	133	0.049		54/45
$P(BA\text{-}MMA)^D_{6\%ME}$	35 000	70 000	2.0	32	122	0.028	4	56/43
$P(BA\text{-}MMA)^A_{6\%ME}$	33 000	55 000	1.7	30	117	0.076		56/43

[a] All samples were synthesized by miniemulsion polymerization and contain 1 wt % methacrylic acid (MAA). [b] Absolute molecular weights were measured by GPC using a Viscotek TDA302 triple detector array. [c] Polydispersity (poly) is a measure of the width of the particle size distribution, taking values close to zero (0.000−0.020) for nearly monodisperse samples and small (0.020−0.080) for narrow size distributions. [d] The T_g values were determined by DSC.

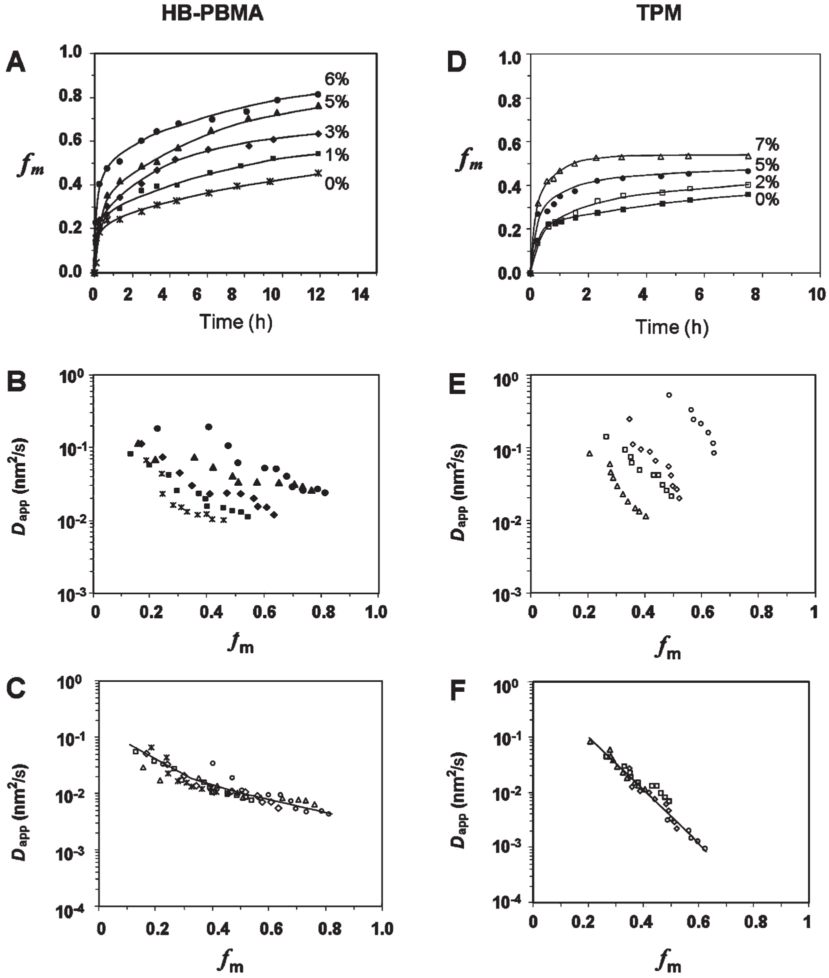

Figure 3. (A) Comparison of the plots of f_m vs annealing time for $P(BA_{55}\text{-}MMA_{44})_{ME}$ latex films at 45 °C containing (∗) 0, (■) 1, (◆) 3, (▲) 5, and (●) 6 wt % HB-PBMA. (B) Plot of D_{app} as a function of f_m for P(BA-MMA) at 45 °C with (∗) 0, (■) 1, (♦) 3, (▲) 5, and (●) 6 wt % HB-PBMA. (C) Master curve of D_{app} for HB-PBMA in P(BA-MMA) films (empty symbols represent the shifted data). (D) Comparison of the plots of f_m vs annealing time for P(BA-MMA) at 45 °C with (∗) 0, (■) 2, (▲) 5, and (●) 7 wt % TPM. (E) Plots of D_{app} vs f_m for P(BA-MMA) at 45 °C with (∗) 0, (■) 2, (▲) 5 and (●) 7 wt % TPM. (F) Master curve of D_{app} for TPM in P(BA-MMA) films (empty symbols represent the shifted data).

expect that there may be phase separation within the particles of the MMA-rich and BA-rich polymer, we found only a single clearly resolved T_g (11 °C, Table 4) by DSC that is likely due to BA-rich polymer. We were unable to resolve a second, higher T_g due to the MMA-rich component.

In order to examine whether the presence of HB-PBMA had any effect on the polymerization of BA and MMA in miniemulsion, we monitored the rate of the polymerization and the conversion rates of BA and MMA in the presence of HB-PBMA (see Supporting Information). These results showed that the conversion of the monomer was well described by ($r_{BA} = 0.39$) and MMA ($r_{MMA} = 2.03$), in accord with values reported in the literature for the same binary system.[33]

Synthesis of HB-PBMA-P(BA_{55}-MMA_{44})$_{ME}$ Latex Particles. In these miniemulsion polymerizations, various amounts of

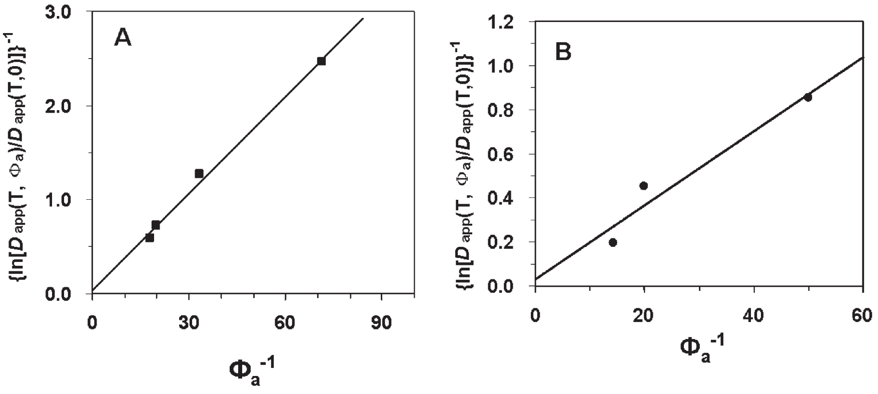

Figure 4. (A) Plot of $1/\ln[D_p(T,\Phi_a)/D_p(T,0)]$ vs $1/\Phi_a$ (eq 6) at 45 °C for the $P(BA_{55}\text{-}MMA_{44})_{ME}$ films containing different amounts of HB-PBMA. (B) Plot of $1/\ln[D_p(T,\Phi_a)/D_p(T,0)]$ vs $1/\Phi_a$ at 45 °C for the $P(BA_{55}\text{-}MMA_{44})_{0\%ME}$ films containing different amounts of TPM.

HB-PBMA (M_n = 40 000 g/mol, M_w/M_n = 1.9) were dissolved in the monomer mixture (BA:MMA:MAA = 55:44:1) plus hexadecane to suppress Ostwald ripening. After addition of an aqueous surfactant solution, the mixture was sonicated to produce droplets which were then the locus of subsequent polymerization. The characteristics of the latex particles obtained by miniemulsion polymerization are summarized in Table 4. They have narrow particle size distributions with mean diameters in the range of 117−136 nm. By GPC, the polymers produced have M_n values in the range of 32 000−46 000 g/mol with values of M_w/M_n less than 2. Values of T_g measured by DSC decreased to a small extent as the weight fraction of HB-PBMA increased. The overall composition of the $P(BA\text{-}MMA)_{ME}$ polymers was measured using ^1H NMR. All of the polymers have similar BA:MMA molar ratio, close to the BA:MMA reactant ratio.

Effect of HB-PBMA on Polymer Diffusion in $P(BA_{55}\text{-}MMA_{44})_{ME}$ Latex Films. Latex films for ET experiments were prepared from 1:1 mixtures of D- and A-labeled latex particles containing the same concentration of HB-PBMA. Two drops of the latex mixture were cast onto a small quartz plate and allowed to dry at 4 °C. The thickness of dried films was ca. 60 μm. All films were transparent and free of cracks. Fluorescence decay measurements were carried out immediately on the freshly formed latex films. Polymer diffusion in these samples was slow at 23 °C. This behavior is very different than that found for polymers of the same overall composition prepared by emulsion polymerization under monomer-starved conditions[18] (see above) and points to the presence of MMA-rich polymer in the latex that is very slow to diffuse at room temperature. Thus, these latex films were annealed at 45 °C, and fluorescence decays were recorded at various periods of time. From these data, values of Φ_{ET} and f_m were calculated. Values of f_m as a function of aging time are plotted in Figure 3A. The plot shows that these f_m values increase as the annealing time increases for all films. The film with the highest concentration of HB-PBMA has greater f_m values than those with a lower HB-PBMA concentration at the same annealing time. For example, it took 12 h at 45 °C to reach f_m = 0.45 for the P(BA-MMA) film without HB-PBMA, whereas for the film containing 6 wt % HB-PBMA, at 12 h, f_m > 0.8. To quantify the effect of HB-PBMA concentration on polymer diffusion rate, we fitted the f_m values to the spherical Fickian diffusion model and calculated apparent diffusion coefficients D_{app}. These D_{app} values for all films are plotted as a function of f_m in Figure 3B. The plot shows that at the same f_m value the film containing the higher fraction of HB-PBMA has a greater value of D_{app}, which indicates that the presence of HB-PBMA significantly enhanced the polymer diffusivity in the latex films.

We hypothesized that the HB-PBMA enhances the polymer diffusion rate by increasing the free volume in the film. In this sense, we treat it like a traditional plasticizer, whose influence on the polymer diffusion rate should follow the Fujita−Doolittle equation (eq 6). To begin this discussion, let us consider the influence of TPM on the diffusion rate of polymers in these latex films. The Fujita−Doolittle equation is derived from the generalized Doolittle equation under the assumption that free volume increases linearly with plasticizer concentration.

For each TPM concentration in Figure 3E, we recorded a shift factor by shifting the curve vertically to superimpose it on the reference curve, the data set for the sample without plasticizer. Each of these shift factors are then set equal to $\{\ln[D_p(T,\Phi_a)/D_p(T,0)]\}^{-1}$ for the corresponding value of Φ_a. Note that the shift factors involve shifting the entire curve for D_{app} vs f_m for the entire range of f_m values for which D_{app} could be determined. We have recently published a more thorough discussion of this treatment.[34] We equated D_p with D_{app} and assumed that we can equate weight fractions of TPM with volume fractions. As shown in Figure 3F, all of the data superimpose onto a single master curve.

In Figure 4B, we plot values of $\{\ln[D_{app}(T,\Phi_a)/D_{app}(T,0)]\}^{-1}$ as a function of $1/\Phi_a$. The linear plot indicates that polymer diffusion in the TPM-containing films followed the behavior predicted by the Fujita−Doolittle model. The intercept yielded a value of $f_p(T,0) = 0.030 \pm 0.002$, a reasonable value for the fractional free volume of P(BA-MMA) itself at 45 °C. From the slope we obtained a value of $\beta(T) = 0.055 \pm 0.004$. This parameter measures the difference in fractional free volume between the TPM additive and the P(BA-MMA) at 45 °C and is a measure of the effectiveness of the additive in promoting polymer diffusion in the films.

To gauge the effectiveness of HB-PBMA as a diffusion promoting additive, we carried out parallel experiments with HB-PBMA. As we described above, to incorporate HB-PBMA into the P(BA-MMA) latex, we had to dissolve different amounts of the polymer in the BA + MMA monomer mixture and carry out separate syntheses for each sample. This is the origin of the small differences in molecular weight and composition distribution in each sample as described in Table 4. Latex films were then cast, and ET experiments were carried out under the same conditions as those used for the TPM-containing films. Values of f_m were calculated from the fluorescence decays and are plotted as a function of annealing time in Figure 3A. We then fitted these f_m values to the

Fickian diffusion model and calculated D_{app} values. These values are plotted as a function of f_m in Figure 3B. The figure shows that D_{app} decreases as f_m increases, and the films with higher concentrations of HB-PBMA have greater values of D_{app}. We then calculated shift factors and used them to create the master curve of D_{app} values shown in Figure 3C.

Master curves presented in Figure 3C,F have different shapes. Under ideal conditions we expect these two master curves to have a common shape. However, one has to appreciate the sensitivity of polymer diffusion rate to various stimuli. In Figure 3, results reported in each column are obtained from the experiments performed in parallel. This means that films of the polymers with different amounts of additive were heated simultaneously in the oven. This ensures that these experiments are carried out at exactly the same temperature. The experiments with TPM as an additive were carried out weeks after the experiments with HB-PBMA as an additive. One can see for the sample without additive in the TPM series (Figure 3E) that D_{app} drops slightly faster that in the HB-PBMA series (Figure 3B). This is likely a consequence of a small difference in temperature history (in the oven and in the air during the FRET measurement) between the two experiments. This is reflected in the shape of the master curve as well; the master curve in Figure 3F shows smaller diffusion coefficient for the same f_m range as the master curve in Figure 3C. There is another difference between the two sets of experiments in that the shape of the master curve depends on the details of molecular weight distribution of the latex polymer. While our results show that the presence of HB-PBMA does not affect the kinetics of miniemulsion polymerization (Figure S2, Supporting Information), we have noted small differences in the molecular weight and composition of the miniemulsion polymer. While these differences are sufficiently small that we can construct a master curve, they can contribute to the details of its shape.

The plot of $\{\ln[D_p(T,\Phi_a)/D_p(T,0)]\}^{-1}$ for HB-PBMA against $1/\Phi_a$ (Figure 4A) yielded a straight line, with fitting values of $f_p(T,0) = 0.034 \pm 0.002$ and $\beta(T) = 0.030 \pm 0.002$. The values of these fitting parameters for HB-PBMA and TPM as additives are compared in Table 5. For this system, for a comparable volume fraction of additive, TPM is a stronger promoter of polymer diffusion than HB-PBMA.

Seeded Emulsion Polymerization Approach. *Seeded P(BA_{55}-MMA_{44}) Latex Particles.* We synthesized P(BA_{55}-MMA_{44}) latex samples using the HB-PBMA latex particles as seeds. Because HB-PBMA is miscible with the P(BA_{55}-MMA_{44}) polymer, we assume that this seeded polymerization does not form a core–shell structure. It is much more likely that the seed polymer becomes uniformly distributed in the P(BA_{55}-MMA_{44}) latex particles during the polymerization reaction at 80 °C. In our notation, the type of fluorescent dye is indicated by a superscript "D" or "A", and the subscript refers to the wt % of HB-PBMA seeds. For example, P(BA_{55}-MMA_{44})$^{A}{}_{5\%S}$ refers to the A-labeled P(BA_{55}-MMA_{44}) containing 5 wt % HB-PBMA seed particles. Table 6 shows that all samples have similar M_n values, broad but similar molecular weight distributions, and narrow particle size distributions. The M_n values are in the range of 22 000–25 000 g/mol, and the values of M_w/M_n are less than 5.0. The values of T_g decrease as the weight fractions of the HB-PBMA seeds increase. The seeded emulsion polymerization offers good control over particle size and size distribution. The average diameters for all samples were in the range of 240 nm. The solids contents were determined by gravimetric analysis, and all latex samples contain ca. 40 wt % solids.

Effect of HB-PBMA Seed Particles on Polymer Diffusion in P(BA_{55}-MMA_{44})$_S$ Latex Films. Latex films for ET experiments were prepared at 4 °C as described above from 1:1 mixtures of D- and A-labeled seeded P(BA_{55}-MMA_{44})$_S$ latex particles containing the same wt % of HB-PBMA seeds. After an initial fluorescence decay measurement on the newly formed film in a cold quartz tube, the films were aged at 23 °C. Donor fluorescence decays were monitored as a function of aging time. Values of f_m for all samples are plotted as a function of annealing time in Figure 5A. These values increase more rapidly with aging time in films formed from latex particles with higher concentrations of HB-PBMA seeds. For comparison, the f_m plots of the P(BA_{55}-MMA_{44})$_S$ films containing 5 and 10 wt % TPM are shown in Figure 5B. Note that these are the same samples used for the experiments in Figure 1A,B. The two figures indicate that the HB-PBMA seeds and TPM have similar effect on f_m. We show the early stages of these f_m plots in Figure 5C,D. It appears that at these early times TPM enhances the growth of f_m more than comparable amounts of HB-PBMA.

Calculated values D_{app} for these experiments are plotted as a function of f_m in Figure 6A for the films containing HB-PBMA seeds and for the self-seeded samples with and without TPM. The plots show that, except at very early times, the films containing 5 wt % HB-PBMA seeds have greater values of D_{app} than the films containing 5 wt % TPM. This effect is even more striking for the films containing 10 wt % HB-PBMA seeds and 10 wt % TPM. D_{app} increases by an order of magnitude. The values of D_{app} of the TPM-containing films decrease more quickly than those of the seeded P(BA_{55}-MMA_{44})$_S$ films.

Using the Fujita–Doolittle fitting procedure described above, we recorded the shift factors $\ln[D_p(T,\Phi_a)/D_p(T,0)]$ and plotted values of $\{\ln[D_p(T,\Phi_a)/D_p(T,0)]\}^{-1}$ as a function of $1/\Phi_a$ for TPM and the HB-PBMA seeds in Figure 6B. Here, we calculated the value of $f_p(T = 23\ °C,0)$ from the Williams–Landel–Ferry (WLF) constants determined previously for this polymer at 50 °C ($C_1 = 9.1$ and $C_2 = 112.6$)[18]

Table 5. Fitting Parameters for the Fujita–Doolittle Equation for Films from Latex Prepared from Latex Synthesized by Miniemulsion Polymerization

	P(BA_{55}-MMA_{44})$_{ME}$/HB-PBMA	P(BA_{55}-MMA_{44})$_{ME}$/TPM
$f_p(T,0)$[a]	0.034 ± 0.002	0.030 ± 0.002
$\beta(T)$[a]	0.034 ± 0.003	0.055 ± 0.004

[a] T = 45 °C.

Table 6. Characteristics of the P(BA_{55}-MMA_{44})$_S$ Latex Polymers and Particles

	molecular weight[a] (g/mol)			particle size[b]			
latex sample	M_n	M_w	M_w/M_n	d (nm)	poly[c]	T_g (°C)	solids content (%)
P(BA_{55}-MMA_{44})$^{D}{}_{5\%S}$	25 000	124 000	5.0	237	0.059	6.6	37.2
P(BA_{55}-MMA_{44})$^{A}{}_{5\%S}$	23 000	100 000	4.3	241	0.042	5.6	41.4
P(BA_{55}-MMA_{44})$^{D}{}_{10\%S}$	22 000	98 000	4.5	251	0.059	3.1	38.1
P(BA_{55}-MMA_{44})$^{A}{}_{10\%S}$	22 000	104 000	4.7	239	0.04	1.9	37.6

[a] Absolute molecular weights were measured by GPC using a Viscotek TDA302 triple detector array. [b] Particle size and size distribution were measured by a BI-90 particle sizer. [c] Polydispersity (poly) is a measure of the width of the particle size distribution, taking values close to zero (0.000–0.020) for nearly monodisperse samples and small (0.020–0.080) for narrow size distributions.

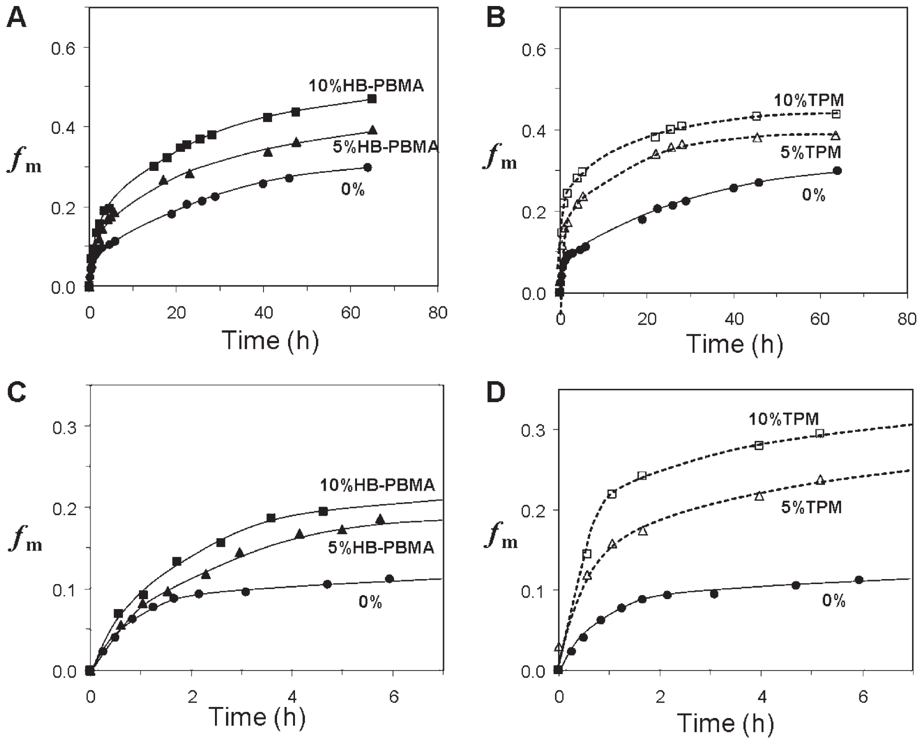

Figure 5. Comparison of the plots of f_m versus aging time for P(BA_{55}-MMA_{44})$_S$ at 23 °C with (●) 0 wt % additives, (▲) 5 wt % HB-PBMA seeds, (■) 10 wt % HB-PBMA seeds, (△) 5 wt % TPM, and (□) 10 wt % TPM. (C) and (D) show the early stages of the f_m plots in (A) and (B), respectively.

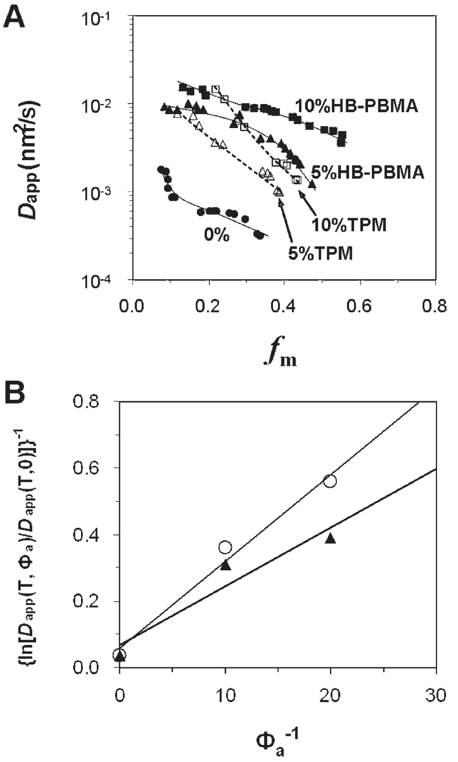

Figure 6. (A) Comparison of the plots of the D_{app} versus f_m for P(BA_{55}-MMA_{44})$_S$ latex films containing (●) 0 wt % additives, (▲) 5 wt % HB-PBMA seeds, (■) 10 wt % HB-PBMA seeds, (△) 5 wt % TPM, and (□) 10 wt % TPM at 23 °C. (B) Plot of $1/\ln[D_p(T,\Phi_a)/D_p(T,0)]$ vs $1/\Phi_a$ at 23 °C for the P(BA_{55}-MMA_{44})$_S$ films containing different amounts of (○) TPM and (▲) HB-PBMA seeds. The intercept for these plots (0.036) was determined from data in ref 15 as described in the text.

based upon G' and G'' measurements. The fractional free volume of the additive-free polymer given by $1/2.3C_1$ when the WLF parameters are shifted to the experimental temperature.[35] Therefore, at T = 23 °C, C_1 = 11.9 and C_2 = 85.6 and $f_p(T = 23\ °C,0)$ takes a value of 0.036 ± 0.002. The slopes of the straight lines gave a $\beta(T = 23\ °C)$ value of 0.050 ± 0.004 for TPM and a $\beta(T = 23\ °C)$ value of 0.070 ± 0.004 for the HB-PBMA seed particles. This result indicates that the HB-PBMA introduced as seed particles are more efficient than TPM for promoting polymer diffusion in P(BA_{55}-MMA_{44})$_S$ films.

Effect of HB-PBMA on Mechanical Properties of the P(BA-MMA) Latex Films. To examine how HB-PBMA incorporated into P(BA-MMA) polymer affects the mechanical properties of the latex films, we carried out tensile tests on the P(BA_{55}-MMA_{44}) latex samples prepared by the three approaches described above. In addition, we carried out parallel experiments in which the P(BA_{55}-MMA_{44}) copolymer contained various amounts of TPM. Latex film samples containing different concentrations of HB-PBMA or TPM were dried in PTFE dishes at room temperature to form films with a thickness of ca. 0.7 mm. After aging several days at room temperature, these films were then cut into strips (35.0 mm × 7.0 mm) for tensile tests. At least five specimens were measured for each sample. Data were plotted as tensile stress vs strain assuming elastomer behavior (Poisson ratio = 0.5). Values of Young modulus were obtained from the initial (3% strain) slope of these plots. Tensile strength is reported as the stress at break, and toughness values were calculated from the areas under these stress−strain curves. Representative tensile stress−strain curves of films prepared from the P(BA_{55}-MMA_{44})/HB-PBMA latex blends are presented in Figure 7, along with corresponding plots for samples of this polymer containing 5 and 10 wt % TPM. A complete tabulation of these data is presented in Table S4 of the Supporting Information.

Films containing TPM show significantly reduced values of Young modulus (Table 8). This result can also be seen in Table 7 for experiments with the miniemulsion polymer. This

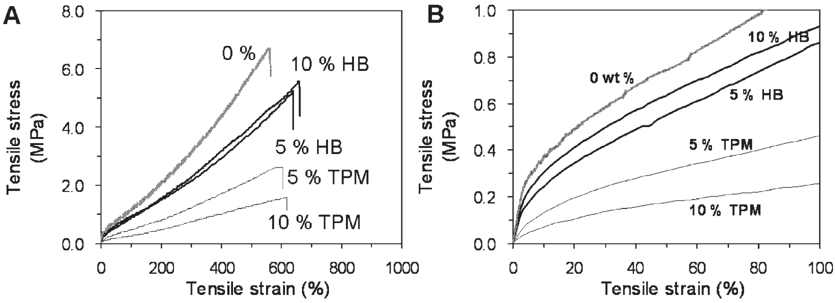

Figure 7. (A) Tensile stress−strain curves for $P(BA_{55}\text{-}MMA_{44})$ films from the $P(BA_{55}\text{-}MMA_{44})$/HB-PBMA latex blends. (B) Early stages of the stress−strain curves in (A).

Table 7. Tensile Testing Results for $P(BA_{55}\text{-}MMA_{44})_{ME}$ Films

samples	ultimate tensile stress (MPa)	Young modulus (MPa)	toughness (MJ/m^3)
$P(BA_{55}\text{-}MMA_{44})_{0\%ME}$	5.1 ± 0.9	0.29 ± 0.08	1156 ± 209
$P(BA_{55}\text{-}MMA_{44})_{1\%ME}$	3.0 ± 0.4	0.28 ± 0.02	555 ± 33
$P(BA_{55}\text{-}MMA_{44})_{3\%ME}$	3.5 ± 0.3	0.42 ± 0.03	981 ± 128
$P(BA_{55}\text{-}MMA_{44})_{5\%ME}$	2.8 ± 0.4	0.23 ± 0.04	687 ± 103
$P(BA_{55}\text{-}MMA_{44})_{0\%ME}$ + 5% TPM	1.6 ± 0.1	0.04 ± 0.00	519 ± 18

Table 8. Tensile Testing Results of $P(BA_{55}\text{-}MMA_{44})_S$ Films

samples	ultimate tensile stress (MPa)	Young modulus (MPa)	toughness (MJ/m^3)
$P(BA_{55}\text{-}MMA_{44})_{0\%S}$[a]	6.76 ± 0.49	0.07 ± 0.01	1790 ± 120
$P(BA_{55}\text{-}MMA_{44})_{5\%S}$	3.78 ± 0.34	0.06 ± 0.02	1490 ± 110
$P(BA_{55}\text{-}MMA_{44})_{10\%S}$	2.39 ± 0.18	0.05 ± 0.01	1400 ± 150
$P(BA_{55}\text{-}MMA_{44})_{5\%T}$[b]	2.50 ± 0.25	0.02 ± 0.00	750 ± 160
$P(BA_{55}\text{-}MMA_{44})_{10\%T}$[c]	1.39 ± 0.20	0.01 ± 0.00	420 ± 100

[a] A self-seeded P(BA-MMA) sample prepared by semicontinuous emulsion polymerization carried out under similar reaction conditions to the other samples in this table, but without the HB-PBMA seeds. [b] The sample *a* with 5 wt % postadded TPM. [c] The sample *a* with 10 wt % postadded TPM.

result is not a surprise. TPM is added to latex dispersions to lower the compression modulus of the polymer in order to facilitate the deformation of latex particles into space-filling polyhedral in response to the forces generated as these dispersions dry. Polymer films containing traditional plasticizers like TPM will also have reduced values of the extensional modulus. As TPM evaporates slowly into the atmosphere, the modulus will increase. As a point of comparison for HB-PBMA as a nonvolatile additive, we take the data for the TPM-containing films to reflect the behavior of latex films containing a nonvolatile low molar mass plasticizer. From this perspective, we note (Figure 7) that the presence of TPM also reduces the tensile strength of the film but has little influence on the strain at break. Thus, the films also suffer reduced toughness.

In contrast, the presence of HB-PBMA has a much smaller influence on the mechanical properties of the films. Values of Young modulus (Table S4, Supporting Information) are similar to that of the additive-free polymer. There is a small reduction in the stress at break and little change in the strain at break. Thus, comparable weight fractions of HB-PBMA as an additive to that of TPM have much less deleterious affects on the elongational modulus, tensile strength, and toughness of these latex films.

Corresponding representative tensile stress−strain curves for the $P(BA_{55}\text{-}MMA_{44})_{ME}$ samples are presented in Figure S3 of the Supporting Information. Calculated values of the tensile properties of these films are shown in Table 7. Here one can see that the tensile stress of the film containing 5 wt % TPM is less than one-third of that of the additive-free film. Note that all of the films containing HB-PBMA have similar ultimate tensile stress values. These are smaller than the value obtained for the additive-free films but twice that of the 5 wt % TPM film. The values of Young modulus of the HB-PBMA-containing films are similar to that of the film without any additives. However, for the film obtained by adding 5 wt % TPM, this modulus decreased by 1 order of magnitude. The toughness values for the HB-PBMA-containing films are smaller than that of the film without additives but greater than that of the film with TPM. There is scatter in the data that originates in sample-to-sample variation in the strain at break.

The results of the tensile tests on films formed from the seeded $P(BA_{55}\text{-}MMA_{44})_S$ samples are compared with those of the TPM-containing films in Table 8. Representative stress−strain curves are presented in Figure S4 of the Supporting Information. These data show the same patterns described above for other HB-PBMA- and TPM-containing $P(BA_{55}\text{-}MMA_{44})$ samples: similar values of Young modulus for the HB-PBMA-containing $P(BA_{55}\text{-}MMA_{44})_S$ films as for the films without any additives, decrease in this modulus for the films with TPM, a reduction in the tensile strength and toughness for the films containing HB-PBMA, but not nearly as severe as in the films containing TPM. One can conclude that the presence of HB-PBMA in $P(BA_{55}\text{-}MMA_{44})$ latex films leads to a much less significant loss of mechanical strength and stiffness than a comparable amount of a traditional small molecule plasticizer.

Summary

We incorporated the hyperbranched polymer HB-PBMA into P(BA-MMA) latex films using three different approaches. In the first approach, we prepared films from blends of HB-PBMA latex with P(BA-MMA) latex. Model experiments indicated that these two different polymers were miscible at the molecular level for a range of BA/MMA compositions. In the second approach, we dissolved HB-PBMA polymer in the monomer mixture used to prepare $P(BA_{55}\text{-}MMA_{44})$ latex particles by miniemulsion polymerization. In the third approach, we used HB-PBMA seed particles to synthesize $P(BA_{55}\text{-}MMA_{44})$ latex particles by semicontinuous emulsion polymerization. The latter two approaches are more likely to lead to latex films in which the HB-PBMA is uniformly dissolved into the matrix polymer at the very early stages of film formation.

Energy transfer measurements of polymer diffusion rates demonstrated that the presence of HB-PBMA strongly promoted the rate of polymer diffusion of the P(BA-MMA) matrix chains. This unexpected result was discovered accidentally and led to the experiments described here to quantify this effect. For the latter two approaches described above, where the HB-PBMA could reasonably be assumed to be uniformly distributed in the latex films, the diffusion data could be fitted to the Fujita−Doolittle equation (based upon a free volume model) that describes the influence of additives on the diffusion rate of polymers in the film. Values of the parameter $\beta(T)$ provide a measure of the diffusion-promoting effectiveness of an additive. For the copolymer synthesized by miniemulsion polymerization, this value (at 45 °C) was somewhat smaller for HB-PBMA (0.035) than for a traditional coalescing agent such as TPM (0.055), whereas for the copolymer synthesized by semicontinuous polymerization under monomer-starved conditions, this value (at 23 °C) was somewhat larger for HB-PBMA (0.07) than for TPM (0.04) While both additives are effective at promoting polymer diffusion, TPM also lowers the T_g of the polymer substantially and reduces the polymer modulus. The mechanical properties of the film are expected to recover when TPM evaporates (as VOC) to the atmosphere. Modern technology calls for a reduction of VOCs in latex films, and the use of nonvolatile small molecule plasticizers would lead to a similar loss of mechanical properties. HB-PBMA as a nonvolatile additive promotes the rate of polymer diffusion in these latex films, enhancing the rate at which the films build their useful mechanical properties. When we measured various mechanical properties of these films, we found little detectable change in Young modulus and only small reductions in tensile strength and toughness.

Because HB-PBMA does not significantly reduce the polymer modulus and has little effect on the polymer T_g, it is not a coalescing agent. It represents a new type of non-VOC additive that promotes polymer diffusion. It will be interesting to see whether this type of polymer can serve a useful function as an additive in environmentally compliant coatings formulations.

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Supporting Information Available: T_g of the P(BA-MMA) blends, a simulation of the kinetics of miniemulsion polymerization of BA/MMA, miscibility of HB-PBMA and P(BA-MMA), and tensile testing results. This material is available free of charge via the Internet at http://pubs.acs.org.

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