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Influence of a hydrogen-bonding co-monomer on polymer diffusion in poly(butyl acrylate-co-methyl methacrylate) latex films

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ABSTRACT

Small amounts of hydrogen-bonding comonomers such as N-(2-methacryloxyethyl)ethylene urea (MEEU) are often included in latex particle synthesis to promote adhesion of latex films to metals and old surfaces. Little is known about how these monomers affect the latex film formation process. Here we examine the influence of 1–7 wt.% MEEU on butyl acrylate-methyl methacrylate copolymer latex films using fluorescence resonance energy transfer (FRET) measurements, in conjunction with donor- and acceptor-labeled latex particles, to study the rates of polymer diffusion in these films. The presence of MEEU in the copolymer leads to small increases in the polymer glass transition temperature (Tg). It also tends to retard the rate of polymer diffusion. This effect, however, is very sensitive to the humidity of the surrounding atmosphere. It appears that moisture taken up in the film minimizes the influence of MEEU groups on the rate of polymer diffusion.

1. Introduction

There has been an increasing demand for the coating industry to reduce the amount of volatile organic compounds (VOCs) in its products [1–3]. These VOCs lead to atmospheric pollution and sick house syndrome. One approach to lower VOCs is to replace solvent-based paints with water-based paints, particularly, latex paints, which use emulsion polymerized resins as the binder. Further refinements are necessary, because most latex paints still contain VOCs consisting of solvents that assist film formation at low temperature by plasticizing the polymer in the latex particles [4]. Of course, one can soften the latex particles by changing the composition to lower the glass transition temperature (Tg). This approach brings about new problems in the dry binder film, such as surface tack and weak abrasion resistance. One needs strategies for synthesizing latexes which have good film formability as the latex dries, but yields films with sufficiently high T_g to provide good mechanical properties. These are seemingly contradictory properties, and achieving this goal remains an outstanding challenge [4,5].

Emulsion copolymers of butyl acrylate (BA) and methyl methacrylate (MMA) are one of the most common binder compositions for commercial latex paints [5]. Many research groups have studied BA-MMA copolymer latex to understand how the synthesis protocol and composition affect latex morphology and film forming properties [6–8]. We collaborated with scientists at Rohm and Haas to explore how blends of BA-MMA latex with oligomeric BA-MMA copolymer latex might promote film formation and polymer diffusion in the blend film [9].

In this study, we examine the idea that including a strong hydrogen bonding (H-bond) comonomer, N-(2-Methacryloxyethyl)ethylene urea (MEEU) in P(BA-MMA) latex compositions might enhance film formability. MEEU has a rigid H-bonding ureido ring consisting of one carbonyl oxygen which acts as a proton acceptor and one NH proton which acts as proton donor. Its structure is shown in Fig. 1. This type of hydrogen-bonding comonomer has been widely used in the coatings industry to promote adhesion, particularly to metal or old substrates and to a lesser extent, to improve the rheological properties of coatings [10–12]. We report the synthesis and properties of dye-labeled MEEU-containing P(BA-MMA) latex particles, and the study by fluorescence resonance energy transfer (FRET) of the rates at which these polymers diffuse in latex films. While one might imagine that the strong hydrogen bonding interactions of MEEU retard polymer diffusion rates in these films, the magnitude of this effect is very sensitive to the presence of moisture in the films.

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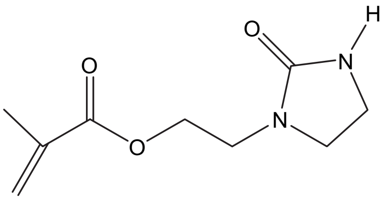

Fig. 1. Molecular structure of MEEU.

2. Experimental

2.1. Materials

Potassium persulfate (KPS), sodium bicarbonate ($NaHCO_3$), n-dodecyl mercaptan (C_{12}–SH), sodium dodecyl sulfate (SDS), and N-(2-Methacryloxy ethyl) ethylene urea (MEEU) were used as received from Aldrich. Methyl-β-cyclodextrin (MCD) was a gift from Rohm and Haas Co. and was used as received. Methyl methacrylate (MMA, Aldrich), and butyl acrylate (BA, Aldrich) were distilled at reduced pressure, and the purified monomers were stored at 0 °C until used. Water was purified by a Milli-Q ion-exchange filtration system. Phenanthryl methyl methacrylate (PheMMA) was used as received from Toronto Research Chemicals Inc. 4′-Dimethylamino-2-methacryloxy-5-methyl benzophenone (NBenMA) is the same sample whose synthesis was described previously [13,14].

2.2. Latex preparation

All latex dispersions were prepared by seeded semicontinuous emulsion polymerization reactions. In the first stage, the non-labeled P(BA_{55}-MMA_{45}) (BA:MMA weight ratio 55:45), seed was prepared batch wise following the recipe shown in Table 1. Water, the surfactant (SDS), and the phase transport catalyst (MCD) were added in a 250 mL three-neck glass flask equipped with a mechanical stirrer, nitrogen inlet, and 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. During the heating process, the monomer mixture and the chain transfer agent (C_{12}–SH) were added to the reactor. After the reactor temperature stabilized at 80 °C, the initiator (KPS) and the pH buffer ($NaHCO_3$) in water solution were rapidly added and kept overnight at 80 °C in order to decompose the unreacted initiator. The reaction was then cooled to room temperature. The seed latex dispersion produced had ca. 10 wt.% solids content, and the particles were 46 nm in diameter with a narrow size distribution.

The final latexes were prepared by semicontinuous emulsion polymerization using the unlabeled P(BA_{55}-MMA_{45}) seed particles. A typical recipe for the synthesis of unlabeled P(BA-MMA-MEEU) latex containing 5 wt.% MEEU is shown in Table 2. The phase transport catalyst (MCD), the seed solution, and water were added to a 50 mL three-neck glass flask equipped with a mechanical stirrer, nitrogen inlet, and condenser as in the synthesis of the seed latex. The system was thoroughly purged with nitrogen while the reaction mixture was heated to 80 °C. After the reactor temperature stabilized at 80 °C, the KPS aqueous solution was rapidly added to the reactor and the monomer pre-emulsion was constantly fed into the reaction solution over 3 h. The monomer feed rate by a Fluid Metering QG50 pump. After the addition was completed, the system was maintained at 80 °C for 1 h. Then the reaction was cooled to room temperature. A latex dispersion with ca. 30 wt.% solids content was produced. The particle size was approximately 120 nm in diameter with a narrow size distribution.

Table 1
Recipe for the synthesis of P(BA_{55}-MMA_{45}) seed.

Ingredients	Weight (g)
Methyl-β-cyclodextrin	0.26
SDS	1.0
Water	170.0
Monomer mixture (BA/MMA = 55/45 w/w)[a]	20.0
C_{12}–SH	0.2
KPS	0.24
$NaHCO_3$	0.24
Water	10.0

[a] by weight.

Table 2
Typical Recipe for the synthesis of non-labeled 5 wt.% MEEU-containing P(BA-MMA-MEEU latex).

Ingredients	Weight (g)
<Initial charge>	
Seed	5.5
Methyl-β-cyclodextrin	0.130
Water	12.95
<Initiator solution>	
KPS	0.060
Water	2.5
<Monomer pre-emulsion>	
Water	5.0
SDS	0.060
Structural comonomer (BA/MMA = 55/45)[a]	9.50
H-Bond containing monomer (MEEU)	0.50
C_{12}–SH	0.10

[a] by weight.

Fluorescent dye-labeled latex samples were synthesized in a similar fashion. For the donor-labeled particles, 1 mol % PheMMA (based on total monomer content) was added into the monomer pre-emulsion. For the acceptor-labeled particles, 0.3 mol % NBenMA (based on total monomer content) was added into the monomer pre-emulsion. Different MEEU-containing copolymers were synthesized by changing the ratio of the structural comonomer (BA/MMA = 55/45, w/w) to the H-bonding monomer (MEEU) using the recipe in Table 2.

2.3. Characterization of latex particles

Particle diameter and size distribution were measured by dynamic light scattering at a fixed scattering angle of 90° at 25 °C with a Brookhaven Instruments model BI-90 particle sizer equipped with a 10 mW He–Ne laser. The solids content of each latex dispersion was determined by gravimetry. Polymer molecular weight and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using a Viscotek liquid chromatograph equipped with a Viscotek model VE3210 UV/VIS detector and Viscotek VE3580 RI double detector. Waters Styragel HR4E columns were used with tetrahydrofuran (THF) as the elution solvent at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration. The glass transition temperature (Tg) of the copolymers were measured using a TA instrument model DSC 2920 with a refrigerated cooling system over a temperature range of −50 to 100 °C at a heating rate of 10 °C/min. Each sample was taken through two runs. T_g values were calculated from the second run.

Gel content was measured by the centrifugation method developed in our laboratory [15]. A latex sample (1.0 g) was dried to a constant weight, W_0. The dried polymer was subsequently immersed in 10 mL of tetrahydrofuran (THF). The mixture was agitated gently at room temperature for 24 h. The resulting solution was then centrifuged at 20,000 rpm for 30 min, and the top transparent layer was poured off. When gel was present, a precipitate remained. The precipitate was washed three more times with excess THF to remove residual sols from the gel. The remaining sample (the gel fraction) was dried and weighed (W_1). The gel content (%) was calculated from the equation

$$\text{Gel content}\,(\%) = (W_1/W_0) \times 100 \tag{1}$$

2.4. Film formation and fluorescence decay measurements

Latex films for fluorescence energy transfer (FRET) experiments were prepared from a 1:9 particle mixture of the donor-and acceptor-labeled dispersions (D/A). Aliquots of the mixed latex dispersions (about 30 wt.% solids content) were spread on small quartz plates (20 × 8 mm). The films were allowed to dry uncovered in a cold room at 12 °C to minimize polymer interdiffusion during the drying process. The films appeared dry by visual inspections after ca. 15 min. The films prepared in this way have a thickness of ca. 35 μm. All films were transparent. Solvent-cast films were prepared from the same polymer mixtures. Approximately 500 mg of the D/A latex dispersion was freeze-dried over 12 h, and then a sample of the dried polymer was dissolved in a small amount of THF. The solution was then cast onto a small quartz plate and allowed to dry at 25 °C and relative humidity (RH) = 45–50% for 24 h [16].

The films on quartz plates were placed directly in an open Petri dish in a closed box with dried silica gel (target RH 0%) or a saturated aqueous salt solution to control the sample relative humidity. We used saturated solutions of magnesium nitrate (target RH 54%), and potassium sulfate (target RH 98%). Most experiments involved sample aging at 25 °C. Some experiments were carried out at higher temperatures ranging from 25.6 °C to 29.5 °C. For these experiments, a sealed box containing the films on the plates was put into an oven preheated to the sample annealing temperature, and the films were annealed for various periods of time. The actual RH and temperature in a closed box were checked by an EAI TMH-250 small portable digital themo-hygrometer. Fluorescence decay profiles of the films at a constant temperature were measured by the time-correlated single photon counting technique using a nanosecond time-correlated single photon counting system from IBH with a NanoLED ($\lambda_{\text{ex}} = 296$ nm) as the excitation source. Each film was placed in a quartz tube for the measurement. The emission was collected from 335 to 366 nm. A 335 nm cutoff filter was mounted in front of the emission monochromator (350 ± 16 nm) 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 measurement time to get a complete fluorescence decay profile of each film was approximately 3 min. After each measurement, the samples were returned to the annealing oven. The donor fluorescence decay data were fitted by nonlinear least-squares using the delta function convolution method [17]. The instrumental response function was obtained using a degassed p-terphenyl solution (0.96 ns lifetime) as a mimic standard [18].

3. Data analysis in FRET experiments

In the absence of benzophenone as an energy transfer acceptor, for all samples containing 1 mol % donor, the phenanthrene decay profiles were exponential, with lifetime $\tau_D = 43.3$ ns. The goodness-of-fit parameter (χ^2) for these single exponential fits ranged from 0.93 to 1.27. In the presence of an energy transfer acceptor, the fluorescence decay curves became non-exponential. The shape of the curve depends on the details of the donor-acceptor (D/A) pair distribution. In a system with uniformly distributed donors and acceptors in three dimensions in the absence of diffusion, the donor fluorescence intensity decay $I_D(t)$ following instantaneous excitation is described by the Förster equation [19]:

$$I_D(t) = A\exp\left[-\frac{t}{\tau_D} - P\left(\frac{t}{\tau_D}\right)^{1/2}\right] \tag{2}$$

where

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

here, $[Q]$ is the concentration of acceptor (quencher), and P is proportional to $[Q]$. R_0 is the critical Förster radius for energy transfer. N_A is Avogadro's number. The orientation factor $<\kappa^2>$ describes the average orientation of dipoles of donor and acceptor molecules. $<\kappa^2>$ has a value of 2/3 in fluid solution, where rotation is rapid. It takes a value of $<\kappa^2> = 0.476$ for a random distribution of immobile chromophores in three dimensions, a situation typical of dyes in polymer matrices [20].

To obtain an accurate area for each decay profile, we fitted each decay curve to the empirical equation (4) and then evaluated the integral analytically from the magnitude of the fitting parameters.

$$I_D(t) = A_1\exp\left[-\frac{t}{\tau_D} - P\left(\frac{t}{\tau_D}\right)^{1/2}\right] + A_2\exp\left(-\frac{t}{\tau_D}\right) \tag{4}$$

from the calculated area data we can calculate the quantum efficiency of energy transfer $\Phi_{\text{ET}}(t_n)$ for samples aged or annealed for a time t_n

$$\Phi_{\text{ET}}(t_n) = 1 - \frac{\int_0^\infty I_{\text{DA}}(t)\text{d}t}{\int_0^\infty I_{\text{D}}(t)\text{d}t} = 1 - \frac{\text{area}(t_n)}{\tau_{\text{D}}} \tag{5}$$

where $I_{\text{DA}}(t)$ and $I_{\text{D}}(t)$ refer to the normalized decay functions of donor fluorescence intensity in the D/A film and in the donor-only film, respectively. Because the unquenched donor decay profile here is exponential, its integral is equal the unquenched donor lifetime τ_{D}.

The "extent of mixing" parameter f_{m} is a useful measure of the extent of polymer interdiffusion

$$f_m(t_n) = \frac{\Phi_{\text{ET}}(t_n) - \Phi_{\text{ET}}(0)}{\Phi_{\text{ET}}(\infty) - \Phi_{\text{ET}}(0)} = \frac{\text{area}(0) - \text{area}(t_n)}{\text{area}(0) - \text{area}(\infty)} \tag{6}$$

this parameter depicts the fractional growth of energy transfer in the D/A films. $\Phi_{\text{ET}}(0)$ refers to the extent of energy transfer across the particle boundaries in the newly formed film, whereas $\Phi_{\text{ET}}(\infty)$ represents the energy transfer efficiency in a fully mixed D/A film, in which the donors and acceptors are randomly distributed. $\Phi_{\text{ET}}(t_n)$ is the degree of energy transfer in a film annealed for time t_n.

4. Results and discussion

4.1. Preparation and characterization of the latex samples

In a recent publication, we reported studies of film formation and polymer diffusion rates in a series of P(BA-MMA) latex of different compositions [7]. In those experiments, all of the latex polymers contained 1 wt.% methacrylic acid (MAA). MAA is commonly added to latex synthesis recipes to enhance the colloidal stability of the latex particles. In the experiments reported here, we wished to focus on the influence of MEEU on the latex properties and the polymer properties. Thus we did not include any MAA in the latex synthesis reactions. To study the influence of copolymer composition on polymer diffusion rates, one has to synthesize a series of latex samples in which the particle size and size distribution are similar in all samples, and in which the latex polymers are all of similar molecular weight. These latex samples should also have a negligible amount of oligomeric and/or residual unreacted monomeric materials. To meet this goal, we used seeded emulsion polymerization in which all dye-labeled latex were synthesized from a common unlabeled seed latex. All but one of the latex samples reported here have similar particle sizes, with mean diameters of 112–123 nm, and narrow particle size distributions (Table 3). The latex sample synthesized to contain 10 wt.% MEEU did not meet these criteria. It exhibited poor colloidal stability, and the formation of aggregates is likely responsible for the larger particle size and polydispersity. Although the seed polymer is unlabeled and has a larger molecular weight than the final latex copolymer, the effects of the seed particles on the film formation process can be ignored because the amount of seed polymer in the final latex samples is only 5–6 wt.% [13,21]

In our initial experiments, we attempted to synthesize MEEU-containing latex at high solids (50 wt.% solids). These latex samples exhibited poor colloidal stability. As a consequence, the samples reported here prepared at a lower solids content (30 wt.% solids). Emulsion polymerization of BA-containing monomer mixtures often leads to branching and to gel formation, as a consequence of chain transfer to polymer. Sayer et al. reported that a starved process gave more gel and lower sol molecular weights than a semi-starved process [6]. To minimize these problems, we added n-dodecyl mercaptan (C_{12}–SH) as a chain transfer agent in the presence of methyl-β-cyclodextrin as a phase-transfer catalyst to assist its transport through the aqueous medium [22,23]. In our previous publication, we reported that P(BA-MMA-MAA) latexes at 50% solid content and M_n of 30,000–50,000, M_w/M_n of 2.0–3.7 could be obtained using only 0.25 wt.% of C_{12}–SH with respect to the monomer content in the second stage under phase-transfer conditions [7]. Asua's group has reported that semi continuous emulsion polymerization of BA/MMA in the presence of 2 wt.% of C_{12}–SH produced a polymer with MWD of 2.9 [8]. In this study, we found that it was necessary to increase the C_{12}–SH level to 1.0 wt.% with respect to the second stage monomer. These conditions produced latexes with M_n of 19,000–25,000 and M_w/M_n of 2.7–3.4. Fig. 2 depicts the relationship between M_n and MWD at various C_{12}–SH concentrations in the synthesis of NBen-labeled latex with 1% MEEU. The plot of $1/M_n$ against [C_{12}–SH] is linear, and the values of M_w/M_n decreased sharply with increasing C_{12}–SH content. It is curious that these synthesis require higher levels of C_{12}–SH than those we reported previously for latex synthesized in the presence of 1 wt.% MAA. Nevertheless, our result here indicates that C_{12}–SH provides good control over polymer molar mass in the presence of the cyclodextrin. We obtained the narrowest MWD in the presence of 1.0 wt.% C_{12}–SH content. Thus, all the latex samples used in the diffusion experiments were prepared in the presence of 1.0 wt.% C_{12}–SH. There was no detectable gel content in these samples.

Table 3
Characteristics of the latex polymers and particles.

Sample name[a]	10^{-4} M_n	M_w/M_n	P/S, nm (PSD)[b]	Solids, %
NBen-MEEU00	1.9	2.7	115 (0.047)	29.2
NBen-MEEU01	2.3	3.2	115 (0.055)	29.6
NBen-MEEU03	2.3	3.4	113 (0.020)	29.4
NBen-MEEU05	2.3	3.4	112 (0.033)	29.0
NBen-MEEU07	2.0	3.1	112 (0.042)	29.0
NBen-MEEU10	2.2	3.0	207 (0.170)[c]	29.1
Phe-MEEU00	2.1	2.6	118 (0.053)	29.6
Phe-MEEU01	2.3	2.9	123 (0.027)	30.0
Phe-MEEU03	2.4	3.3	116 (0.030)	28.9
Phe-MEEU05	2.5	3.1	116 (0.031)	29.7
Phe-MEEU07	2.5	3.1	115 (0.031)	29.0
Phe-MEEU10	2.0	3.0	211 (0.069)[c]	28.9

[a] The abbreviations NBen and Phe in the sample names refer to the latex particles labeled NBen and Phe chromophores, respectively. The numbers in the sample name indicate the wt.% of N-(2-methacryloxy ethyl) ethylene urea in the monomer feed for synthesis of the latex samples. We show that the final latex composition is consistent with this feed ratio. For example, NBen-MEEU00 is a NBen (acceptor) labeled BA/MMA = 55/45 copolymer containing no MEEU.

[b] P/S and PSD refer to particle diameter and the particle size distribution, respectively. P/S and PSD were measured just before preparing latex films for the fluorescent film decay measurements.

[c] The initial particle size of NBen-MEEU10, measured immediately after synthesis, was 171 nm and that of Phe-MEEU10 was 172 nm.

Fig. 3 compares the refractive index (RI) signal and the UV signal from a GPC measurement of the molecular weight distribution of NBen-labeled MEEU10. The shapes of the two curves are very similar, indicating that the NBen dye (UV signal) is distributed homogeneously in the latex polymer molecule synthesized under monomer-starved conditions [7,14,24]. The absence of peaks at long retention volumes confirms that this sample contains negligible amounts of oligomeric and monomeric units.

Fig. 4 compares the ^{1}H NMR spectra of P(BA-MMA) with that of the NBen-MEEU10 polymer. In these copolymers, the $-OCH_2$- peak of BA at 3.8–4.4 ppm and the $-OCH_3$ peak from MMA units at 3.5–3.7 ppm are clearly resolved [7]. The presence of MEEU groups in the NBen-MEEU10 sample contributes additional signals at 3.5 and 6.7 ppm [12]. While it is difficult to integrate this peak quantitatively, its magnitude is consistent with full incorporation into the polymer. Based upon this result, we assume that the MEEU content of the latex polymer is equal to that of the monomer feed.

We carried out differential scanning calorimetric (DSC) experiments to determine the T_g of all freeze-dried latex samples. Representative DSC thermograms of NBen-MEEU00 and NBen-MEEU10 are shown in Fig. S1 (Supplementary Data). For dry films, the presence of MEEU in the polymer led to a small but regular increase in Tg, as shown in Fig. 5, with a 4 °C increase in T_g for the sample containing 8 wt.% MEEU. One can explain this result in terms of the strong H-bonding interactions between the MEEU units and between MEEU and the ester groups of the P(BA-MMA) polymer [12].

4.2. *Energy transfer studies of polymer diffusion*

Films for FRET experiments were prepared from a 1:9 mixture Phe- and NBen-labeled latex particles. Aliquots of the latex mixtures were cast onto a small quartz plates and allowed to dry

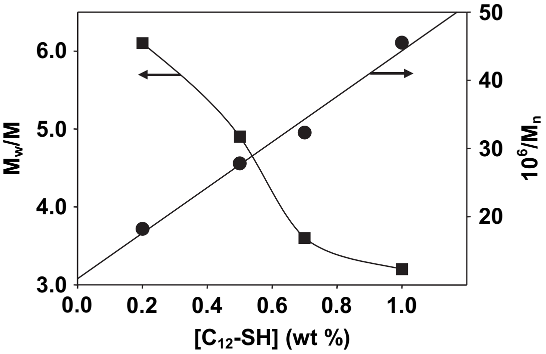

Fig. 2. Plots of molecular weight distribution (M_w/M_n) and $1/M_n$ against concentration of C_{12}–SH wt.%, with respect to the second stage monomer content of NBen-MEEU01 latex sample.

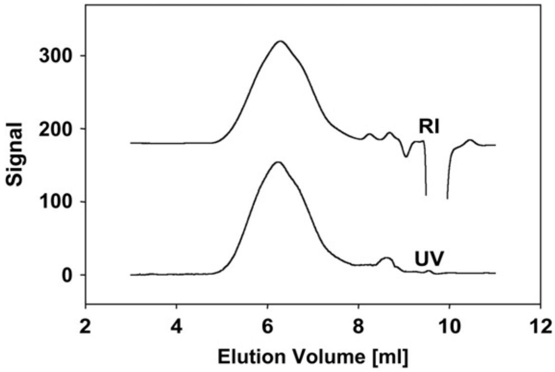

Fig. 3. Apparent molecular weight distribution from a GPC measurement on a sample of NBen-labeled MEEU10 showing both the refractive index (RI) signal and the UV signal measured at 350 nm.

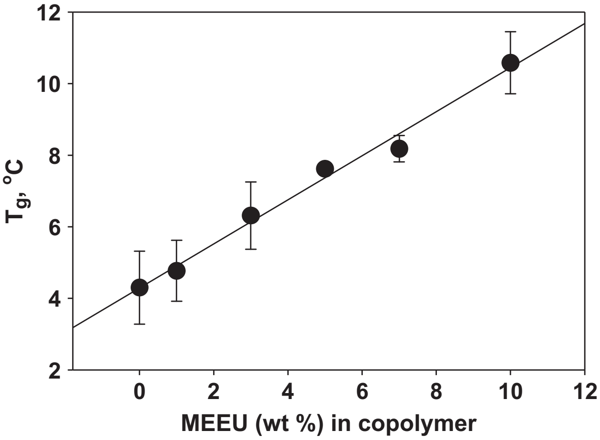

Fig. 5. Relationship between MEEU content in the copolymer latexes and T_g measured by DSC.

over about 15 min in a cold room at 12 °C to yield films ca. 35 μm thick. All of the films were transparent and free of cracks. Freshly formed latex films were transferred to the sample chamber of the fluorescence decay instrument in a cold quartz tube, and donor fluorescence decays were measured immediately. Individual decay measurements took less than 3 min. The films were then annealed in a preheated oven for various periods of time at 25 °C. The fluorescence decays were monitored as a function of annealing time at a series of temperatures.

Fig. 6 shows representative series of donor fluorescent decays for a Phe-MEEU05 latex film [curve (1)], D/A mixed MEEU05 latex films aged for various periods of time at 25 °C and RH = 45–50% [curves (2–4)], and a solvent-cast film of D/A mixed MEEU05 latex [curve (5)]. The decay curve (1) in Fig. 5 is exponential with a lifetime of 43.2 ns. The magnitude of the unquenched donor lifetime is independent of the MEEU content of the polymer, as shown in Table S1 in the supplementary data. Curve (2) in Fig. 6 is the decay profile of a newly formed film from a 1:9 D/A mixture. As we explain below, the curvature of this plot indicates that some interparticle polymer diffusion took place as the film dried. Curves (3) and (4) are the decay profiles of the film after 1.5 h and 100 h annealing time, respectively at 25 °C and RH = 45–50%, and curve (5) represents the donor decay profile for a film cast from a THF solution. It serves as a model for a film in which complete diffusive mixing of the donor- and acceptor-labeled polymer has occurred.

Values of the energy transfer efficiency Φ_{ET} for each sample were calculated via Eq. (5) by comparing the area the donor decay profile for that sample to that for the donor-only film. A plot of Φ_{ET} vs. annealing time at 25 °C and RH = 45–50% is presented in Fig. S2 in the supplementary data. To interpret our FRET data, we need a value for $\Phi_{ET}(0)$ to describe the amount of ET that would take place in a newly formed film in the absence of any polymer diffusion. We use a theoretical approach as described in Ref. [25] for a system of cells formed from particles of the size studied here, in which the donor and acceptor chromophores are separated by a sharp boundary. In this way we obtain a value of $\Phi_{ET}(0) = 0.04–0.05$ for all samples. From the solvent-cast films, we obtain values of $\Phi_{ET}(\infty) = 0.65$ to 0.67. These values are consistent with a theoretical value of $\Phi_{ET}(\infty) = 0.67$ expected for a random distribution of acceptors and a Förster radius $R_o = 2.5$ nm. In Table S1 (Supplementary data), we present values of τ_D, $\Phi_{ET}(0)$, and $\Phi_{ET}(\infty)$ for the various P(BA-MMA-MEEU) copolymer latex films.

For all of the polymers we examine here, we find that in newly formed films dried at 12 °C values of Φ_{ET} were in the range of 0.14–0.19. These large values indicate that some polymer diffusion occurred as the films dried. To quantify this process, we calculate

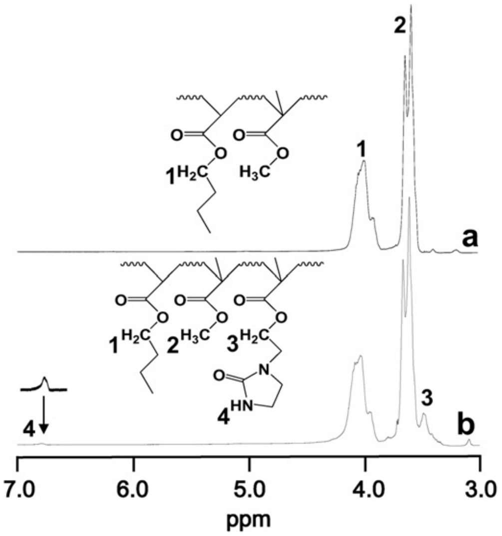

Fig. 4. ^{1}H NMR spectra of (a) NBen-MEEU00, and (b) NBen-MEEU10 in $CDCl_3$. The intensity of peak 4 shown in the inset of (b) was magnified 10 times.

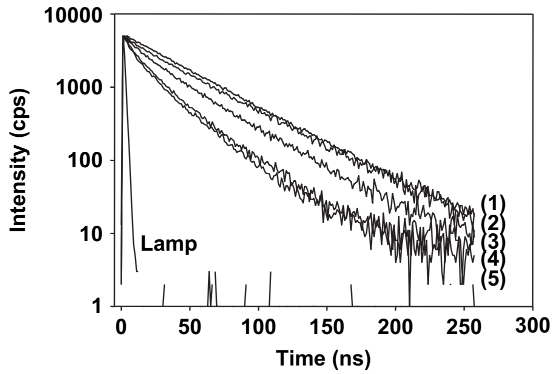

Fig. 6. Phenanthrene (donor) fluorescence decay curves [$I_D(t)$] measured at room temperature for Phe-MEEU05 latex films: (1) Phe-labeled latex only, (2) a newly formed film dried at 12 °C, consisting of a 1:9 ratio of Phe-MEEU05 and NBen-MEEU05, (3) the same film as in (2) aged for 1.5 h at 25 °C and RH = 45–50%, (4) the same film as in (2) aged for 100 h at the same condition, (5) a solvent-cast film from 1:9 mixture of the two freeze-dried polymers dissolved in THF and then annealed at the same condition for 24 h.

values of f_m (Eq. (6)) using the values of $\Phi_{ET}(0) = 0.05$ and $\Phi_{ET}(\infty) = 0.67$. In this way, we obtain for MEEU05 a value of $f_m(0) = 0.19$ as a measure of the extent of diffusion that occurred as the film dried. Values of f_m as a function of annealing time for each of the samples examined are plotted in Fig. 7 for experiments carried out at 25 °C and RH = 45–50%.

To compare polymer diffusion rates for the films of different composition in a meaningful way, we calculate apparent diffusion coefficients, D_{app} by fitting the f_m data to a spherical Fickian diffusion model as we have described previously [14,21,26]. D_{app} values calculated in this way for each film are plotted as a function of f_m in Fig. 8. These D_{app} values decrease with increasing f_m as the latex copolymers with lower diffusivity make their contribution to the ET signal. In the data plotted in Fig. 8, the films with higher concentrations of MEEU tend to have lower values of D_{app}. While the differences are not large, we will find it useful to shift these curves along the y-axis to create a master curve. We have employed this type of master curve analysis to investigate the dependence of D_{app} on temperature [7], and humidity [16,27]. We selected the data for MEEU00 as the reference curve and then multiplied the D_{app} values by an MEEU-content dependent shift factor (a_{MEEU}). Values of a_{MEEU} were adjusted until the data overlapped with the MEEU00 data. These shift values are given in the caption to Fig. 8.

4.3. *Experiments at constant T–T$_g$ and at variable humidity conditions*

In this section, we consider the influence of temperature and of relative humidity on the rate of polymer diffusion. As we will see below, both elevated temperature and moisture absorbed from the air enhance the rate of polymer diffusion in our films. These effects are due to the influence of temperature and water as a plasticizer [16] on the effective friction coefficient for polymer diffusion. The relationship between the diffusion coefficient D_R and temperature T for unentangled polymer dynamics can be described by the Rouse model, which is obtained from the Einstein relation [28].

$$D_R = \frac{kT}{\zeta_R} \qquad (7)$$

here, k is the Boltzmann constant and ζ_R is the friction coefficient of the Rouse chain.

In Fig. 5, we showed that latex polymers with higher MEEU content have higher values of T_g. In Fig. 7 we show that these polymers exhibit lower diffusivities when compared at the same temperature to latex copolymers containing smaller amounts of MEEU. For polymers of similar composition, ζ_R is proportional to $T-T_g$. To compare the influence of MEEU on polymer diffusion rates, we repeated the FRET measurements of polymer diffusion different temperatures for each sample, with $T-T_g = 21.7$ °C. The film samples were aged in a sealed box containing a saturated solution of magnesium nitrate to control the relative humidity at 45–50%. The overall variation in temperature was small enough (from 25.0 °C to 29.5 °C) that we ignore the influence of this temperature change on RH. We checked this assumption by measuring the humidity in the box using a portable thermo hygrometer, The resulting D_{app} data and the master curve obtained from these data are plotted in Fig. 9. While the effect of MEEU on D_{app} is small, all of the MEEU-containing copolymer latex films show smaller D_{app} values than MEEU00.

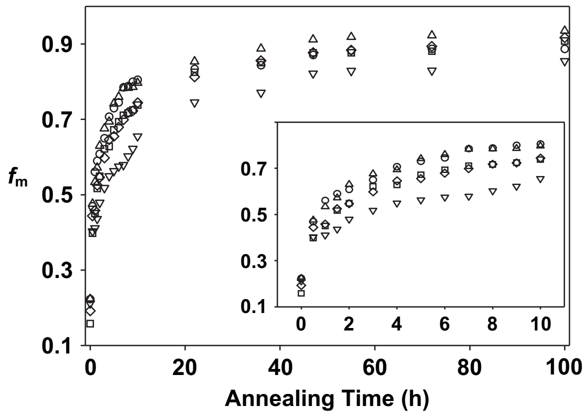

Fig. 7. Plots of f_m vs annealing time for latex films annealed at 25 °C and RH = 45–50%. The inset shows the same curves at short times. The results are taken from five different latex copolymers: MEEU00 (○), MEEU01 (△), MEEU03 (□), MEEU05 (◇), MEEU07 (▽).

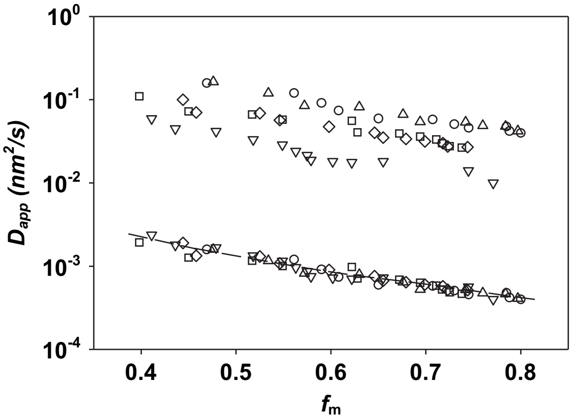

Fig. 8. Plots of the apparent diffusion coefficient D_{app} and master curve of the D_{app} values as a function of f_m for latex films annealed at 25 °C and RH = 45–50%, The results are taken from five different latex copolymers: MEEU00 (○), MEEU01 (△), MEEU03 (□), MEEU05 (◇), MEEU07 (▽). In constructing the master curve, all the D_{app} values were multiplied by a_{MEEU} and then vertically shifted down by two log units for clarity. Values of the shift factors employed are $a_{MEEU00} = 1$, $a_{MEEU01} = 0.97$, $a_{MEEU03} = 1.75$, $a_{MEEU05} = 1.9$, $a_{MEEU07} = 4.0$. The line drawn through the data points of the master curve is intended as a guide for the eye.

To explore the effect of humidity further, we carried out additional experiments at 25 °C and RH = 75–95%, using a saturated solution of potassium sulfate to control RH. Under these conditions,

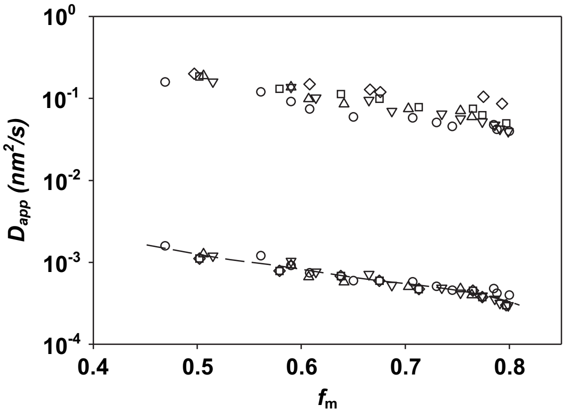

Fig. 9. Plots of the apparent diffusion coefficient D_{app} and master curve of the D_{app} values as a function of f_m for latex films annealed at $(T-T_g) = 21.7$ °C and RH = 45–50%. The results are taken from five different latex copolymers: MEEU00 (○), MEEU01 (△), MEEU03 (□), MEEU05 (◇), MEEU07 (▽). In constructing the master curve, all the D_{app} values were multiplied by a_{MEEU} and then vertically shifted down by two log units for clarity. Values of the shift factors employed are $a_{MEEU00} = 1$, $a_{MEEU01} = 0.67$, $a_{MEEU03} = 0.6$, $a_{MEEU05} = 0.45$, $a_{MEEU07} = 0.75$. The line drawn through the data points of the master curve is intended as a guide for the eye.

the films become turbid, indicating that some water taken up by the latex films is present in microdomains large enough to scatter light. In the coatings industry, this phenomenon is known as "water whitening". By visual observation, we noted that the films containing the greater content of MEEU became turbid more quickly than those with lower or zero amount of this polar monomer. The data obtained from FRET studies on these films are plotted in Fig. 10. In this high-moisture state, the difference in diffusivity among the samples is dramatically reduced. This effect can be attributed to hydroplasticization of the latex polymer.

To test the other extreme of dry films, samples were aged at 25 °C in a sealed box filled with silica gel. The humidity measured by inserting the portable thermo hygrometer into the box was in the range 10–25%. FRET experiments on these films led to the data plotted in Fig. 11. For these dry films, we see much larger differences in the magnitude of D_{app} values between samples at comparable values of f_{m}. More important, we also find that the polymer diffusivity decreases as the content of MEEU increases. At low humidity, the MEEU in the polymer slows down its rate of diffusion.

We summarize the effect of humidity on the polymer diffusion rate in Fig. 12, where we plot the magnitude of the shift factors for the different polymers at different relative humidities. Even at higher T_g, MEEU01 shows higher or similar diffusivity compared to MEEU00, which might come from H-bonding induced interactions between the polymer chains. Except MEEU01, MEEU-containing copolymers show lower diffusivity because of high T_g and they show a stronger dependence on water for film formation compared to MEEU00.

It would be even better if we could connect the shift factors in Fig. 12 to the actual water content of the films. This is very difficult to do. Under the high humidity conditions of the experiments in Fig. 10 (ca. 90% RH), we measured the weight uptake of water compared to the dry films. We found 6.4% in MEEU7, 3.8% in MEEU3 and 2.0% is MEEU0. These numbers, however, are not meaningful, because the water in these films is present both as molecularly dissolved water and as water pools that make the films turbid. Only the molecularly dissolved water acts as a diffusion promoter by plasticizing the polymer and disrupting MEEU hydrogen bonds. Under normal atmospheric conditions (45% RH), the situation is not so bad because the films are clear. Nevertheless, it is difficult to establish without more detailed studies, that the moisture uptake (2.6% in MEEU7, 1.9% in MEEU3 and 1.2% is MEEU0) is present entirely as molecularly dissolved water molecules. This point is discussed in more detail in Ref [27].

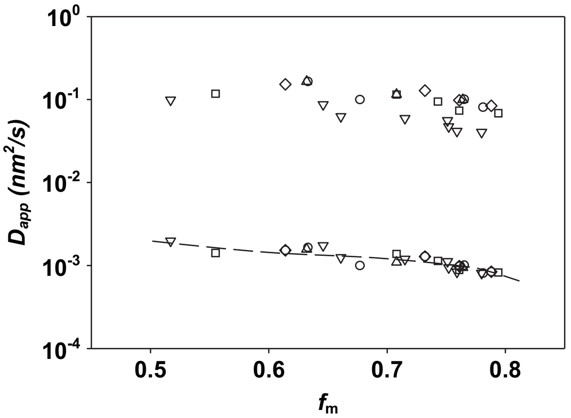

Fig. 10. Plots of the apparent diffusion coefficient D_{app} and master curves of the D_{app} values as a function of f_{m} for latex films annealed at 25 °C and RH = 75–95%, The results are taken from five different latex copolymers: MEEU00 (○), MEEU01 (△), MEEU03 (□), MEEU05 (◇), MEEU07 (▽). In constructing the master curve, all the D_{app} values were multiplied by a_{MEEU} and then vertically shifted down by two log units for clarity. Values of the shift factors employed are $a_{\mathrm{MEEU00}} = 1$, $a_{\mathrm{MEEU01}} = 0.95$, $a_{\mathrm{MEEU03}} = 1.2$, $a_{\mathrm{MEEU05}} = 1.0$, $a_{\mathrm{MEEU07}} = 2.0$. The line drawn through the data points of the master curve is intended as a guide for the eye.

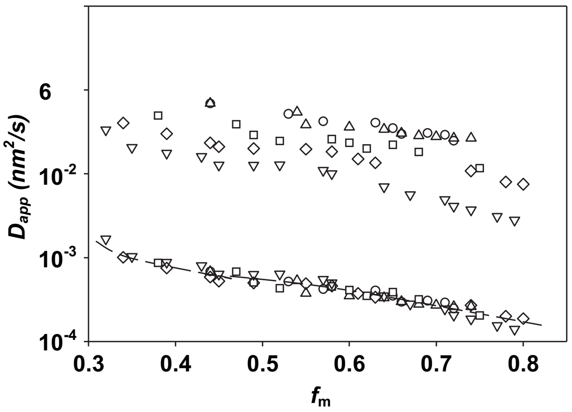

Fig. 11. Plots of the apparent diffusion coefficient D_{app} and master curves of the D_{app} values as a function of f_{m} for latex films annealed at 25 °C and RH = 10–25%, The results are taken from five different latex copolymers: MEEU00 (○), MEEU01 (△), MEEU03 (□), MEEU05 (◇), MEEU07 (▽). In constructing the master curve, all the D_{app} values were multiplied by a_{MEEU} and then vertically shifted down by two log units for clarity. Values of the shift factors employed are $a_{\mathrm{MEEU00}} = 1$, $a_{\mathrm{MEEU01}} = 0.98$, $a_{\mathrm{MEEU03}} = 1.75$, $a_{\mathrm{MEEU05}} = 2.5$, $a_{\mathrm{MEEU07}} = 5.0$. The line drawn through the data points of the master curve is intended as a guide for the eye.

5. Summary

We synthesized P(BA-MMA-MEEU) copolymer latexes using a MEEU monomer which has a hydrogen bonding capable moiety. The copolymer latexes were prepared through two-stage emulsion polymerization using seed particles under monomer-starved conditions to control particle size and conversion. We also added a chain transfer agent, C_{12}-SH plus a phase transport catalyst, MCD, to suppress gel formation and to control the molecular weight distribution. The latexes were colloidally stable at 30% solids content for samples containing up to 7 wt.% MEEU. One latex sample containing 10 wt.% MEEU formed small aggregates in water upon standing. These latex samples, both dye-labeled and unlabeled, showed good monomer conversion, modest molecular weight distributions, and only small differences in particle size and molecular weight between the samples.

We used FRET measurements to study the rates of polymer diffusion in these latex films. Polymers containing MEEU tended to diffuse more slowly as the MEEU content increased. This effect was very sensitive to atmospheric humidity. MEEU showed the greatest

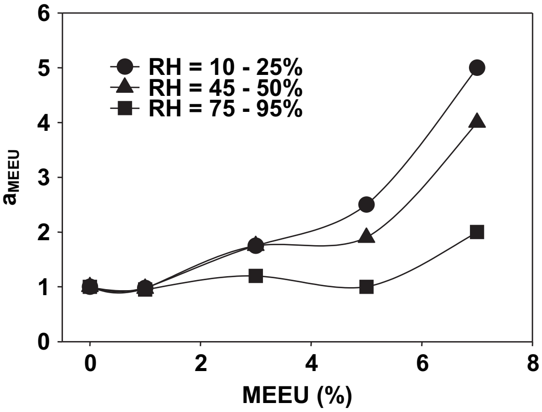

Fig. 12. Plots of shift factor a_{MEEU} change as a function of MEEU content for the latex films for different values of the relative humidity (RH).

retardation under dry humidity conditions. At high humidity (ca. 90% RH), conditions under which the films became turbid due to the presence of phase separated water in the films, the differences in polymer diffusion rate of the various MEEU-containing films nearly disappeared and became comparable to that of films formed from latex without any MEEU. The retardation effect of MEEU is almost certainly a consequence of its ability to donate a proton in a hydrogen bonding interaction with ester groups in the polymer backbone, increasing the friction coefficient for polymer diffusion. In the presence of atmospheric humidity, water molecules dissolve in the film and disrupt hydrogen bonding between MEEU groups and the carbonyl groups of the latex polymer.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.04.028

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