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Effect of Water on Polymer Diffusion in Latex Films

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ABSTRACT: The role of water in polymer diffusion in latex films was examined. For a hydrophobic polymer (poly(butyl methacrylate), PBMA), water has little influence on the polymer diffusion rate. Water absorption in PBMA latex films does increase film turbidity, both for nascent and for well-annealed films. For a hydrophilic polymer (a copolymer of 5 wt % methacrylic acid and 95 wt % butyl methacrylate, P(MAA-*co*-BMA)], the presence of water (e.g., 5 wt %) increases the diffusion coefficient by a factor of 5 at 60 °C. Upon neutralization of the carboxylic acid groups of P(MAA-*co*-BMA) with NaOH, the polymer diffusion is much retarded in dry films but greatly enhanced in wet films: the polymer diffusion coefficients for the wet films are about 2 orders of magnitude larger than those for the corresponding dry films. Neutralization with NH_3 results in intermediate diffusion rates, between those of unneutralized and NaOH-neutralized films under both dry and wet conditions.

Introduction

Latex film formation is a process in which the polymer microspheres initially dispersed in water are transformed into a solid film. The process has been pictured phenomenologically as occurring in several steps.[1,2] First, water evaporation brings the polymer particles into close contact. Then the particles deform to fill the interstitial spaces and to form a continuous solid structure. With time, healing of the interfaces occurs as the polymer molecules diffuse across the interparticle boundaries.

Among various ingredients in latex systems, water is the indispensable component. It is present in varying concentrations throughout the process from a liquid dispersion to a solid film. A major role of water in the latex film formation process is to provide a stabilizing and suspending medium for the particles that allows for thermal motion of the system to permit approach to close packing of the particles. During drying, water evaporates, leading to the concentration of polymer particles and the formation of films. For many years, scientists have been concerned with the role played by water in the film formation process and the development of film properties. Much of this attention has been focused on the drying process itself and the forces that lead to particle deformation and the formation of dense and transparent films. More recently, questions have been posed about the possible role of residual water, either from the drying process or from absorption of moisture from the atmosphere, on the rate of polymer diffusion in latex films. In this paper we examine the role of moisture on the diffusion rates of polymer molecules in poly(butyl methacrylate) (PBMA) latex films, comparing results for PBMA itself with BMA copolymers containing polar groups. To put this work in context, we first provide a brief review of the influence of water on the latex film formation process itself.

In 1956, Brown[3] proposed that water evaporation at the water−air interface leads to capillary compression, which serves as the principal force driving the deformation of latex particles. Another view of this process is that particle deformation and compaction are driven by the polymer−air surface tension, the so-called dry-sintering theory proposed by Bradford and co-workers.[4] A third point of view is that compaction can be driven under water by the polymer−water interfacial tension.[5] There has been a long debate about which forces, the capillary force in relation to the presence of water, the polymer−air surface tension, or the polymer−water interfacial tension, play the dominant role in particle deformation under normal film-forming conditions.[6−8]

Holl and co-workers[9] examined coalescence for a styrene/butyl acrylate based latex ($T_g = 40$ °C) at 36 °C under different conditions. They found that drying the wet latex dispersion in air at 94% relative humidity (RH) for 2 h gave a clear film, while exposing the same particles from which water had been preremoved at 23 °C /0 RH to 94% RH gave only an opaque film after 2 h. Only after 24 h did the film obtained from the predried particles turn slightly transparent. Sperry et al.[10] investigated the role of water and humidity in latex film formation via minimum film formation temperature (MFT) measurements. They observed that the dependence of MFT on water content was different for hydrophobic and hydrophilic polymers. With hydrophobic polymers (e.g., a copolymer of 47 wt % ethyl acrylate/52 wt % styrene/1 wt % acrylic acid), the MFT values for films dried in open air (65% RH) from wet dispersions were almost identical to those for films produced in a high flow of dry air from predried particle deposits. In contrast, when more hydrophilic polymers (e.g. a copolymer of 43 wt % ethyl acrylate/56 wt % methyl methacrylate/1 wt % acrylic acid) were used, the MFT values for films dried at high RH were about 10 °C lower than those for films dried and aged in a dry environment. In Sperry's view, the effect of water on particle deformation was simply the hydroplasticization of hydrophilic polymers, which decreases the deformation resistance of the viscoelastic polymers and thus reduces the minimum temperature (or time) required for the formation of compact films.

Another interesting issue is how exposure to water influences latex films after they are dried, i.e., after the compaction process. Joanicot and co-workers[11,12] reported that in films newly formed from hydrophobic latex particles with a polar surface shell, the polar material forms an interconnected membrane. This membrane could be rehydrated with H_2O or D_2O. When the membranes took up water, the films lost their cohesive strength and became brittle. Stress−strain tests showed that breakage of the samples occurred at

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both low stress and low strain. Note that their latex particles contained a hydrophobic core, made of 50 wt % butyl acrylate/50 wt % styrene, surrounded by a thin hydrophilic shell (4 wt % based on core polymer), made mainly of acrylic acid monomer copolymerized with the core polymer. In their samples, the decrease in strength might be due to the water plasticization of the membrane, decreasing the overall strength for the composite. As the membranes swell, water can occupy the interstitial spaces between adjacent cells and loosen the film structure.

Eckersley et al.[13] found by dynamic mechanical analysis that their latex films, made of a copolymer of 49.5 wt % butyl acrylate/49.5 wt % methyl methacrylate/1 wt % methacrylic acid, showed a decreased modulus when immersed in water compared to its behavior when placed in a dry environment. They attributed the reduced modulus in the presence of water to water plasticization of the polymer. Plasticization (lowering of T_g) implies water solublization into the latex polymer. Water concentrated in the interstitial spaces will decrease the intimacy of polymer contact and lead to a decrease in film stiffness.

Here our concern is with the influence of water on polymer diffusion rates in latex films. It is widely believed that the mechanical properties of latex films develop through the diffusion of polymer molecules across the interparticle boundaries, leading to the healing of the initial interparticle interfaces.[14] Since there is normally some water in latex films, either from the original dispersion or from air, it is of great importance to understand the role of water in the polymer diffusion process in latex films. For example, if water were to act as a plasticizer, it should enhance the diffusion rate of the polymer, and the data should fit theories relating the polymer diffusion coefficient to the plasticization effect, as exemplified by the Fujita–Doolittle free-volume model.[15–17] Thus measuring the change in polymer diffusion properties may be able to provide important, molecular level information about the influence of water on the films.

Here we study the influence of water on polymer diffusion in latex films. In our experiments we monitor polymer diffusion by the fluorescence energy transfer technique. We compare the diffusion rates between latex films aged or annealed in dry environment and those treated under wet or humid conditions. We also compare the effect of moisture on diffusion between hydrophobic and hydrophilic latex polymers.

Experimental Section

Materials. Butyl methacrylate (BMA, Aldrich) and methacrylic acid (MAA, Aldrich) were vacuum distilled under a N_2 atmosphere and stored in the refrigerator before use. The fluorescent comonomers were synthesized in our laboratory. 9-Anthryl methacrylate (AnMA) was prepared by reacting anthrone (Aldrich) with methacryloyl chloride (Aldrich) in dry THF catalyzed by dry pyridine, as described previously.[18] 9-Vinylphenanthrene (V-Phe) was obtained via a Wittig reaction between 9-phenanthrenecarboxaldehyde (Aldrich) and methyltriphenylphosphonium iodide (Aldrich) in a mixture of benzene and 5 N NaOH in water.[19] Dodecyl mercaptan (DM, Aldrich), sodium dodecyl sulfate (SDS, Aldrich), potassium persulfate (KPS, Aldrich), and sodium bicarbonate (Fisher) were used as supplied.

Latex Preparation. Latex particles were prepared by semicontinuous emulsion polymerization. The latex polymers used in this study included poly(butyl methacrylate) (PBMA), regarded as a hydrophobic polymer, and a copolymer of butyl methacrylate and methacrylic acid (P(MAA-*co*-BMA)), as the more hydrophilic polymer. The polymers were labeled either with a fluorescence donor, phenanthrene (Phe), or a fluorescent acceptor, anthracene (An), respectively. In the case of PBMA latex, the synthesis is described as follows: A small amount of PBMA latex seed (diameter ca. 55 nm) was prepared in the first stage. KPS, SDS, and $NaHCO_3$ were used as the initiator, surfactant, and pH buffer, respectively. DM (2 wt %), based upon monomer weight, was used as a chain transfer agent to adjust the molecular weights for all the latex polymers. In the second stage of polymerization, a monomer solution composed of 1 mol % of a fluorescent comonomer (AnMA or V-Phe), 2 wt % DM, and the rest of the BMA was continuously fed into the seed latex dispersion. The monomer feeding rate was kept identical (0.1 mL/min) for all samples, controlled by metering pumps, with a total feeding time of 5 h for each reaction. KPS and SDS dissolved in water were added into the reactor concurrently. Table 1 shows the recipe for the preparation of the labeled PBMA latex samples. To prepare a more hydrophilic latex, 5 wt % MAA (based upon BMA) was premixed in the monomer solution and the monomers were then polymerized in the second stage under identical conditions to those shown in Table 1, to give a copolymer of 5 wt % MAA/95 wt % BMA [P(MAA-*co*-BMA)]. A high conversion of the monomers (>98.5%) was obtained for all reactions, as evaluated gravimetrically.

Table 1. Recipe for the Preparation of Phe-Labeled PBMA Latex

first stage		second stage	
BMA (mL)	3.5	BMA[a] (mL)	32
DM (mL)	0.074	DM (mL)	0.68
water (mL)	60	V-Phe[b] (g)	0.48
KPS (g)	0.062	water (mL)	26
SDS (g)	0.11	KPS (g)	0.060
$NaHCO_3$ (g)	0.060	SDS (g)	0.60
temp (°C)	80	temp (°C)	80
time (h)	1	time (h)	20–24

[a] For preparing the P(MAA-*co*-BMA) copolymer, a mixture of 32 mL (28.6 g) of BMA + 1.5 g of MAA was used to replace pure BMA. [b] For preparing the An-labeled latex, 0.58 g of AnMA was used to replace 0.48 g of V-Phe.

Particle size and size distribution were determined by dynamic light scattering using a Brookhaven BI-90 particle sizer. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC), using Ultrastyragel columns (10^4A+500A), THF as the eluent, and a flow rate of 0.8 mL/min. Monodisperse poly(methyl methacrylate) standards (Polysciences) were used as the calibration standards. In the GPC signal acquisition, a refractive index detector was coupled with a fluorescence detector, the latter serving as a monitor for the fluorescent dye. Negligible fluorescence signal was detected at long elution times where unreacted dye would appear. A large peak appeared in the fluorescence trace in the high molar mass region which had the same time position and shape (intensity distribution) as the peak in the refractive index trace, indicating that essentially all dye molecules were bound to polymer chains in a random manner. As a consequence, the labeling content in all polymer samples is 1 mol % (based on the base monomer units), close to the molar ratio of dye comonomer to the base monomers added during polymerization.

The important characteristics of all the latex samples used are listed in Table 2. Since we prepared all the latex samples using almost the same recipe and under strictly identical conditions, we obtained similar particle sizes and size distributions for all samples and, more importantly, the molecular weights and molecular weight distributions of all samples are very similar. Even the addition of 5 wt % MAA in BMA in the monomer feed did not change the molecular weights significantly. Note that in the second stage reaction our monomer addition rate was quite low and the reactions were carried out under monomer-starved conditions. Owing to the similar characteristics of our samples, we are able to make meaningful comparison of the diffusion properties of the polymers under various sets of conditions.

Table 2. Latex Characteristics

	PBMA		P(MAA-*co*-BMA)	
	Phe-	An-	Phe-	An-
diameter[a] (nm)	125	125	132	132
size polydispersity[a]	0.02	0.02	0.03	0.03
M_w (×1000)	35	34	39	37
M_n (×1000)	17	18	16	16
M_w/M_n	2.1	1.9	2.4	2.3

[a] The particle sizes are nearly identical with both a narrow size distribution for each pair of Phe- and An-labeled latex samples, and the results shown here were measured for 12:1 An/Phe mixtures of the pairs of ion-exchanged samples, which are thus directly used in our diffusion analysis.

Film Formation and Characterization. Before film formation, all latex dispersions were treated several times with an ion exchange resin (AG-501-X8 mixed bed resin, Bio-Rad) to remove the surfactant and other ionic substances. The procedure for cleaning the latex samples was similar to that described elsewhere.[20] The latex samples remain stable in dispersions during the procedure. For PBMA samples, we found it necessary to dilute the original dispersion (30 wt % solids) by at least a factor of 2, otherwise the dispersion became too viscous upon cleaning the latex. For P(MAA-*co*-BMA) samples, the latex showed higher stability after the washing process. In both cases, we were able to obtain a final "clean" latex with (within experimental error) the same size and size distribution as the original latex.

Films were formed by spreading mixed dispersions of Phe-labeled particles and An-labeled particles (solids content ca. 15 wt %) onto thin quartz plates and dried in a temperature-controlled oven. The typical thickness of our films was ca. 150 μm. The number ratio of Phe- to An- labeled particles in the films was 1:12. This was chosen to ensure that each donor-labeled particle is surrounded primarily by acceptor-labeled particles, and yet there is still sufficient donor fluorescence signal to be detected.[21−23] For P(MAA-*co*-BMA) samples, some films were formed when the −COOH groups were in the protonated form, and others were prepared from dispersions of the latex mixed with NH_3 or NaOH (mole ratios NH_3/−COOH or NaOH/−COOH ≈ 2.5) to neutralize the −COOH groups. To minimize interparticle polymer diffusion during the drying process, the drying conditions were chosen such that a minimum temperature and time were required for drying, which still led to the formation of clear and crack-free films. PBMA latex samples were dried at 25 °C, close to room temperature, whereas P(MAA-*co*-BMA)-based samples required 32 °C. An inverted Petri dish was used to cover the latex dispersions to increase the drying time for film formation, and the fan in the oven was used to circulate the air to ensure uniform drying time for each dispersion. Drying times were typically 3 h. The air humidity in the laboratory was ca. 45% RH. For each set of samples which we compare, the films were dried under identical conditions.

Some films were further dried under vacuum for 2−3 days to remove possible residual water and then kept in a dry environment in a sealed test tube. Some were placed, using glass beads as a support, on the top of a water layer in a test tube covered with a rubber septum and, thus, had an internal humidity of 100% RH. Other samples were immersed in liquid water. These films were kept in a wet environment for 2 days to ensure an equilibrium water content. The dry and wet films were then annealed at 60 °C in an oven for various times. To minimize the water loss from the wet films upon heating, the wet films were either supported on top of a water layer inside a sealed test tube to maintain high humidity (100% RH), or heated directly in water. To prevent an increase in water vapor pressure during heating, the internal vapor pressure was bled to the open air via a small needle inserted through the rubber septum. After fluorescence decay measurements for each annealed wet film, it was returned to its wet environment at room temperature again to reach a saturated water content, and then heated for an additional amount of time. For each set of samples to be compared, the films were heated simultaneously.

Table 3. Water Contents (wt %) in Latex Films Treated in Water Vapor (100% RH) or in Liquid Water

		P(MAA-*co*-BMA)		
	PBMA	−COOH	+NH_3	+NaOH
newly dried film	1.4	1.4	5.3	8.9
immersed in liquid water (2 days)	15.0	16.2	*c*	*d*
exposed to wet vapor (∼100% RH, 2 days)	3.4	5.7	5.9	13.8
heated at 60 °C in water vapor[a]				
40 min	2.3	5.4	5.0	13.7
90 min	2.2	4.6	3.3	10.5
heated for 2 h at 60 °C and exposed to wet vapor again[b]	3.5	5.5	5.8	14.0

[a] Water content was measured immediately after heating the sample prior to allowing the sample to cool. [b] The films were annealed and then placed in water vapor again to reach an equilibrium water content. [c] Swollen. [d] Highly swollen.

The water contents of the films were measured gravimetrically. Film transparency was determined with a UV-vis spectrometer (Hewlett-Packard 8452A Diode Array). The film was mounted in front of the sample window of the spectrometer, and its transmittance (%*T*) was scanned in the visible range (400−700 nm). Fluorescence decay measurements were carried out by using the time-correlated single-photon-counting technique. The measurements conditions were similar to those described previously.[18]

Results and Discussion

Film Transparency and Water Content. We first describe the influence of water on the optical clarity of latex films. We measured both the film transparency and water content for samples treated under different humidity conditions.

(a) Water Content in Latex Films. In the fresh films of PBMA prepared under our conditions, the films had an initial water content of 1.4 wt %. Similar values were found for newly formed P(MAA-co-BMA) films with the acid groups in the protonated form. Much larger values were found (up to 8.9 wt %) when the carboxylic acid groups were neutralized by NH_3 or by NaOH. The water content of these carboxylated films increased significantly when all these films were exposed to a vapor of high water content (100% RH). When immersed directly in liquid water, ca. 15 wt % water could be detected. Table 3 shows the water content measured for our latex films when exposed to water at room temperature and when heated at 60 °C in high humidity. When the wet films are heated, water is evaporated out from the film. When the heating was carried out in a wet environment (i.e., air vapor of 100% RH), a significant amount of water remained in the film (Table 3), which allowed us to observe its effect on polymer diffusion.

(b) Film Transparency. When dense, crack-free films are formed from latex dispersions, they are often transparent, or sometimes semitransparent, depending on the film microheterogeneity, film thickness, or water content. Due to the microheterogeneous nature of the newly formed films, the transparency of latex films is in many cases somewhat lower than that of films cast from homogeneous solution. In other cases highly transparent films are obtained, with a percent transmittance (%T) over 85%, especially when the temperature of film formation is well above the MFT. In the films formed at high temperatures, some interparticle polymer diffusion may have occurred during the film formation process.

Films dried under our conditions were fairly transparent with 70%T over the visible wavelength range.

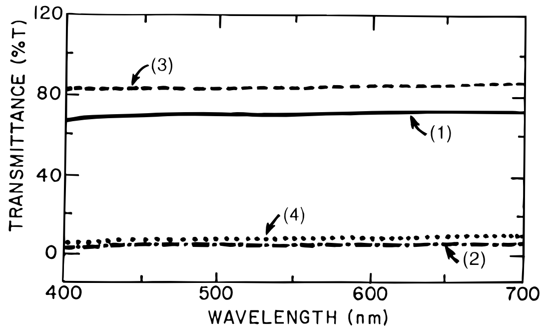

Figure 1. Visible transmittance spectra for PBMA films: (1) a newly formed film; (2) a nascent film exposed to 100% RH for 2 days; (3) a film heated in low humidity at 60 °C for 2 h; (4) the well-heated film exposed once again to 100% RH for 2 days.

This value would be higher if thinner films were prepared. For both PBMA and P(MAA-*co*-BMA) based samples, annealing at elevated temperatures (e.g., 60 °C) in dry environment leads to an increase in transmittance to over 80%T.

When PBMA films are exposed to water vapor or immersed in liquid water for a sufficient time (e.g., 2 days), they become turbid, with %T < 20%. The water content for a PBMA film exposed to 100% RH water vapor was 3.5 wt % and that for a film immersed in liquid water could be as high as 15 wt %. The film immersed in liquid water also showed large cracks and became too brittle to resist mechanical forces. This result is similar to that seen by Joanicot et al.[12] We infer from this result that water becomes more concentrated in the interparticle boundary region richer in polar groups (e.g., $-OSO_3H$). This inhomogeneity of water distribution in the films would lead to turbidity for films exposed either to water vapor or to liquid water.

When the water-containing, turbid PBMA films are heated in a low humidity environment and water is evaporated, the film transmittance increases to higher values and the films soon become clear. When these heated clear films are placed back into water vapor or liquid, they once again become highly turbid. What is surprising here is that turbidity under wet conditions was found for films that had been well-annealed and the polymer molecules had reached a high extent of mixing. A similar behavior was found for films of the latex polymer cast from dioxane solution. Figure 1 shows the visible transmittance spectra for a newly formed PBMA film, a film exposed to water vapor, then heated for 2 h at 60 °C at low humidity, and then placed into a high humidity atmosphere again. What one would expect is that as polymer molecules are well mixed, the heterogeneity in the initial latex films would gradually disappear and the hydrophobic polymer matrix would become more resistant to water. From our results, we infer that while the molecular mixing increases overall the homogeneity of the system, some degree of nonuniform distribution of polar groups exists in the polymer. When the films are exposed to water, domains rich in polar substituents take up more water and these regions must be sufficiently large to scatter light. As a consequence, the water-containing films remain turbid, no matter how much polymer diffusion has taken place.

Polar group aggregation in latex films has certain features in common with inverse micelle formation from ionic surfactants. Our PBMA latex polymers are hydrophobic chains with polar end groups ($-OSO_3H$ groups from the initiator). When the polymer molecular weights are much higher than that of typical common surfactants, the tendency for the hydrophilic ends to assemble can be overcome by the tendency toward random distribution of the chain ends driven by the polymer conformational entropy. In these experiments, however, the molecular weights ($M_w = 35\,000$, $M_n = 17\,000$) are smaller than those of normal latex polymers. Some polymer components have M values only 1000 to several thousand. In these molecules, each chain contains only a few tens of monomer units and one or two polar end groups, which may be able to aggregate into hydrophilic domains distributed in the hydrophobic matrix. This aggregation process would be enhanced when the films are heated.

The presence of water in P(MAA-*co*-BMA) films has a different effect on transparency than in PBMA films. When clear P(MAA-*co*-BMA) films are subject to water treatment, the saturated amount of water was ~5.7% in 100% RH vapor and >15% in liquid water. However, these water-containing films remain transparent, with almost identical transmittance to those films in the dry state. This implies that there is a relatively uniform distribution of water in the film. This may be related to the distribution of polar groups in the latex. In this type of samples, the polar groups (mainly carboxylic acids) should be statistically distributed along each polymer chain. In each particle, the density of polar groups ($-OSO_3H$ and $-COOH$) at the surface may be comparable to that within the particle, since 5 wt % MAA incorporated into the polymer under monomer-starved conditions throughout the second stage of polymerization. There is a seed core made of PBMA, corresponding to ~10 wt % of the entire particle, but it ought to be well mixed with the second-stage polymer during polymerization (at 80 °C). Thus, on a microscopic level, there maybe no preferred domains in which the polar substituents are highly concentrated in the films.

Films prepared from dispersions of P(MAA-*co*-BMA) neutralized by NH_3 and NaOH also showed good transparency either in the dry state or under wet conditions. When the wet films were heated, differences were observed between NH_3- and NaOH-neutralized films. The NH_3-neutralized films remained transparent throughout the molecular mixing process upon heating, similar to those films with protonated carboxyl groups. In the case of NaOH-neutralized films, transparency was preserved when the water-containing films were heated to some intermediate stage (e.g., at 60 °C for 30 min), but increasing turbidity (e.g., %T ~ 30%) was seen when these films were annealed more extensively. When a latex film of the same composition was dissolved in a good solvent (1,4-dioxane), recast onto a quartz substrate, and exposed to 100% RH, a similar turbidity of the film was observed.

One reason for the turbidity of NaOH-neutralized films in the wet state would be that the amount of water absorbed in the films was much larger than for the NH_3-neutralized films or the unneutralized films (Table 3). Since turbidity was observed mainly for well-heated films, it might be related to the phase rearrangement involved in the molecular mixing process. These Na^+ neutralized films are in fact ionomers, and ion clustering would be expected.[24,25] These ion-pair clusters are natural centers for water pickup to occur. The difference between the NH_3 neutralization and NaOH neu-

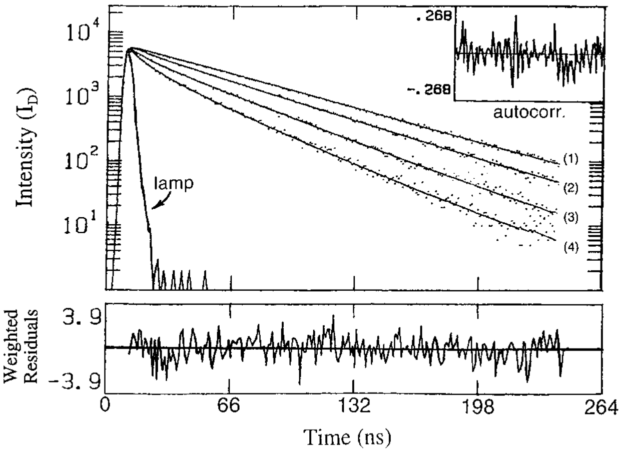

Figure 2. Representative donor fluorescence decay profiles for dry P(MAA-*co*-BMA) films. Curve 1 corresponds to a film with donor particles only, and curve 2 is for a film freshly prepared with a 1:12 mixture of Phe- and An-labeled particles. Curves 3 and 4 are for the acceptor-containing films annealed in a dry environment at 60 °C for 40 and 190 min, respectively. These curves are integrated to obtain the areas under them as described in the text. The decay function used for this study is $I_D(t) = A_1 \exp(-t/\tau_D{}^o) + A_2 \exp[-t/\tau_D{}^o - B(t/\tau_D{}^o)^{1/2}]$, where A_1, A_2, and B are fitting parameters and $\tau_D{}^o$ is the unquenched donor lifetime (45 ns). In this figure we also display the weighted residuals and their autocorrelation for curve 4 when fitted to the above expression.

tralization would be that NH_3 can evaporate with time or upon heating, causing the behavior of the NH_3 films to become closer to that of the protonated films.

Energy Transfer and Diffusion Data Analysis. Fluorescence decay measurements were carried out on our film samples as a means of assessing the extent of energy transfer as a function of annealing history and of film composition. Figure 2 shows examples of fluorescence decay profiles obtained for a set of our P(MAA-*co*-BMA) films in the dry state before and after annealing. Films prepared from a dispersion of Phe-labeled particles, excited at 300 nm, exhibit an exponential decay profile (top curve) with a lifetime of 45 ns. Films prepared from a mixture of Phe- and An-labeled particles show a slightly increased curvature at early times in the decay profiles followed by a long exponential tail (curve 2). This curvature corresponds to a small amount of energy transfer between donors and acceptors across the interparticle boundary region in the nascent films. When these films are annealed at elevated temperatures, this increased curvature becomes more pronounced, as seen in curves 3 and 4 for films heated at 60 °C for 40 and 190 min, respectively. This indicates that molecular mixing has occurred between donor- and acceptor-labeled polymers. The extent of energy transfer is increased, leading to a faster decay of donor fluorescence.

The quantum efficiency of energy transfer, Φ_{ET}, can be evaluated by integrating the fluorescence decay profiles $I_D(t)$ after first normalizing them to unit intensity at $t = 0$.[21] Φ_{ET} is usually obtained through eq 1

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D(t)\,dt}{\int_0^\infty I_D{}^0(t)\,dt} = 1 - \frac{\text{Area}}{\text{Area}^0} \qquad (1)$$

where $I_D(t)$ and $I_D{}^o(t)$ represent the donor fluorescence decay functions in the presence and absence of acceptors and Area and Area^0 are the integrated areas under the decay profiles for films in the presence and absence of energy transfer, respectively. In this way one can monitor the extent of energy transfer in the latex film samples without assuming a specific model to parametrize the $I_D(t)$ decay profile. One only needs to compare areas under the respective decay profiles to monitor the increase in energy transfer due to polymer diffusion. We calculate these areas by fitting the decay profiles to the stretched exponential form described previously[22] and then integrate the parameterized expressions.

There are various ways that one can define the extent of mixing in the heated films from the energy transfer data.[21-23] One of the most convenient is to define the fraction of mixing, f_m, in terms of the fractional growth in energy transfer efficiency from annealing time zero to t_a, as follows

$$f_m = \frac{\Phi_{ET}(t_a) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} \qquad (2)$$

f_m can be rewritten in terms of the areas under the donor decay curves according to eqs 1 and 2

$$f_m = \frac{\text{Area}(0) - \text{Area}(t_a)}{\text{Area}(0) - \text{Area}(\infty)} \qquad (3)$$

The term f_m represents the "quantum efficiency" of mixing and provides a measure of the degree of polymer interdiffusion which occurs when the films are annealed. Representative data of f_m values for our films as a function of annealing time will be presented in the following sections. These were obtained by measuring the decay profiles and comparing the areas under the profiles for films without annealing [Area(0)], annealed for certain times [Area(t_a)], and annealed for sufficiently long time to approach a minimum value of area [Area(∞)].

In many cases a single value of Area(0) or Area(∞) can be used for different samples when the labeling content of the polymers is the same. In our cases, the presence of water (e.g., 5 wt %), either in the interstitial spaces or in the well-mixed polymer matrix, might alter these values by decreasing the intimacy between dyes at various states of the interdiffusion process. In our experiments we found that this amount of dilution does not affect the extent of energy transfer significantly. Nevertheless, we measured these areas separately for each set of our samples so that by normalization to obtain f_m values through eq 3 these effects from different sample conditions were minimized.

To proceed more deeply into the analysis of the diffusion process, it is useful to calculate the apparent mean diffusion coefficient D_{app} characterizing the rate of movement of the polymers in the samples. The diffusion coefficients were calculated by fitting the data obtained from energy transfer to a spherical diffusion model which satisfies Fick's laws of diffusion.[26] The details of the analysis and discussions have been presented previously.[21,27,28] In the analysis, a parameter, f_D, namely the fraction of substance (donor-labeled polymer under consideration here) which has diffused across the initial boundaries after a certain time, is needed. The key step for us is thus to find a relation between f_D and the growth in energy transfer efficiency (i.e. f_m) which characterizes the extent of mixing.

In the analysis of polymer diffusion in latex films previously carried out in our laboratory, we have most often used films with a number ratio of An- to Phe-labeled particles (N_{An}:N_{Phe}) of 1. As discussed previously, we find that it is acceptable to assume that the mass fraction of diffusion f_D is equal to the extent of mixing f_m expressed in terms of quantum efficiencies of energy transfer in 1:1 An/Phe mixtures.[21,27,28] In other cases in which we intend to analyze the diffusion by more sophisticated models, a N_{An}:N_{Phe} ratio of 12 is preferred.[22,23] In the films described in this study, we chose a N_{An}:N_{Phe} ratio of 12 to match the conditions for spherical diffusion model, as described in refs 22 and 23. The f_D value we use for the diffusion coefficient calculations is $(1/2)f_m$. One notices that the relationship between f_D and f_m for 12:1 An/Phe mixture differs by a factor of 2 from that for the 1:1 mixture. From a geometric consideration, this is not difficult to understand. In the case of N_{An}:N_{Phe} = 12, each donor particle is surrounded by an acceptor-containing medium, whereas in 1:1 mixtures, each Phe-labeled particle has only half the number of An-labeled neighboring particles. Thus for the same mass fraction of diffusion (f_D), the energy transfer signal one would observe in the $N_{An}/N_{phe} = 1$ film is half of that for the $N_{An}/N_{Phe} = 12$ film.

We have found experimentally that the diffusion coefficients obtained from films of $N_{An}/N_{Phe} = 12$ by assuming $f_D = f_m/2$ are very close to those obtained from films of $N_{An}/N_{phe} = 1$ by setting $f_D = f_m$, especially at early times of diffusion. We also found that the diffusion data analyzed by using $f_D = f_m/2$ for $N_{An}/N_{Phe} = 12$ are very similar to those analyzed by a model considering the concentration profile developed by Liu et al. for the same samples.[22,23] We thus obtain f_D values, from energy transfer data by setting $f_D = {}^1/_2\ f_m$, for each sample ($N_{An}/N_{Phe} = 12$) at each diffusion time and are able to calculate the diffusion coefficients of the polymers.

Effect of Water on Polymer Diffusion. Figure 3 shows the diffusion data at 60 °C for PBMA films annealed in a dry environment and in the presence of water vapor at high humidity. In Figure 3a we plot the fraction of mixing f_m vs annealing time, and in Figure 3b we plot the apparent diffusion coefficient D_{app} vs time. We see that the extent of mixing in the films increases with time and approaches unity on a time scale of 2−3 h in both sets of samples. The diffusion coefficients obtained are on the order of 0.1 nm^2/s (10^{-15} cm^2/s) at early times and become somewhat lower at later times. This decrease in D_{app} can be explained by the fact that our samples have a range of chain lengths, and the shorter chains have higher diffusivity and make their contribution to the measurement at the early times. The larger molecules having smaller diffusion coefficients contribute to donor−acceptor mixing at later times. Comparing the data between the dry and wet PBMA films, we see that the diffusion rate for the wet film may be slightly higher than the dry film, but the difference is not significant, with the diffusion coefficients essentially falling in the same range. This indicates that water has little effect on the diffusion rate of PBMA. The only exception, observed repeatedly in our experiments, is that at the very beginning of annealing (e.g., the first 10 min), the f_m for the wet film is significantly larger than that for the dry film, and the calculated diffusion coefficient for the wet film is also noticeably larger (e.g., 2 times, see Figure 3). We suspect that this behavior is related to the presence of a small portion of molecules having shorter chain lengths than the average. This portion of molecules not only has high diffusivity but may also have a higher hydrophilicity because of the relatively high polar end group content. These combined factors lead to a faster mixing at early times in the wet films than in the dry films. Over most of the times of annealing, however, the influence of water on diffusion of PBMA is quite small, indicating that the hydrophobic PBMA exhibits little plasticization from water.

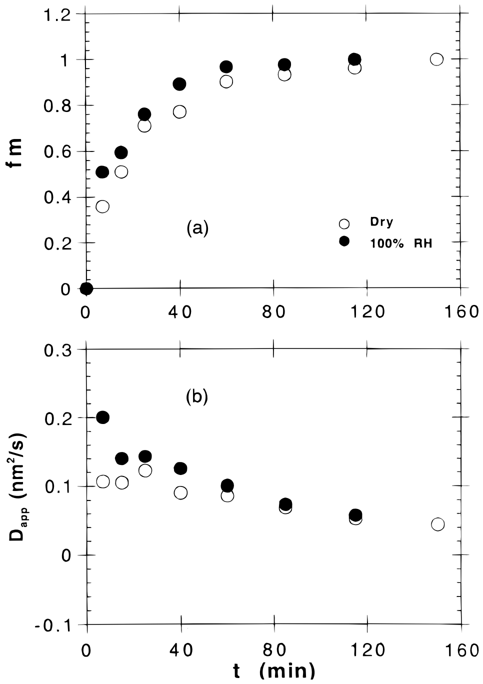

Figure 3. Comparison of diffusion rate of PBMA at 60 °C between dry samples (○) and wet films (●) treated in high humidity: (a) plots of the fraction of mixing (f_m) and (b) the mean apparent diffusion coefficient (D_{app}, in nm^2/s), respectively, as a function of annealing time (in min). Similar types of plots are presented in the following figures.

For P(MAA-*co*-BMA) samples, the diffusion data for films under dry and wet conditions are presented in Figure 4. Three sets of films are under consideration here: one is in dry state, one is in wet vapor, and the other is immersed in liquid water. The wet films, either exposed to high humidity or immersed in water, show similar diffusion rates upon heating at the same temperature. Note that the amount of water in the film was 5 wt % during heating at 100% RH and larger when the film was immersed in liquid water (see Table 3). Although there is an excess of water present in the film immersed in water compared to that in equilibrium with water vapor at 100% RH, this does not impose a further hydroplastic effect on the polymer. We also notice here again that the diffusion coefficient for the wet films at the very beginning of annealing (e.g., 10 min) is distinguishably larger than at later times, an effect similar to that found for PBMA samples, pointing to a contribution from the relatively more diffusive, hydrophilic short-chain molecules. The most important result here is that diffusion occurs much faster for these films under wet conditions than in the dry state. As seen in Figure 4a, the f_m values for the wet films are much larger (typically twice as large for times up to 2 h) and approach unity sooner than those for the dry films. The diffusion coefficients calculated for the dry P(MAA-*co*-BMA) film are about 0.01 nm^2/s, whereas those for the wet films are about 5 times larger (Figure 4b). This difference is significant. This clearly indicates that the presence of water in P(MAA-*co*-BMA) films enhances the diffusion rate of the polymers.

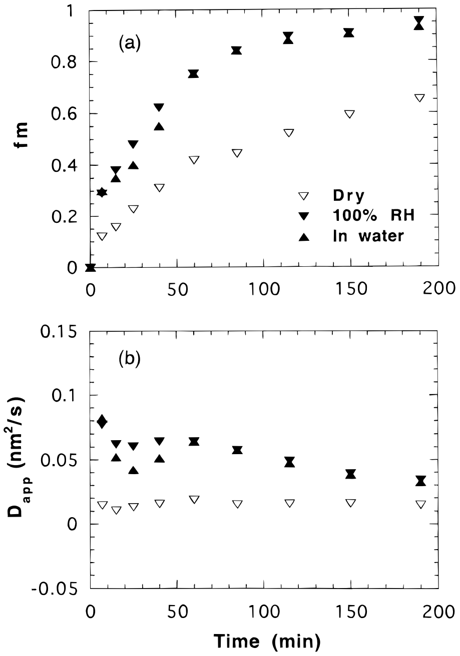

Figure 4. Comparison of diffusion rate at 60 °C between dry and wet films for P(MAA-*co*-BMA). The symbols ▽, ▼, and ▲ represent films treated in a dry environment, exposed to water vapor at 100% RH, and immersed in liquid water, respectively.

Comparing the data for PBMA samples (Figure 3) with those for P(MAA-*co*-BMA) (Figure 4) of similar molecular weights examined under the same conditions, we see that PBMA diffuses faster than P(MAA-*co*-BMA). We have previously attributed this to an increase in T_g and a decrease in mobility when the MAA component is incorporated into the PBMA.[27,28] In the dry state, the D_{app} values for PBMA are 10 times larger than those for P(MAA-*co*-BMA), whereas in the wet state, the ratio of diffusion coefficients between the same polymers becomes only a factor of 2. This comparison further demonstrates that water has much larger effect on the diffusion of the hydrophilic P(MAA-*co*-BMA) than the hydrophobic PBMA. Note that even in the wet state, PBMA has a higher diffusivity than P(MAA-*co*-BMA).

Diffusion of Neutralized P(MAA-*co*-BMA) versus Water Content. The P(MAA-*co*-BMA) films described above were prepared from ion-exchanged dispersions in which the carboxylic acid groups were in the protonated form. Here we consider films prepared from dispersions in which the −COOH groups were neutralized with NH_3 or NaOH. We added to each dispersion 2.5 equiv of base with respect to the total COOH content of the latex.

(a) Effect of Neutralization of P(MAA-*co*-BMA). Figure 5 compares diffusion data for dry P(MAA-*co*-BMA) films without addition of base, with those neutralized by NH_3 and NaOH. We see that the diffusion rate for NaOH-neutralized sample is much smaller than that for the unneutralized (−COOH) film, with the diffusion coefficient ratio of almost an order of magnitude (0.001 vs 0.01 nm²/s). NH_3-neutralization also leads to some retardation of the diffusion, but the difference is not as large as for the NaOH film. We attribute the decrease in diffusion rate upon neutralization of the −COOH to the increase in T_g when the polymer changes from its normal state to an ionomer.[24,25,28] The difference between NH_3- and NaOH-treated films is likely related to the ability of NH_3 to evaporate upon heating, leading to partial regeneration of MAA groups in the protonated form.

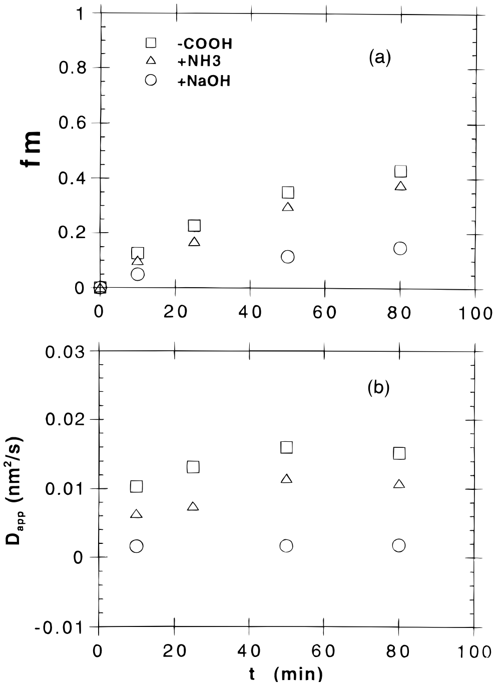

Figure 5. Comparison of the diffusion rate at 60 °C for dry films of P(MAA-*co*-BMA) in which the carboxyl groups are fully protonated (□) and neutralized with NH_3 (△) and with NaOH (○), respectively.

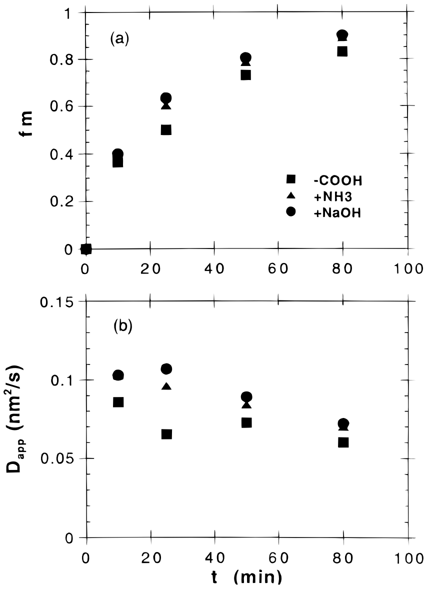

Figure 6. Comparison of diffusion rate of P(MAA-*co*-BMA) at 60 °C in water vapor for samples fully protonated (■) and neutralized with NH_3 (▲) and with NaOH (●), respectively.

(b) Effect of Water on Diffusion of Neutralized P(MAA-*co*-BMA). Figure 6 displays the results for films similar to those shown in Figure 5 but treated under wet conditions (in wet vapor). The films in Figures 5 and 6 were annealed and examined simultaneously. Here one sees that diffusion rates in the wet films for all sets of samples are larger than those in dry films. This indicates that water plasticizes all these samples. What is interesting here is that in the dry state diffusion in the NaOH-neutralized film is slower than that in the −COOH film, whereas under wet conditions this situation is reversed: the polymer in the NaOH-neutralized film sample diffuses faster than that in the −COOH film sample in the presence of water. What is impressive is that the ratio of diffusion coefficients between wet and dry NaOH-treated samples is about 80−100 times (ca. 0.1 vs 0.001 nm^2/s). A large change is also observable between wet and dry NH_3-neutralized films. For −COOH films, this ratio between wet and dry samples is still significant (5- to 8-fold) but much smaller than for the neutralized films. These results indicate that water has a much larger enhancement effect on the P(MAA-*co*-BMA) diffusion in neutralized samples than on those in the protonated form.

Some other observations may be also instructive to the understanding of the above results. For example, we found that the unneutralized P(MAA-*co*-BMA) sample could preserve its film identity when exposed both to water vapor and to liquid water, while the NaOH-neutralized film was only physically stable in the wet vapor but not stable when immersed in liquid water. When a NaOH-neutralized P(MAA-*co*-BMA) film is immersed in water, it gradually loses its film features and becomes a white suspension of small polymer pieces, indicating that a large amount of water swells the film and causes fragmentation and delamination from the substrate.

We have also found that most of these low molecular weight films, either PBMA- or P(MAA-*co*-BMA)-based, show significant polymer interdiffusion when they are aged at room temperature for several days or weeks, yet the films obtained do not appear to be sticky or blocky. This may be very useful information for practical coatings applications, and it will be interesting to examine ambient diffusion of these polymers in future experiments.

Conclusion

The effects of water on polymer diffusion in latex films were examined. Polymer diffusion was monitored by the fluorescence energy transfer technique. We compared the diffusion rates of latex films in the dry state with those exposed to water vapor or liquid water. For a hydrophobic polymer (PBMA), water has little influence on the polymer diffusion rate. Some water absorbed in these PBMA films increases film turbidity, both for nascent films and for well-annealed films in which polymer molecules have undergone extensive diffusion. For a hydrophilic polymer [P(MAA-*co*-BMA)], water absorption does not change significantly the film transparency. The diffusion rate of P(MAA-*co*-BMA) is significantly increased due to the presence of water (5 wt %). Water shows a more pronounced effect on the diffusion rate of NaOH-neutralized P(MAA-*co*-BMA) samples: the polymer diffusion coefficients measured for the neutralized wet films are about 2 orders of magnitude larger than those for the corresponding dry films. Neutralization with NH_3 results in intermediate diffusion rates between unneutralized and NaOH-neutralized films under both dry and wet conditions.

In latex films, there is always some amount of water present. Commercial latex polymers almost always contain significant amounts of hydrophilic comonomer, typically carboxyl groups, present initially in the shell or distributed within the particles. Thus the above results are also of importance for practical latex coatings systems.

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