Effect of Surface Acid Group Neutralization on Interdiffusion Rates in Latex Films[1]

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ABSTRACT: We report measurements of the kinetics of polymer diffusion in latex films prepared from two pairs of poly(butyl methacrylate) (PBMA) latex particles. One set contains only a small amount of sulfate groups at the surface; the other contains a significant amount of carboxylic acid groups at the surface. Neutralization of these acid groups with ammonium, sodium, and barium hydroxide retards the interdiffusion rate at 100 °C but does not suppress it. In these experiments, we employ pairs of particles identical in size, with very similar molecular weights, molecular weight distributions, and surface charge densities, that differ only in the fluorescent chromophore [phenanthrene (Phe) or anthracene (An)] used to label the polymer. Each pair of latex allows us to use direct nonradiative transfer (DET) experiments to follow polymer interdiffusion in films prepared from their dispersions. Acid group neutralization in the latex converts an acid-rich phase at the interparticle boundary in the film into an ionomer phase. Ba^{2+} salts are more effective than Na^+ at slowing down the polymer diffusion rate, and both metal ions are much more effective than NH_4^+. In the case of the carboxylated latex, this may point to loss of NH_3 during film annealing, regenerating free COOH groups.

Introduction

There has been a substantial interest over the past decade in the diffusion of polymer molecules across interfaces. The key features of interest for homopolymer interdiffusion are the influence of the interface on the kinetics of interdiffusion and the connection between the extent of interdiffusion and the growth of strength of the joint.[3-7] One of the reasons for the broad interest in this topic is that polymer diffusion across interfaces represents the essential feature of a number of technologically important processes. These include the welding of polymer slabs,[8] crack healing,[7] the sintering of polymer powders,[9] strength development during annealing of objects prepared by compression molding of polymer powders,[10,11] and the formation and aging of latex films.[12,13]

From a theoretical point of view, the aspects we understand with greatest confidence include homopolymer interdiffusion and the interdiffusion of miscible pairs.[3-7] The aspect that we understand the least involves the kinetics and extent of mixing between immiscible and partly miscible polymers. Important contributions here include the work of Green and Doyle[14] and Steiner et al.,[15] who examined interdiffusion of protonated and deuterated polymer pairs near the phase separation temperature. They found evidence for thermodynamic slowing down near the critical temperature and limited interdiffusion in the two-phase region of the phase diagram. In both of these examples, the two polymers have virtually identical glass transition temperatures. Thus no effects due to differences in the microscopic friction coefficient on the kinetics of interdiffusion would be expected.

A very different situation is expected in the case of films prepared from latex particles containing a significant amount of polar material at the latex particle surface.[16] This layer will form a separate phase in the newly formed film. In the language of foams, this phase acts as an interconnecting membrane separating cells containing the core polymer of the original latex particles. The membrane in the dry film is composed of a different material than the core polymer. Since it likely has a different T_g, there will be both thermodynamic factors and friction effects contributing to the interdiffusion kinetics.

In contemporary industrial practice,[17] acrylic acid or methacrylic acid is often introduced as a comonomer into the emulsion polymerization with the idea of putting surface acid groups on the latex to enhance its colloidal stability. If the acid content of the particle surface is sufficiently rich, these dispersions will form films with an interconnecting membrane of polar material. It is widely believed in the coatings industry that the presence of these acid groups, for certain applications, enhances the properties of the films formed. Two of the variables that enter into product development in the coatings industry are control over the amount of acid added to an emulsion polymerization reaction, and the timing of its addition to the reaction. Studies of polymer interdiffusion in latex films offer an opportunity to study two aspects of the issue of diffusion kinetics of partially miscible or immiscible polymer pairs: One could examine the ability of the surface polymer to act as a barrier to retard or inhibit interdiffusion of the core polymer, and one could also in principle examine the rate and extent of intermixing of the core and shell polymers in the films.

Recently, a group of Rhône Poulenc in France reported electron microscopy (TEM) and small-angle neutron scattering (SANS) studies of films prepared from poly(styrene-*co*-butyl acrylate) (S–BA) latex containing a shell very rich in acrylic acid.[18] They examined the integrity of the interconnecting membrane by SANS, reswelling the films with D_2O following annealing of the films at 50, 110, and 140 °C. In this system it appears that the membranes remain intact in the dry film until the annealing temperature is well above the T_g of the membrane polymer. For poly(acrylic acid) (PAA), $T_g = 105$ °C, and for poly(sodium acrylate) (PNaA), $T_g = 230$ °C.[18] For films prepared at low pH, the array of membranes was stable when the films were heated 24 h at 110 °C, but their characteristic diffraction peak disappeared when the films were heated at 140 °C. For films prepared at high pH, the membrane array persisted even when the films were annealed at 140 °C. Once the membrane polymer becomes mobile, the membrane breaks up into droplets which

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Table 1. Characteristics of PBMA Latex Particles

	particle size (nm)	$10^5 M_w$ (M_w/M_n)	charge density (μ equiv/g)[a]			parking area (Å^2 per acid)	wt % solids
			Q_s(SO$_4$H)	Q_s(CO$_2$H)	Q_b		
An-MA0	129	4.8 (3.6)	10	0	35	730	30
Phe-MA0	127	4.1 (3.2)	9.9	0	32	750	30
An-MA6	149	4.9 (3.0)	4.2	112	260	55	37
Phe-MA6	146	4.3 (2.6)	4.8	116	270	54	37

[a] Q_s(SO$_4$H) and Q_s(CO$_2$H) are the surface charge densities of sulfate and carboxylate groups, respectively. Q_b is the total content of both acid groups in the latex.

coalesce, and this process brings the core polymers into intimate contact. According to the French group, interdiffusion is suppressed until the membranes break up.

At almost the same time, we reported results on interdiffusion in films prepared from latex particles containing a shell rich in methacrylic acid (MAA).[19] Our results were very different. We observed interdiffusion by energy transfer to occur at the earliest stages of the annealing process. Interdiffusion was retarded by the presence of the acid groups, but not suppressed. The extent of slowing down depended both on the extent of interdiffusion and on the acid content of the original latex. Our material is significantly different in composition from that studied by the French group. It was prepared from a seed of poly(butyl methacrylate) (PBMA) to which a mixture of MAA–BMA was added under monomer-starved emulsion polymerization conditions. In a series of latex particles, the composition of the "shell" polymer did not exceed 9 mol % MAA, but this phase comprised about one-third of the polymer in the latex. Thus our material has a thicker "shell" composed of a material likely to be more miscible with the core polymer than the S–BA–PAA latex examined by the French group.

In the preceding paragraph we placed quotation marks around the word shell to indicate that these latex particles may not have a sharply delineated core–shell structure. Characterizing latex particle morphology is always a very challenging task. From titration experiments on the latex in water we found that nearly half of the acid groups were readily titratable, and thus presumably very close to the surface. The remainder were buried in the latex interior and could be titrated only after dissolution of the freeze-dried latex polymer in an organic solvent.

In the experiments described above, we were able to prepare pairs of particles identical in size, with very similar molecular weights, molecular weight distributions, and surface charge densities, that differed only in the fluorescent chromophore used to label the polymer. One set of particles was labeled with phenanthrene (Phe) groups, which can act as a donor in direct nonradiative transfer (DET) experiments.[20,21] The other set was labeled with anthracene (An) groups, which act as the corresponding acceptor. Each pair of latex allows us to use DET experiments to follow polymer interdiffusion in films prepared from their dispersions.[11,12,21] With several such pairs differing only in surface functionality, we can assess the influence of groups at the latex surface, or in the shell region of the latex, on polymer interdiffusion in latex films.

In this paper, we examine the effect of acid group neutralization on polymer interdiffusion. In the dry film, the salts should form an ionomer phase[22] which will have lower miscibility with PBMA and a higher T_g than in the case where the acid groups are fully protonated. Two types of comparisons should be particularly interesting: first, ammonia vs sodium hydroxide as monovalent neutralizing agents, and second, these bases vs barium hydroxide to assess the effect of mono- vs divalent cations in the ionomer phase.

We compare two pairs of latex. The first, MAO, contains only sulfate groups at the surface. The second pair, MA6, was prepared using the MAO samples as seeds, and the final stage of the emulsion polymerization contains 9 mol % methacrylic acid in the monomer mixture. The mean volume for MAO is 1.13×10^6 nm^3/particle, whereas for MA6 it is 1.75×10^6 nm^3/particle. Thus the carboxylated copolymer represents ca. 35 vol % of the polymer in the particle.

The characteristics of the latex are given in Table 1. One sees that in the MAO samples about one-third of the sulfate groups are titratable, implying that they lie either at the surface or just beneath the surface so that they become neutralized upon exposure to excess base. The rest of the sulfate groups remain buried in the interior of the particle. In the MA6 sample, only about 10% of the sulfate groups are found in the surface region of the latex. There is, however, a significant surface concentration of carboxylic acid groups. About 43% of the COOH groups are to be found in the surface region of the latex. From a slightly different perspective, if the area occupied by a COOH group is 25 Å^2, then half the total surface area of the particle is occupied by carboxylic acid functionality.

Experimental Section

The latex samples MAO and MA6 are the same samples whose synthesis and characterization have been previously reported.[19] Relevant details are given in Table 1. Films were prepared from a dispersion containing an equal number of Phe- and An-labeled particles. To this mixture (0.30 g) was added a known amount of base, either aqueous ammonia or sodium or barium hydroxide, and the sample was allowed to stand for ca. 30 min at room temperature. Except in one experiment, the amount of base was chosen to be equal to the amount of titratable acid groups, referred to as Q_s in paper 1 in this series.[19] A few drops of dispersion were placed on a small quartz plate (ca. 5 mm × 10 mm) previously warmed on a hot plate to 32 °C. A Petri dish was inverted over the film to slow down the drying process. Drying occurred over a period of ca. 4 h to yield transparent and void-free films 30–50 μm thick. To anneal films for short periods of time, the quartz substrates supporting the films were placed directly on a high-mass aluminum slab inside a convection oven prewarmed to 100 ± 1 °C. For films annealed for longer periods of time, steps were taken to prevent polymer and chromophore oxidation. The films were placed inside small test tubes which were sealed with septa. Using flowing gas and syringe needles, an argon atmosphere was introduced into the test tube, and the test tube was placed into the oven at 100 °C. Samples were removed from the oven and cooled to room temperature for fluorescence measurements.

Samples for fluorescence decay measurements were placed in a small quartz test tube under an argon atmosphere. Decay profile measurements were carried out using the single photon timing technique[23] as described previously.[12,21] Phenanthrene decay profiles were monitored at 366 nm, with $\lambda_{ex} = 300$ nm. Decays were fitted to the expression

$$I(t') = A_1\left[\exp\left(-\frac{t'}{\tau_D} - P\left(\frac{t'}{\tau_D}\right)^{\beta}\right)\right] + A_2\exp\left(-\frac{t'}{\tau_D}\right)$$

with $\beta = 0.5$, and integrated as described in ref 19. Since here we are only interested in the integrated area under the $I(t')$ pro-

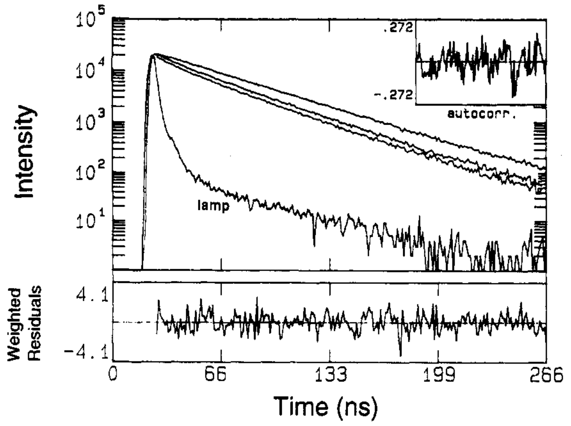

Figure 1. Representative fluorescence decay traces measured at room temperature for a film of MA6 (neutralized with 1 equiv of NaOH based upon titratable acid), as initially prepared (top) and annealed for various amounts of time at 100 °C: (middle) 60 min; (lower) 130 min. These curves are fitted to the expression given in the Experimental Section. Weighted residuals and their autocorrelation for the uppermost curve are displayed in the figure. The fitting parameters are not accorded any specific meaning; rather, the curves are integrated to obtain the areas as described in ref 19.

file, i.e., the total fluorescence intensity,[19,21] no meaning is associated with the individual parameters obtained from each decay curve.

Results and Discussion

All of the latex films prepared were transparent and free of cracks. Fluorescence decay measurements were carried out on these samples as a means of assessing the extent of energy transfer in each film as a function of its annealing history. Films prepared from a dispersion of Phe-labeled particles exhibit an exponential decay profile with a lifetime (τ) of 44.5 ns when excited at 300 nm. It is for this reason that Phe is chosen as the donor in our DET experiments. Films prepared from a mixture of Phe- and An-labeled particles exhibit a small fast component to the decay followed by a long exponential tail with the same lifetime as that found in films containing only the Phe chromophore. In these nasecent films, this fast component is due to energy transfer across the interparticle boundary.[12b,21] Energy transfer is a fluorescence quenching process. As a consequence, the total intensity of Phe fluorescence in the presence of An is smaller than in its absence.

Data Analysis. While the extent of quenching is in principle available through steady-state fluorescence measurements,[24] various artifacts make these measurements unexpectedly difficult. A much more reliable approach involves integrating the Phe fluorescence decay profiles $I_D(t')$ after first normalizing them to unit intensity at $t' = 0$.[21]

$$\text{area} = I = \int_0^\infty I_D(t')\,dt' \qquad (1)$$

In this way one can monitor the extent of energy transfer in any latex film sample, without assuming a specific model to parameterize the $I_D(t')$ decay profile.[25] One only has to compare areas under the respective decay profiles to monitor the increase in energy transfer due to polymer interdiffusion. Thus we calculate the volume fraction of mixing f_m from the expression

$$f_m = \frac{\text{area}(t) - \text{area}(0)}{\text{area}(\infty) - \text{area}(0)} \qquad (2)$$

Representative decay profiles are presented in Figure 1.

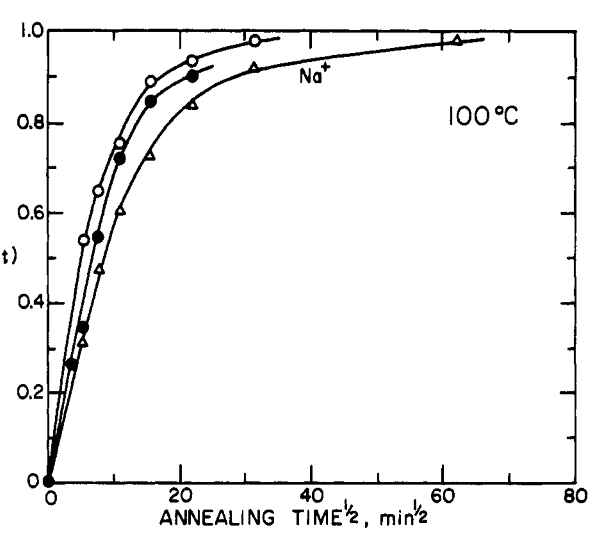

Figure 2. Plot of f_m vs the square root of annealing time for latex films of MA0 annealed at 100 °C: top curve, films prepared from ion-exchanged latex, with all the exchangeable sulfate groups in the protonated form; middle curve, latex sample treated with aqueous NH_3, 1 equiv based upon titratable sulfate groups; lower curve, latex sample treated with the same quantity of NaOH.

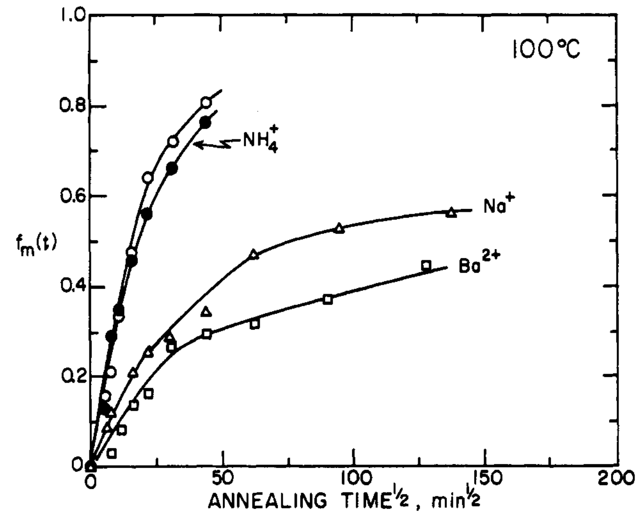

Figure 3. Plot of f_m vs the square root of annealing time for latex films of MA6 annealed at 100 °C: top curve, films prepared from ion-exchanged latex; upper middle curve, latex sample treated with aqueous NH_3; lower curves, latex sample treated with NaOH and $Ba(OH)_2$, respectively.

There are two time scales in this experiment. $I_D(t')$ measures events which occur on the time scale (t') of nanoseconds. Each $I_D(t')$ profile provides a snapshot of the system following annealing of a sample for a time t at a temperature T. The term f_m measures the degree of polymer interdiffusion which occurs on the time scale (t) of minutes, hours, or days.

Polymer Interdiffusion. Values of f_m, obtained for latex film samples of MAO annealed different periods of time at 100 °C, are presented in Figure 2. The data are plotted as a function of $t^{1/2}$ to emphasize that the major portion of the interdiffusion does indeed follow a square root of t dependence.[8] The uppermost curve is that obtained from a film prepared from ion-exchanged latex. The middle curve is from a film sample prepared from latex fully neutralized with ammonia, and the lowermost curve is obtained from a film sample in which the surface acid groups have been neutralized with NaOH. It is clear that neutralization of acid groups slows down polymer interdiffusion.

In Figure 3 we present similar data obtained for latex films prepared from samples of MA6 and annealed at 100 °C. Comparison of Figures 2 and 3 reveals that polymer interdiffusion is noticeably slower for the MA6 film sample prepared from ion-exchanged latex than for the corresponding MAO film. The carboxyl groups at the latex surface act to slow the polymer diffusion. These results are consistent with those reported previously for experiments carried out at 90 °C for the complete series of carboxylated latex.[19] Acid group neutralization with ammonia has a small effect on retarding polymer diffusion. In this respect it resembles the effect of ammonia on the MAO films. Sodium hydroxide, however, has a more pronounced effect on polymer diffusion, and that due to barium hydroxide is even more severe. Not only has diffusion slowed markedly but deviations from the linear dependence of f_m on $t^{1/2}$ occur much sooner.

Diffusion Coefficients. To proceed with the analysis, we need to be able to compare rates of interdiffusion among the various experiments carried out. The most appropriate way of making these comparisons is to calculate diffusion coefficients from the mixing data. In films prepared from multicomponent latex, we expect a distribution of diffusion coefficients. This distribution will reflect the compositional heterogeneity in the system, i.e., the fraction of carboxylic acid or carboxylate groups in each polymer, as well as the molecular weight distribution in the sample. Based upon our previous experiments,[19] we also expect the diffusion of PBMA through an acid-rich phase or an ionomer phase will also contribute to a slowing down of the PBMA homopolymer diffusion. Thus the diffusion coefficients calculated by fitting the f_m data to any diffusion model will not have the same rigorous meaning as measures of the self-diffusion coefficient in a monodisperse homopolymer sample. Following arguments discussed previously,[12,21] we fit the data to a spherical diffusion model which satisfies Frick's laws of diffusion[26]

$$\frac{\partial C(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial C(r,t)}{\partial r}\right) \qquad (3)$$

so that at time t we have

$$C(r,t) = \frac{C_0}{2}\left\{\mathrm{erf}\left(\frac{R+r}{2(Dt)^{1/2}}\right) + \mathrm{erf}\left(\frac{R-r}{2(Dt)^{1/2}}\right)\right\} - \frac{C_0}{r}\left(\frac{Dt}{\pi}\right)^{1/2}\left\{\exp\left(\frac{(R-r)^2}{4Dt}\right) - \exp\left(-\frac{(R+r)^2}{4Dt}\right)\right\} \qquad (4)$$

D values are calculated by equating f_m with the fractional mass which has diffused across the interface, M_t/M_∞, where M_∞, where $M_\infty = (4/3)\pi R^3 C_0$, and carrying out a numerical integration to find the best D value which satisfies the equation

$$M_t = M_\infty - \int_0^R C(r)(4\pi r^2)\,\mathrm{d}r \qquad (5)$$

Note that these are cumulative diffusion coefficients which describe the time necessary for the system to achieve a certain extent of mixing.

D values calculated in this way from the data in Figure 1 are presented in Figure 4. For the ion-exchanged sample, whose sulfate groups are in the protonated form, D values are approximately constant over the entire range of f_m and have a magnitude of 2×10^{-15} cm^2 s^{-1}. The corresponding film with the sulfate groups present as the NH_4^+ salt are characterized by a somewhat smaller D value, 1.5×10^{-15} cm^2 s^{-1}. When the latex surface sulfate groups are present as the sodium salt, diffusion is slowed even further.

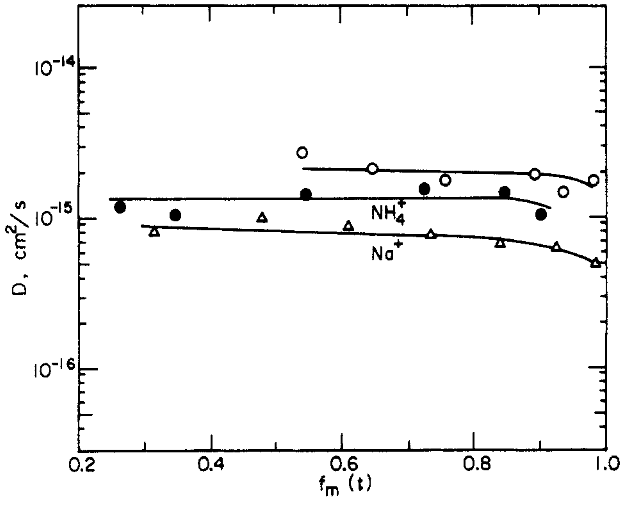

Figure 4. Plot of D values calculated from the data in Figure 2 for the MA0 samples as a function of f_m.

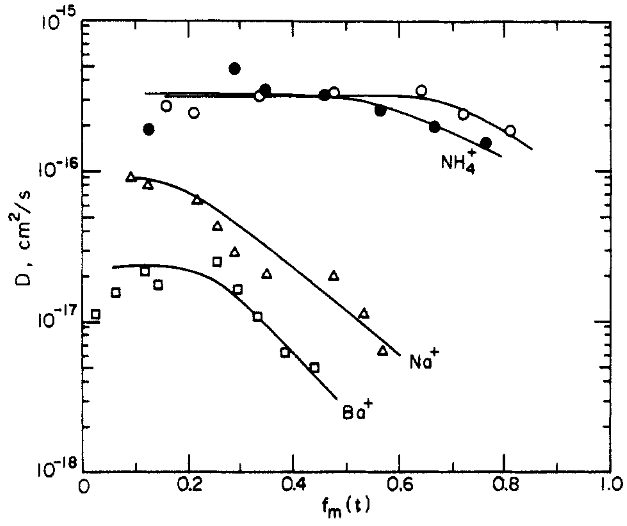

Figure 5. Plot of D values calculated from the data in Figure 3 for the MA6 samples as a function of f_m.

Here $D = 8 \times 10^{-16}$ cm^2 s^{-1} and exhibits a slight downward curvature at large extents of intermixing.

D values for the carboxylated latex films are shown in Figure 5. As anticipated from the data in Figure 3, the diffusion coefficients of the polymers with acid groups present in the protonated form and those present as the ammonium salt are essentially identical at early stages of the interdiffusion. Their magnitude, 3×10^{-16} cm^2 s^{-1}, is nearly an order of magnitude smaller than that for the MAO films shown in Figure 4. There is a certain amount of scatter in the latter set of data for $f_m < 0.4$, but for more extensive interdiffusion two differences are apparent. First, there is a trend toward decreasing D with increasing f_m. Second, the film prepared from ammonia–neutralized acid groups also exhibits a further decrease in D at $f_m \geq 0.5$.

In the case of the sodium carboxylate films, one observes not only a further decrease in D compared to the film sample with protonated carboxyl groups but also a very pronounced decrease in D throughout the interdiffusion process. Here D decreases from ca. 1×10^{-16} cm^2 s^{-1} in the initial stages of annealing to 7×10^{-18} cm^2 s^{-1} at $f_m = 0.6$. Diffusion is retarded even further in the case of the barium carboxylate films. The initial D value is ca. 10^{-17} cm^2 s^{-1} and appears to increase before decreasing. There differences in D values in the early stages of interdiffusion in the case of the barium salts may well be within experimental error. The major conclusion to be drawn from

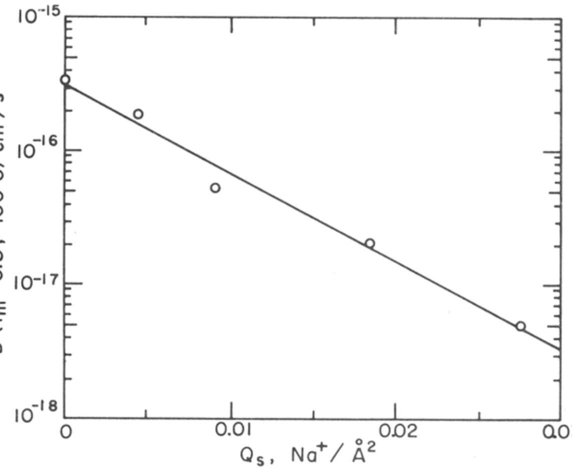

Figure 6. Plot of D values for films prepared from MA6 as a function of the amount of NaOH added to the dispersion prior to film formation. The x-axis is in units of number of Na^+ ions per Å² of latex surface area. The amounts of base added correspond to 0, 25, 50, 100, and 150% of the number of moles of titratable acid groups in the latex.

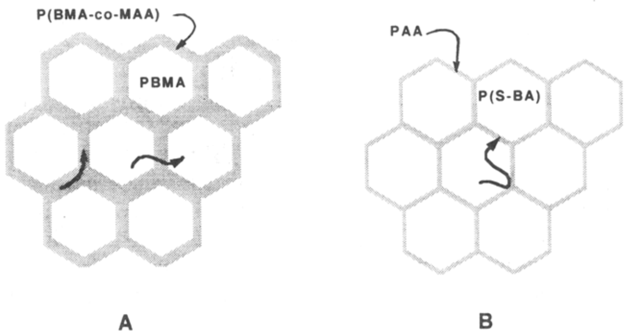

Figure 7. Drawings of a cross section of films prepared from (A) MA6 and (B) the P(S–BA) latex described by Joanicot et al. in ref 18. We depict the thicker shell of lower acid group content in the film A. Interdiffusion begins instantaneously at 100 °C, both across and within the polar interphase. In film B, the interphase, has a much higher T_g than the P(S–BA) core. Interdiffusion is suppressed until the film temperature exceeds T_g of the interphase.

these data is that neutralization of the carboxylic acid groups at the latex surface with NaOH or $Ba(OH)_2$ induces a pronounced decrease in the interdiffusion rate and that the divalent Ba^{2+} salts are more effective than Na^+ at retarding interdiffusion.

Another interesting question is how the interdiffusion rate depends upon the amount of base added to the latex dispersion prior to film formation. We prepared a series of films from samples of MA6 treated with various amounts of NaOH. These amounts correspond to ca. 25, 50, 100, and 150% of the moles of titratable acid groups (Q_b) in the system. To make comparisons among these experiments, each system should be examined at a similar extent of interdiffusion. In Figure 6 we plot D values obtained at f_m = 0.5 for these five samples, where the x-axis represents the number of Na^+/CO_2^- groups per square angstrom of surface area of latex.

One sees that the cumulative D values decrease with increasing extent of neutralization, and when the data are plotted in this way, the dependence appears to be linear. It is interesting to note that there is no break in the data corresponding to the sample to which the largest amount of NaOH was added. Here a 50% excess of NaOH was added over the number of titratable COOH groups, indicating that carboxyl groups initially buried within the latex are neutralized and that these ionic groups make a similar contribution to retarding interdiffusion as those groups at the particle surface.

A final point concerns the effect of ammonia as the base used to neutralize surface acid groups in the latex dispersion. In Figure 4 we see that neutralization of the sulfate groups in MAO with ammonia leads to a small decrease in D values. This effect is significant and remains significant throughout the film annealing. For this reason, we infer that ammonia is not driven off as the film dries. In this sample there are only a small number of NH_4^+–OSO_3^- groups in the boundary region of the film. Thus the effect of ammonium salt formation on interdiffusion rates is relatively small.

In the case of the carboxylated latex, Figures 3 and 5, the effect of ammonia is even smaller. Here the local concentration of carboxyl groups in the latex and in the film is rather large. The absence of a significant effect of NH_3 on polymer D values points to a tendency for the ammonium groups to dissociate. This might occur upon drying or annealing of the film. The net effect would be for ammonia to evaporate, regenerating MAA groups in the film in their protonated form. Some differences are seen in the diffusion kinetics between films prepared from NH_3-neutralized latex and those prepared from ion-exchanged latex. This difference may point to incomplete loss of NH_3 from the film during annealing.

This contrast in behavior, whereby NH_4^+ carboxylate groups in the film dissociate and NH_4^+ sulfate groups persist upon annealing, is related to the strength of the conjugate acids, and is consistent with the thermal stability of corresponding simple ammonium salts in the dry state.[27]

Summary and Conclusions

The experiments reported here examine interdiffusion in films prepared from latex dispersions of PBMA particles. One set of particles (MA6) has a surface region rich in polar groups, carboxylic acid groups introduced as a BMA–MAA copolymer, and its salt formed by neutralization by inorganic bases. This phase comprises 35% of the polymer in the latex. The other latex material (MA0, the seed from which MA6 was prepared) contains only a small fraction of sulfate groups at the particle surface.

In all samples, but particularly MA6, we find that polymer interdiffusion begins as soon as the films are heated to 100 °C. In these samples, the polar component serves to slow down interdiffusion. Neutralization of the carboxyl functions retards further the rate of interparticle polymer diffusion. Diffusion is also apparent at 90 °C, but it is very slow. This result appears to be quite different from that reported by Joanicot et al.[18] for P(S–BA) latex films in which the original latex had a much thinner shell of poly(acrylic acid) or poly(sodium acrylate) much richer in polar groups.

We present a drawing in Figure 7 in which we compare latex film prepared from MA6 with that of a styrene–butyl acrylate film of the sort examined by the French group. They found no interdiffusion until they raised the film temperature well above the T_g of the surface polymer. In their system, if the film morphology is as shown in Figure 6, there should be a large difference between the T_g's of the core polymer (ca. 65 °C) and the polar shell (106 °C for PAA, 230 °C for PNaA). Thus Joanicot et al.[18] picture the film as a foam of liquid polymer droplets separated by a rigid membrane that breaks up once its T_g is exceeded. In MA6, the carboxyl content of the third-stage polymer is 9 mol %. We can estimate the T_g of this phase using the Flory–Fox equation and find values near 40 °C for the films formed at low pH[19] and not much above 50 °C for films formed from the neutralized dispersions. Both phases would be expected to be mobile at 100 °C. Thus our results and those of Joanicot et al.[18] are in fact consistent with one another.

Two additional aspects of our observations are noteworthy. First, in every case, the extent of interdiffusion is always very high. Since both the PBMA homopolymer phase and P(BMA-*co*-MAA) phase were labeled identically with Phe or An groups, this result does not necessarily mean that the homo- and copolymer phases are completely miscible, but rather that the individual phases on adjacent particles are able to interdiffuse. Second, the kinetics of mixing involves a fast component which persists for a certain fraction of the extent of intermixing and then undergoes a decrease. In terms of cumulative D values calculated from the data, these remain constant over much of the early time interdiffusion and then exhibit a decrease. These results are consistent with a distribution of diffusion coefficients in the system. Both the initial rate of interdiffusion and the magnitude of the decrease depend upon the number of carboxyl groups and their state of neutralization. Metal ions ($Ba^{2+} > Na^+$) are more effective than NH_4^+ at retarding diffusion.

We are unable at this point to distinguish T_g effects from thermodynamic effects as the origin of the decrease in diffusion rates. If we assume that the early time diffusion is due to mixing of PBMA homopolymer which has to diffuse through an acid-rich or ionomer phase, it may very well be the magnitude of the local friction coefficient rather than the χ-parameter that plays the larger role. We have some indication that D values can be scaled by functions of $(T - T_g)$.[28] This will be the subject of a future publication.

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References and Notes

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(25) In actual practice, we fit $I_D(t')$ to the stretched exponential expression presented in the Experimental Section and used in our previous experiments.[12,19,21] Its integral is given in ref 19. One might think that one could arbitrarily fit $I_D(t')$ to any easily integratable expression such as a sum of exponentials to obtain the requisite areas. Based upon extensive simulations, we have come to appreciate that sums of exponentials are particularly sensitive to a scattered light component in the detected signal. It turns out to be more reliable to correct for light scattering when the fitting function is smoothly varying at early times in the decay profile where scattering of the excitation source may be important.

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