...g$^+$tg$^-$...: and the remaining all-trans portion of the chain. When the data from Table I, 90.0 and 200.4 GPa for the kink B chain and the all-trans modulus, respectively, are used, eq 3 yields 28.9 GPa for the bare modulus of the three -bond kink sequence. This indicates that the kink defect yields an element about 7 times more elastic than that of the all-trans structure. The bare defect modulus effectively includes all changes in the deformational response of the zigzag segment that were brought about by an introduction of the defect into the segment.

Very little information is available on the moduli of chains with conformational defects. An unrealistically high modulus of 245 GPa was calculated[22] for the three-bond kink defect assuming a strictly symmetrical (i.e., $\phi_3 = -\phi_5$) deformation of torsional angles. Using the original parametrizaton of Boyd's method, Reneker and Mazur[9] calculated moduli in the range of 30–70 GPa or several six- or seven-bond crystallographic defects characterized by a full reentry of the chain ends into the lattice points of the original all-trans chain. It is our expectation that calculations of moduli for the some additional segments involving torsional defects will be useful in the interpretaton of the mechanical properties of polymeric materials.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research, Grant No. 88-001.

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Registry No. Polymethylene, 25038-57-7; hexadecane, 544-76-3.

Molecular Aspects of Latex Film Formation: An Energy-Transfer Study[1]

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ABSTRACT: Poly(butyl methacrylate) (PBMA) latex labeled with either phenanthrene or anthracene derivatives in low concentrations (1 or 2 mol %) was prepared by semicontinuous emulsion polymerization. The latex film formation process was studied by analysis of the nonradiative energy transfer from phenanthrene (donor) to anthracene (acceptor). Initially, when the latex film dries, there is little energy transfer, indicating that the particles conserve their individual identity. With increasing time at temperatures above the glass transition temperature of PBMA, the extent of energy transfer increases. This is a clear indication that interdiffusion of polymer chains across particle boundaries occurs. The diffusion coefficient D of the polymer was evaluated by using models based upon Fick's second law. In each sample, the magnitude of D decreases with time. Initial D values increase with increasing temperature, taking values between 1×10^{-14} to 1×10^{-18} cm^2/s, yielding an apparent activation energy of 38 kcal/mol. The diffusion data also fit well to the Williams–Landel–Ferry equation. The results demonstrate the great potential of fluorescence techniques in the study of polymer diffusion processes during latex film formation.

Introduction

The topic of film formation from aqueous latex dispersions is of both fundamental and technological importance.[3,4] Recent concern about the deleterious environmental impact of solvent-based coatings has led to an even more intense effort to develop high-performance coatings based upon aqueous dispersions. Much of the early work on latex film formation focused on the early stages of the process: particle concentration accompanying water evaporation followed by particle coalescence and deformation to produce continuous and transparent films.[5,6] Particle deformation occurs only above a certain temperature, the minimum film formation temperature (MFFT), which is usually close to the glass transition temperature of the polymer.

The drying of aqueous latex to produce a film usually takes from several minutes to several hours, depending on the film thickness and the environmental conditions. After this period, both film aspect and film properties often improve with time.[7,8] This phenomenon is referred to as "further coalescence". One explanation of this process is the interdiffusion of polymer chains across particle

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boundaries.[9] There is indirect experimental evidence for interparticle polymer diffusion. For example, it serves to explain the improvement of the mechanical and permeation properties of latex films. In many cases, one also observes by transmission electron microscopy (TEM) the disappearance of the individual particle contours with time.[10] In some instances, however, particle boundaries persist.

The TEM studies by Kanig et al.[11,12] clearly demonstrate that for some latex films, particle contours do not disappear, even for films aged for over a year. This extraordinary observation is perturbing. It leads one to question whether polymer diffusion across the particle boundary actually occurs in these cases. If polymer diffusion takes place under some circumstances but not under others, what are the determining factors?

To answer this question, one needs experimental methods for following the diffusion of polymer molecules across the particle boundary. There are two obvious approaches to this problem. On one hand, one could prepare deuterated latex, mix it with perprotio latex, and follow the diffusion of the deuterated polymer by small-angle neutron scattering (SANS). Alternatively, one could prepare one batch of latex labeled with a small amount of one fluorescent dye (the donor, D), prepare another batch of latex labeled with a second dye (the acceptor, A), and study polymer diffusion by direct nonradiative energy transfer (DET) measurements.

Hahn et al.[13,14] recently reported their studies by SANS of a poly(butyl methacrylate) (PBMA) latex system. They studied films prepared from very small particles (ca. 60 nm in diameter), some of which were deuterated. By following the radius of gyration of the deuterated latex particles, they were able to show that polymer chains did diffuse across the particle boundaries. Both the temperature for film formation and the degree of cross-linking of the polymer had a large impact on the extent of polymer diffusion in the film. More recently, Sperling and co-workers[15] have used the SANS technique to examine film formation at elevated temperatures from polystyrene particles. They, too, observed the growth in radius of gyration of deuterated particles, consistent with polymer diffusion.

We have carried out a preliminary study using DET measurements of polymer diffusion during film formation from micron-size poly(methyl methacrylate) (PMMA) particles labeled with donor and acceptor groups.[16] The particles were prepared by nonaqueous dispersion polymerization.[17] Films were formed below the MFFT to give turbid or opaque coatings which were subsequently heated. These experiments did detect interparticle polymer diffusion and serve to establish the validity of the DET measurements applied here to the study of latex film formation. They were not, however, focused on the central issues raised in the opening paragraph of this paper.

These DET measurements are based upon the pioneering experiments of Morawetz and co-workers,[18] who showed how steady-state fluorescence measurements of nonradiative energy transfer can be used to study interface structure in polymer blends and also to examine various types of polymer diffusion. We have used various fluorescence techniques, including energy transfer, to study morphology in polymer colloid systems.[19] These techniques are very adaptable to the study of diffusion in latex film formation. In order to avoid problems associated with radiative energy transfer, the method we have developed relies on fluorescence decay measurements.

Table I
Emulsion Polymerization Recipe and Conditions

seed		second stage	
water	45.0 mL	water	20.0 mL
BMA	3.25 mL	KPS	0.0361 g
KPS	0.0428 g	SDS	0.4722 g
$NaHCO_3$	0.0816 g		
SDS	0.0810 g	PheMMA	0.4460 g
		BMA	24.0 mL
temp	80 °C	temp	80 °C
time	1 h	time	19 h

In this paper we report on the application of nonradiative direct energy transfer techniques to study the film formation process for an aqueous PBMA latex system. We are able to confirm that polymer chain diffusion does occur and is prominent in the process of "further coalescence". Diffusion coefficients are obtained by fitting the data to a diffusion model, and values, over a range of temperatures, show an apparent activation energy of 38 kcal/mol. These data are in accord with predictions of the Williams–Landel–Ferry (WLF) equation.

Experimental Section

(9-Phenanthryl)methyl methacrylate (PheMMA) was prepared by reacting phenanthrylmethanol (from reduction of 9-phenanthracenecarboxaldehyde, Aldrich) with methacryloyl chloride in dry THF in the presence of dry triethylamine.[20] The product was recrystallized twice from cyclopentane, mp 75–76 °C.

The preparation of (9-anthryl)methacrylate (AnMA) from anthrone (Aldrich) and methacryloyl chloride is novel to this work. Anthrone (5 g, 25.7 mmol) was dissolved in a mixture of dried pyridine (10 mL) and dried THF (15 mL) by warming at 35 °C under argon (base promotes stabilization of the enol form[21]) and then stirred at room temperature overnight. To this cloudy solution was added dropwise 3.5 mL (31.3 mmol) of methacryloyl chloride over 1 h. The mixture was warmed to 50 °C (10 min) and then stirred at room temperature for another 2 h. After water (20 mL) was added, the reaction mixture was extracted repeatedly with diethyl ether, and the etheral solution was washed several times with 5% aqueous HCl, 5% Na_2CO_3, H_2O, and saturated NaCl and subsequently dried over magnesium sulfate. After evaporation of diethyl ether, the crude product was purified by column chromatography (silica gel Kieselgel 60, Merck) with benzene as eluent. The product was collected as the first band off the column and recrystallized twice from 95% ethanol to yield pale yellow crystals (17%), mp 139–140 °C. Calcd for AnMA ($C_{18}H_{14}O_2$): C, 82.4; H, 5.385. Found: C, 82.32; H, 5.46. Mass spectrum: *m/e* 262 (M^+), 193, 165, 139, 115. IR peaks: 1736, 1125 cm^{-1}. 60-MHz ^1H NMR in $CDCl_3$: δ 2.21 (s, 3 H, CH_3), 5.90 (s, 1 H, =CH), 6.66 (s, 1 H, =CH), 7.33–8.30 (m, 9 H, aromatic H).

BMA monomer was vacuum distilled immediately before use. Potassium persulfate (KPS) (>99%, Aldrich) and sodium dodecyl sulfate (SDS) (98%, Aldrich) were used as received. Sodium bicarbonate was used as a buffer.

Emulsion copolymerizations of BMA and PheMMA or AnMA were carried out by a two-step seeded polymerization technique.[22] A latex seed was first prepared by using a small fraction of pure BMA. The rest of the surfactant and initiator in water plus the fluorescent monomer in BMA was then added continuously into the reactor. The recipe and polymerization conditions are given in Table I.

The final latex particle size was measured by photon correlation spectrometry (Brookhaven Instruments Model BI-90 particle sizer). Molecular weights were determined by GPC (Waters Styragel columns, THF as eluent, monodisperse PMMA samples as standards) coupled with tandem refractive index and fluorescence detectors. The latter also served as a means of monitoring the product for the presence of unreacted fluorescent monomers (FLM). Under the experimental conditions given above, no detectable amount of unreacted FLM (<0.1% of the total FLM) was present in the samples examined here. The particle sizes of the latexes and the molecular weights of their constituent polymers are given in the Results and Discussion section.

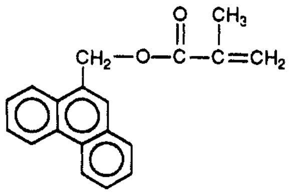
Polymer latex films (ca. 50 μm thick) were first formed by drying a thin layer of aqueous latex on a clean quartz plate (dimensions: 12 mm × 20 mm × 2.5 mm) at room temperature (22 °C). The drying process takes ca. 20 min. The quartz plate supporting a latex film was inserted into a quartz tube of ca. 12 mm in diameter and sealed with a rubber septum. The quartz tube was then purged with oxygen-free nitrogen for at least 10 min before the fluorescence decay profiles were measured. The quartz plate was then tempered at a chosen temperature (between 50 and 124 °C) for a certain time (4 min to 16 days). An oven (VWR Scientific Inc.) was used to control the temperature. Humidity was not controlled; further studies will take this parameter into account.

Fluorescence decay profiles were measured by using the time-correlated single-photon-counting technique.[23] The excitation wavelength was 298 nm and the emission wavelength 366 nm for phenanthrene. A band-pass filter (transparent at 320–390 nm) was mounted in front of the phototube detector in order to minimize light scattering. Fluorescence decays were fitted to eq 4; see below. All fits have a χ^2 value less than 1.3. Details of the model for curve fitting will be discussed in the following sections.

Results and Discussion

Latex Synthesis. The synthesis of fluorescent-labeled latex particles by free-radical emulsion polymerization poses four different types of problems: (i) stability of the dye under the reaction conditions, (ii) solubility of the dye in the aqueous medium and in the polymer matrix, (iii) parasitic influences of the dye derivative on the free-radical polymerization process, and (iv) the possibility of unreacted dye comonomer or other low molecular weight fluorescent species present in the system at the end of the reaction. In these experiments, only problems iii and iv proved troublesome. To avoid the possibility of unreacted fluorescent monomer, we employed a relatively high initiator concentration.

The most serious problem we faced was the tendency of dye comonomers containing allylic hydrogens (e.g., 1, 2) to act as chain-transfer agents. This turned out not to be problematic for 1, but our initial experiments with 2 led to cross-linked particles. As a consequence, we synthesized 3, previously unreported, and found that it allowed us to prepare the An-labeled particles needed for these experiments.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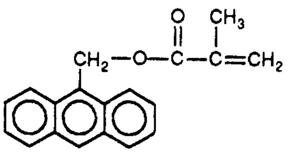
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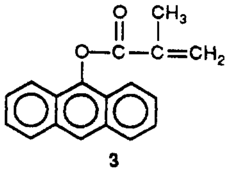
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Latex Characterization. Figure 1 shows the GPC chromatograms of the two latex polymers labeled with 1 mol % of PheMMA (PPheMMA-BMA, upper curves) and 2 mol % of AnMA (PAnMA-BMA, lower curves), respectively. The polymers were isolated by directly freeze-drying the corresponding aqueous latex dispersions and dissolving the solid in THF. The absence of a peak at ca. 17 min of elution time detected by the fluorescence detector indicates that we have a complete incorporation of the FLM into PBMA. This is essential for the interpretation of the data in terms of polymer chain diffusion. There is a small shoulder on the high molecular weight side of the refractive index signal of PPheMMA-BMA, not seen by the fluorescence detector. This peak probably derives from the seed polymer. The peaks at 18.5 and 19.5 min detected by the refractive index detector could be due to the surfactant and other residues present in the latex. We calculate molecular weights of M_w = 440 000 and M_n = 87 000 for PPheMMA-BMA and M_w = 420 000 and M_n = 96 000 for PAnMA-BMA, based upon monodisperse PMMA standards. The two latexes have an average diameter of 110 nm as measured by photon correlation spectroscopy.

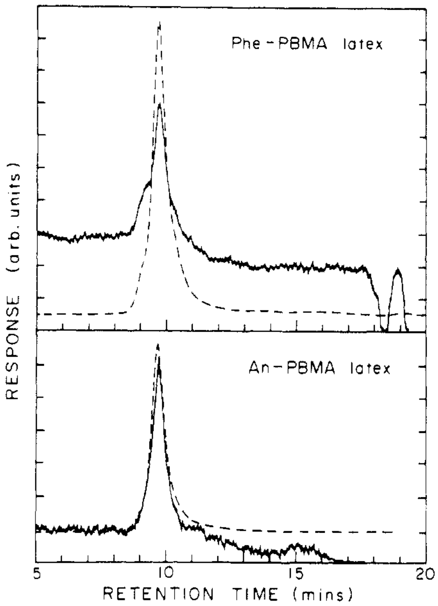

Figure 1. GPC chromatograms in THF solution of PheMMA-labeled PBMA (upper curves) and AnMA-labeled PBMA (lower curves): (- - -) fluorescence detector; (—) refractive index detector.

Spectroscopy. When phenanthrene is excited at a wavelength of 290–300 nm, the decay of the fluorescence emission (340–400 nm) follows a first-order mechanism. That means the fluorescence intensity decreases exponentially with time following a pulsed excitation as described by eq 1. A typical decay profile of the PheMMA-labeled PBMA is shown in Figure 2. The fluorescence lifetime (τ_0) is 45.4 ns.[24]

$$I(t) = I(0) \exp(-t/\tau_0) \quad (1)$$

In the presence of an energy acceptor (A), anthracene in this case, whose absorption spectrum overlaps the emission spectrum of the donor (D) phenanthrene, nonradiative energy transfer occurs. This process depends upon a dipole–dipole interaction between D* and A. When the excitation duration is sufficiently brief that the random distribution of distances from D* and A is not significantly perturbed, the decay of the donor fluorescence can be described by the following equation:[25,26]

$$I(t) = I(0) \exp[-(t/\tau_0) - \beta(t/\tau_0)^{1/2}] \quad (2)$$

where $I(0)$ is the fluorescence intensity at time zero, τ_0 is the fluorescence lifetime of the donor in the absence of

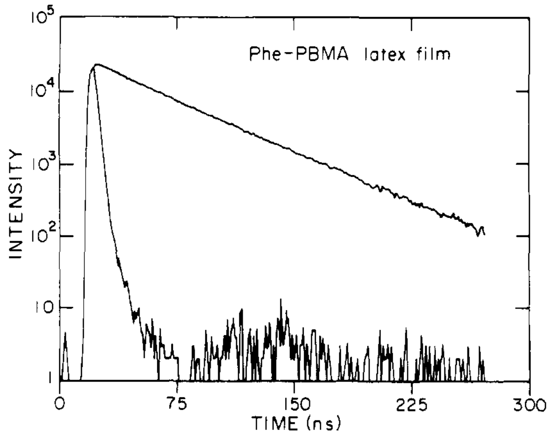

Figure 2. Fluorescence decay profile of PheMMA-labeled PBMA latex film. τ_0 = 45.4 ns.

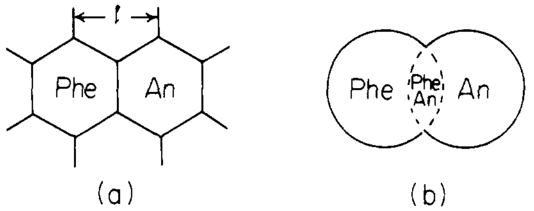

Figure 3. Conception of the mixing region caused by diffusion during latex film formation.

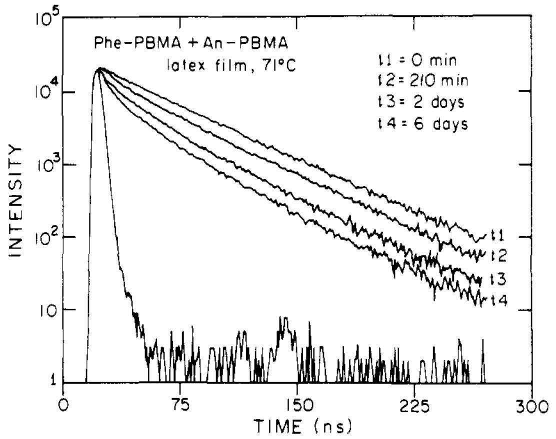

Figure 4. Fluorescence decay profiles of PBMA latex films annealed at 71 °C for different times.

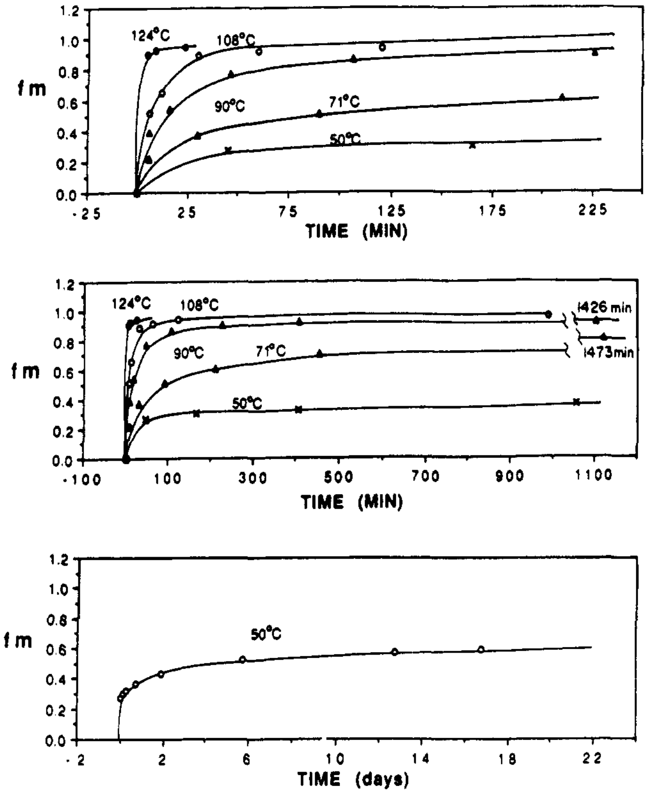

Figure 5. Volume fraction of mixing (f_m) as a function of time at different temperatures.

acceptor, and β is defined as

$$\beta = 4N_A R_0^3 \pi^{3/2}[A]/3000 \qquad (3)$$

where N_A is Avogadro's number, and [A] is the acceptor concentration in moles/liter. This expression presumes a globally uniform distribution of D and A in three-dimensional space.

When we mix an equal amount of PheMMA-labeled latex and AnMA-labeled latex to form a film, the degree of energy transfer will be very low and will occur only in the interfacial regions if there is no polymer chain diffusion across particle boundaries. If there is polymer chain diffusion (cf. Figure 3), the fluorescence decay of the donor will have two contributions characterizing respectively the mixed region where energy transfer occurs and the unmixed region where energy transfer does not occur:

$$I(t) = B_1 \exp[-(t/\tau_0) - \beta(t/\tau_0)^{1/2}] + B_2 \exp(-t/\tau_0) \qquad (4)$$

The volume fraction of mixing (f_m) can be calculated by the expression

$$f_m = B_1/(B_1 + B_2) \qquad (5)$$

We derive eq 5 in the Appendix.

In Figure 4 are shown a series of decay profiles, measured at various times, for a polymer latex film annealed at 71 °C. At time zero, which corresponds to a film formed at room temperature after water evaporation, the decay is almost singly exponential. A small amount of energy transfer can be detected. When the decay curve is fitted to eq 4, the fraction of mixing, f_m, is very small (3.4%).

With increasing time for film formation, the fluorescence decay becomes faster as a result of energy transfer. This signifies that mixing of PheMMA-labeled polymer chains and AnMA-labeled polymer chains is taking place. The increase of fluorescence decay rate is accompanied by a decrease of the fluorescence intensities of the energy donor. The decay curves fit well to eq 4.

In Figure 5, we present a plot of f_m versus time for film formation at different temperatures. Temperature has a dramatic influence on the film formation process. The higher the temperature, the faster the rate of mixing. At 124 °C, it takes only 23 min for 90% of the particle volume to mix. At 50 °C, which is much closer to the glass transition temperature (T_g) of PBMA (T_g = 27 °C), it takes more than 16 days to achieve 58% mixing.

The results in Figure 5 are very important. They demonstrate that polymer chains from different particles do indeed diffuse across particle boundaries, provided the temperature is high enough and the time is long enough. This type of molecular-level information cannot be obtained from electron microscopy or permeativity measurements.

Polymer Diffusion. The results described above demonstrate that polymer diffusion across the particle boundary takes place. To obtain quantitative information, we must fit these data to a model describing the diffusion. Several models are possible, and the problem is made more delicate by the expected molecular weight dependence of

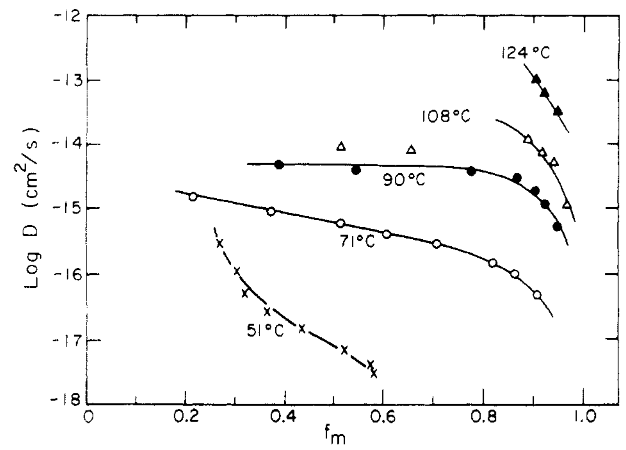

Figure 6. Diffusion coefficient D as a function of f_m at different temperatures.

the polymer self-diffusion coefficient, coupled with the polydispersity in molecular weight of the samples. This problem is common to all studies of latex film formation, and it is clear that in the long term, one will have to pay considerable attention to the issue of which model and what type of data analysis best describe the physics of the coalescence process.

Here we fit our data to a spherical diffusion model.[27] This model assumes that the diffusing substance is initially distributed uniformly in a sphere of radius R with an initial concentration C_0. The concentration $C(r,t)$ at radius r and time t is given by

$$\frac{C(r,t)}{C_0} = \frac{1}{2}\left\{\operatorname{erf}\left(\frac{R+r}{2(Dt)^{1/2}}\right) + \operatorname{erf}\left(\frac{R-r}{2(Dt)^{1/2}}\right)\right\} - \left(\frac{Dt}{\pi}\right)^{1/2}\frac{1}{r}\left\{\exp\left(\frac{-(R-r)^2}{4Dt}\right) - \exp\left(\frac{-(R+r)^2}{4Dt}\right)\right\} \quad (6)$$

M_t, the amount of substance that has diffused across the boundary at time t, can be calculated through eq 7 provided D is known:

$$M_t = M_\infty - \int_0^R C(r)(4\pi R^2)\,\mathrm{d}r \quad (7)$$

where $M_\infty = (4/3)\pi R^3 C_0$.

Experimentally, we determined f_m at different times t and set this value equal to M_t/M_∞. A numerical method was then used to obtained the best D value that satisfies eq 7. For each sample, D decreased with increasing time. For example, the film sample annealed at 71 °C gave a value of $D = 1.6 \times 10^{-15}$ cm^2 s^{-1} at early times, decreasing to $D = 4.7 \times 10^{-17}$ cm^2 s^{-1} after 140 h. This decrease of D is shown in Figure 6, where we have chosen to plot log D vs f_m, the volume fraction of mixing. One feature of our data made apparent in Figure 6 is that at high annealing temperatures we are unable to detect the early stages of polymer diffusion.

The time dependence of D for polymer diffusion is an important observation, in accord with the neutron scattering results reported by Hahn[13,14] on much smaller PBMA latex particles. We believe that the origin of this effect is associated with the expected strong molecular weight dependence of D. If short chains dominate diffusion at short times with diffusion of longer chains becoming more prominent at long times, one would expect D to decrease with time. Emulsion polymers usually have large molecular weight polydispersities (cf. Figure 1), and this type of behavior should be an important and ubiquitous aspect of latex film formation.

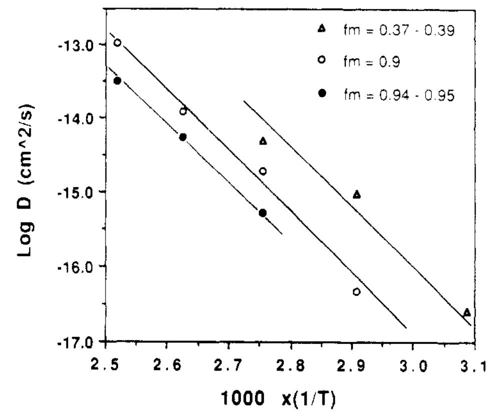

Figure 7. Arrhenius plot of log D versus $1/T$.

Other effects can become prominent in small particles, particularly those composed of high molecular weight polymer whose polymer dimensions are compressed relative to the mean dimensions of chains in the melt. Conformational distortion provides an additional entropic driving force for chain diffusion (expansion) during the early stages of the particle fusion process. This is a particularly important factor in the experiments reported by Sperling.[15] This factor may be important here, since chains at the surface of latex particles may have different diffusional properties, especially at early times, than those in bulk.

Temperature Dependence of Polymer Diffusion

The temperature dependence of polymer diffusion can be described in terms of the WLF equation,[28] with parameters close to those obtained from viscoelastic relaxation measurements.[29,30] Over a limited temperature range both the viscoelastic and diffusion data will fit an Arrhenius plot, with an apparent activation energy given by

$$E_a = 2.302R'C_1C_2T^2/(C_2 - T - T_0) \quad (8)$$

Here R' is the gas constant, T_0 is a reference temperature, and C_1 and C_2 are parameters associated with a given polymer structure. The quantity E_a, instead of being temperature independent as reaction rate theory would predict, increases rapidly with decreasing temperature and at T_g attains the value $2.302R'C_{1g}T_g^2/C_{2g} = R'T_g^2\alpha_f/f_g^2$. Thus E_a is predicted to be independent of chemical structure except as reflected by T_g itself and in minor variations in the fractional free volume f_g and the thermal expansion coefficient α_f in the vicinity of T_g. It is of the order of 62 kcal/mol if T_g = 200 K and 250 kcal/mol if T_g = 400 K.

In Figure 7 we construct Arrhenius plots of our diffusion data. We have chosen to compare D values associated with equal extents of mixing. These generate three essentially parallel lines and an apparent E_a of 38 kcal/mol. This value can be compared with results of dynamic mechanical measurements of PBMA by the Ferry group.[31,32] When they fit their data to the WLF equation, they obtain an apparent activation energy for backbone motion that depends upon temperature and is characterized by a value of 37 kcal/mol at 100 °C.

When the temperature dependence of diffusion properties is measured, the WLF equation can be applied in the following form:

$$\log a_T = \log (DT_0/D_0T) = C_1(T - T_0)/(T - T_\infty) = C_1(T - T_0)/(C_2 + T - T_0) \quad (9)$$

where D_0 is the diffusion coefficient at reference

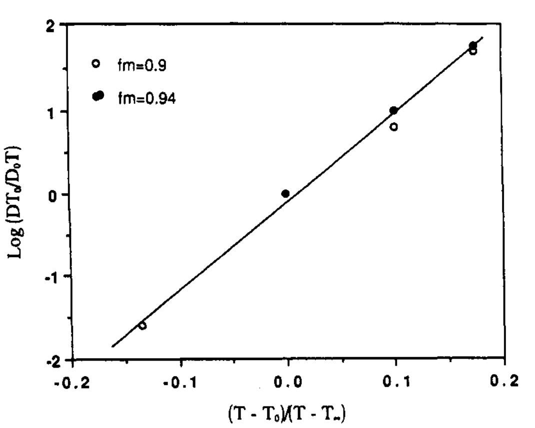

Figure 8. Plot of the reduced diffusion coefficient log (DT_0/D_0T) vs $(T - T_0)/(T - T_\infty)$, with T_0 = 363 K.

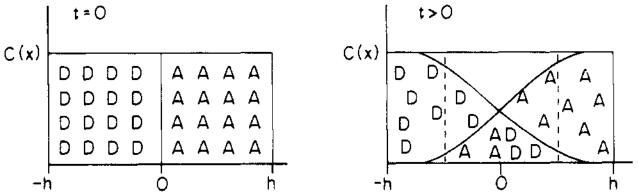

Figure 9. Depiction of diffusion during latex film formation and the evolution of labels in terms of the planar sheet diffusion model. In a real experiment, the sample is removed from the oven and diffusion ceases during measurement of the Phe fluorescence decay profile.

temperature T_0 and T_∞ is the Vogel temperature, corresponding to an infinite viscosity or relaxation time. We choose T_0 = 363 K as the reference temperature and $D_0 = 1.9 \times 10^{-15}$ cm^2/s for f_m = 0.9 and $D_0 = 0.52 \times 10^{-15}$ cm^2/s for f_m = 0.94. T_∞ = 203 K for PBMA. We obtain a linear plot (Figure 8) of log (DT_0/D_0T) against $(T - T_0)/(T - T_\infty)$, with C_1 = 10.5. If the reference temperature is chosen as T_0 = 373 K, we find C_1 = 15.2 and C_2 = 254.3. These values are in excellent agreement with values reported by Child and Ferry from their dynamic mechanical measurement for PBMA (C_1 = 14.53, C_2 = 255).

Conclusion

Using the nonradiative direct energy transfer technique in conjunction with fluorescence decay measurements, we are able to show that polymer chain diffusion across the interparticle boundary takes place during film formation from poly(butyl methacrylate) latex particles. Both temperature and time have dramatic influences on the diffusion process. The temporal decrease in D is due, at least in part, to molecular weight effects, with short chains dominating the diffusion process at early times. Temperature effects can be described quantitatively by the WLF equation. The apparent activation energy for diffusion (38 kcal/mol at 51–124 °C) has been evaluated and is nearly identical with that (37 kcal/mol) determined from dynamic mechanical measurements and attributed by Ferry to backbone motion of the PBMA chains.

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Appendix

Figure 9 depicts the situation anticipated for two adjacent deformed latex particles, labeled with donor (D) and acceptor (A) groups, in terms of the planar sheet diffusion model. From Figure 9 we may define the following quantities: V_D as the volume that contains only the Phe-labeled polymers of a concentration C_D, V_A as the volume that contains only the An-labeled polymers of a concentration C_A, and V_{AD} as the volume that contains both the Phe-labeled and An-labeled polymers with a Phe-labeled polymer concentration C'_D. The volume fraction of mixing is then given by $f_m(t) = V_{AD}/(V_{AD} + 2V_D)$, where we assume that $V_A = V_D$. From eq 5, we know that the component B_1 describes the amount of donor-labeled polymers in the mixed domain and that the component B_2 describes the donor-labeled polymers that have not undergone mixing with the acceptor-labeled polymers. If we assume further that $C_D = 2C'_D$, i.e., a twofold dilution in the mixing domain, we can make the following connection between the volume fraction of mixing and the B_1 and B_2 values obtained by analyzing the Phe fluorescence decay profile at an annealing time (t) using eq 1:

$$f_m(t) = \frac{V_{AD}}{V_{AD} + 2V_D} = \frac{B_1/C'_D}{B_1/C'_D + 2B_2/C_D} = \frac{B_1}{B_1 + B_2} \qquad \text{(A1)}$$

References and Notes

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