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Introduction

Over the past decade, concern for the environment has generated many instances where there is a need to turn from a more polluting technology to one that is more benign. One example of this situation is the impact on coatings technology of stricter regulation of volatile organic compound (VOC) emissions. Because of these restrictions, the use of waterborne latex-based coatings is expanding into areas, such as automotive and industrial coatings. While latex-based coatings are currently available in the market place, most formulations still contain significant amounts of VOCs (typically 15−30 wt %). The latex particles in these formulations typically have a T_g above 30 °C, and will not form films at room temperature. Organic solvents are added to the formulations to plasticize the latex particles, lowering their T_g. Such additives are referred to as "coalescing aids."

We[1] and others[2] have shown that these solvents also promote polymer diffusion rates in latex films. This effect is coupled to the contribution of the plasticizer to the overall free volume in the polymer matrix. We have shown that the Fujita−Doolitle model,[3] originally developed to describe the influence of free volume on the rate of plasticizer diffusion in polymer films, is also able to describe the influence of plasticizing solvents on the polymer diffusion rates in these films.[4] Other substances can act as nonvolatile plasticizers. Examples include alkylphenol ethoxylates ($C_nPhO-EO_x$) where n is the number of carbons in the substituent and x is the mean degree of ethoxylation. For example, Kawaguchi et al.[5] showed that NP20 ($n = 9$, $x = 20$) at 90 °C acts as a plasticizer for poly(butyl methacrylate) (PBMA) latex films and increases the rate of polymer diffusion. In subsequent experiments, Odrobina et al.[6] showed that temperature plays an important role in the surfactant−

polymer interaction: up to 76 °C, NP20 has only limited miscibility in PBMA. At room temperature its solubility is limited to slightly more than 2 wt % in PBMA. At 90 °C NP20 appears to be fully miscible with PBMA. In contrast, simple ionic surfactants such as sodium dodecyl sulfate and sodium dihexyl sulfosuccinate have little effect.[7]

In this paper we are concerned with Pluronics surfactants. The term Pluronics refers to a series of commercially available water-soluble triblock copolymers of ethylene oxide (PEO) and propylene oxide (PPO). There is a vast literature describing the properties of these polymers, arising from both their interesting behavior in self-assembly[8] and their important practical applications.[9] PEO−PPO−PEO block copolymers are an important class of surfactants and find widespread industrial applications in detergency, dispersion stabilization, emulsification, lubrication, and formulation of cosmetics and inks, along with more specialized applications in, for example, pharmaceuticals, bioprocessing, and separations.[10] In this paper, we are interested in their influence on polymer diffusion in latex films. We choose two low molar mass polymers of nearly identical chain length and composition but different microstructure, PEO−PPO−PEO and PPO−PEO−PPO samples of $M \approx 2000$ and approximately 50 wt % of each component.

Experimental Section

The synthesis and characterization of the poly(butyl methacrylate) (PBMA) latex particles employed here are described elsewhere.[11] Two similar materials were prepared by seeded semicontinuous emulsion polymerization from a common unlabeled seed latex. The cross-linked seeds[12] (diameter $d = 21$ nm) represent 3 wt % of the final latex particles. One latex consists of 1 mol % phenanthrene- (Phe-) labeled particles to act as a donor (D) dye; the other consists of 0.5 mol % 4′-*N,N*-dimethylaminobenzophenone- (NBen-) labeled particles[13] to act as the acceptor (A) dye. The two dispersions at 19 wt % solids consisted of particles of $d = 130$ nm and polymer of $M_w \approx 125\,000$, $M_w/M_n = 2.5$.

The polymers PPO−PEO−PPO ($M_n \approx 2000$ g/mol, 50 wt % EO) and PEO−PPO−PEO ($M_n \approx 1900$ g/mol, 50 wt % EO) were purchased from Aldrich. ^{1}H NMR measurements (Varian model HA-200) indicated that PPO−PEO−PPO is 53.9 wt % EO, whereas PEO−PPO−PEO is 53.4 wt % EO. Latex films were prepared from dispersion mixtures of 1:1 weight ratio of Phe- and NBen-labeled particles. The dispersions were first cleaned by treating them with a prepurified[14] ion-exchange resin (AG-501-X8 mixed-bed-resin, Bio-Rad) to remove the ionic surfactant and other ionic species before film formation. A few drops of this mixed dispersion containing different amounts of Pluronic surfactant) were spread on a small quartz plate. The film was allowed to dry at room temperature in the open air overnight before annealing. Films were dry and transparent.

Differential scanning calorimetry (DSC) traces were measured with a TA Instruments Universal V2.6D. The samples were run under N_2 with a 10 °C/min average heating and

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cooling rate. For each samples three scans were performed: scan 1 (heating from −20 to +56 °C); scan 2 (cooling from +56 to −20 °C); scan 3 (reheating from −20 to +56 °C). T_g values were calculated automatically using the instrument software. Samples of 5 ± 1 mg were used.

Fluorescence decay profiles were measured at room temperature by the time-correlated single photon counting technique.[15] The donor phenanthrene was excited at 300 nm, and its emission was recorded over the range 350−400 nm. A bandpass filter (310−400 nm) and a cutoff filter (335 nm) were mounted in the front of the photomultiplier tube detector to minimize the interference due to scattered light. For fluorescence decay measurements, each sample was placed in a small quartz tube and degassed with N_2 for 5 min before the measurement. In the absence of NBen as an energy transfer acceptor, Phe decay profiles $I_D°(t)$ were exponential, with $\tau_0 = 46.1$ ns. For other samples annealed for a time t, we fit each decay curve to a stretched exponential, and used the fitting parameters to evaluate the integrated area (Area(t)) under the decay profile. All fits in this article have goodness-of-fit χ^2 values less than 1.3. From the integrated area we calculate the quantum efficiency of energy transfer $\Phi_{ET}(t)$.

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D(t')\,dt'}{\int_0^\infty I_D^0(t')\,dt'} = 1 - \frac{\text{Area}(t)}{\text{Area}(D)} \qquad (1)$$

We define the extent of mixing f_m that occurs upon annealing a sample for a time t in terms of the fractional evolution of the quantum efficiency of energy transfer.

$$f_m = \frac{\Phi_{ET}(t) - \Phi_{ET}(t_0)}{\Phi_{ET}(t_\infty) - \Phi_{ET}(t_0)} = \frac{\text{Area}(t_0) - \text{Area}(t)}{\text{Area}(t_0) - \text{Area}(t_\infty)} \qquad (2)$$

In eq 2, $[\Phi_{ET}(t) - \Phi_{ET}(t_0)]$ represents the change in energy transfer efficiency between the freshly prepared film and that annealed for time t. $[\Phi_{ET}(t_\infty) - \Phi_{ET}(t_0)]$ is the difference in energy transfer efficiency between the fully mixed film and the newly formed film. To obtain values of $\Phi_{ET}(t_\infty)$, representing full mixing, we took a latex film sample, dissolved it in THF, and then recast a film onto a quartz plate.

Results and Discussion

In this paper we compare the influence of two different Pluronics block copolymers on the rate of poly(butyl methacrylate) diffusion in PBMA latex films. By ^{1}H NMR, both Pluronics samples have identical compositions, 53.5 wt % PEO. According to the vendor's specifications, they have very similar molar masses: for PEO−PPO−PEO, $M_n \approx 2000$, and for PPO−PEO−PPO, $M_n \approx 1900$. A series of films were prepared from a 1:1 particle mixture of donor- (Phe-) labeled latex and acceptor- (NBen-) labeled latex containing different amounts (0, 3, 6, 9 wt %) of the two block copolymers. The particle diameters (130 nm) and constituent polymer molar masses ($M_w \approx 125\,000$, $M_w/M_n = 2.5$) of the Phe- and NBen-labeled latex were essentially identical. The films were dried in the open air, and fluorescence decay profiles were measured for each sample. For all of these samples, irrespective of the amount or type of Pluronics added, the Area(t_0) values were 42.4 ± 0.5 ns. This value corresponds to $\Phi_{ET}(t_0) = 0.08$ and represents energy transfer from donors on one side of the boundary in newly formed latex films to acceptors on the other side. We note that the added block copolymer has a negligible effect on this value. This is the result one would expect if the additive dissolved in the PBMA matrix or if it formed large immiscible domains. If the block copolymer became trapped as a thin continuous phase that occupied the spaces between adjacent cells
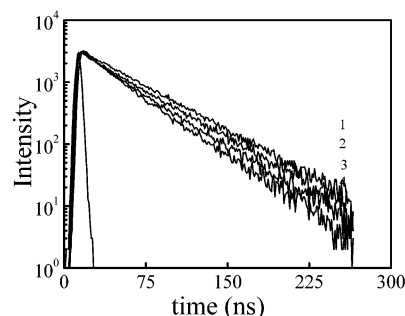

Figure 1. Donor fluorescence decay profiles of (1) a Phe-labeled PBMA film, (2) a film formed at room temperature from a 1:1 ratio of Phe- and NBen-labeled PBMA latex containing 6 wt % PPO−PEO−PPO and then annealed for 5 min at 70 °C, (3) the film shown in part 2 annealed for 254 min at 70 °C, and (4) a film of this material cast from a solution in tetrahydrofuran.
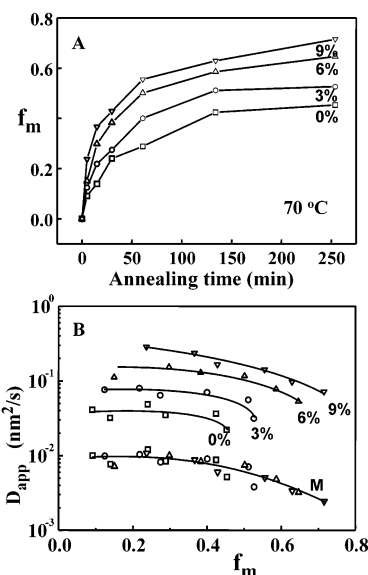

Figure 2. Comparison of the diffusion rates for PBMA at 70 °C with and without the addition of PPO−PEO−PPO. The amounts present in wt % are indicated adjacent to each curve. Plots show (A) the extent of mixing (f_m) vs time and (B) D_{app} vs f_m. In part B, the curve labeled M is a master curve of the D_{app} data shifted to 0% additive as described in the text. For visual clarity, this curve is arbitrarily translated along the D_{app} axis.

in the latex film,[16] it would serve to separate cells containing donor- and acceptor-labeled polymer. One would expect Area(t_0) values to increase and $\Phi_{ET}(t_0)$ to become smaller in the presence of increasing amounts of added block copolymer.

In Figure 1, we show representative fluorescence decay curves from some of the samples. The top curve, from a film of Phe-PBMA, is exponential with a lifetime $\tau_0 = 46.1$ ns. The second and third curves are obtained from films containing 6 wt % PPO−PEO−PPO annealed for 5 and 254 min, respectively, at 70 °C, and then cooled to room temperature for the measurement. The lowermost curve is a model for complete mixing obtained from a similar sample dissolved in THF and then cast as a film. This decay curve is used for the calculation of Area-(t_∞) and $\Phi_{ET}(t_\infty)$.

In Figure 2A, we plot values of f_m as a function of annealing time for a series of PBMA latex films containing different amounts of PPO−PEO−PPO. One sees,

as expected, that the f_m values increase with annealing time at 70 °C. Even in the absence of PPO–PEO–PPO, these values will eventually reach 1.0. Complete mixing corresponds to polymer diffusion over a length scale comparable to the radius of the original latex particles.

We are interested in the influence of the Pluronics additive on the rate of polymer diffusion. It is clear that even small amounts of PPO–PEO–PPO increase the PBMA diffusion rate. To quantify this effect, we calculate apparent diffusion coefficients D_{app} from the f_m values, using a spherical diffusion model.[17] As we have discussed previously, this calculation involves making severe assumptions about the nature of the polymer diffusion in the system. As a consequence, the D_{app} values are at best proportional to the true polymer diffusion coefficients appropriate for a system with a broad molar mass polydispersity. Our experience has shown that the influence of external variables such as temperature or plasticizers on the magnitude of D_{app} provide a realistic measure of the changes in the diffusion rates of the polymers in the system.[18]

Values of D_{app} calculated in this way are plotted against the extent of mixing f_m in Figure 2B. One sees first that for a given concentration of PPO–PEO–PPO, D_{app} values decrease as f_m increases. We understand that this effect is a consequence of the fact that the fastest diffusing species in the system make their contribution to the growth in Φ_{ET} at early times.[19] Here we also see clear evidence for the influence of PPO–PEO–PPO on the increase in PBMA diffusion rates. The D_{app} values increased about 2 times with the addition of 3 wt % PPO–PEO–PPO and by similar factors for films with 6 and 9 wt % additive. This indicates that the PPO–PEO–PPO plasticized the PBMA polymer and enhanced its diffusivity.

In experiments in which temperature is the variable, free-volume models lead naturally to the concept of time–temperature superposition.[20] For plasticizing additives, the free-volume-based Fujita–Doolittle[3] model predicts time–composition superposition, where the important variable is the volume fraction of additive Φ_a.

$$\left[\ln\frac{D_p(T,\Phi_a)}{D_p(T,0)}\right]^{-1} = f_p(T,0) + \frac{f_p^2(T,0)}{\Phi_a\beta(T)} \qquad (3)$$

In this expression, D_p is the polymer diffusion coefficient; $f_p(T,0)$ is the fractional free volume of the polymer with no added plasticizer, and $\beta(T)$ is the difference in free volume between the polymer and additive at temperature T. The term $\ln[D_p(T,\Phi_a)/D_p(T,0)]^{-1}$ is a shift factor that should allow us to superimpose data in Figure 2B to a common value of the additive concentration Φ_a. We set $D_{app} = D_p$ for each concentration of additive and used the value 1.06 g/mL as the density of PPO–PEO–PPO. The lowermost curve in Figure 2B, labeled M and arbitrarily translated along the D_{app} axis, is the master curve obtained by shifting the data at finite additive concentrations to the curve at $\Phi_a = 0$.

To find the appropriate value of $\beta(T)$, we selected data for $f_m = 0.38$ and plotted values of $\{\ln[D_p(T,\Phi_a)/D(T,0)]\}^{-1}$ vs $1/\Phi_a$ (not shown) and obtained a straight line. The intercept yielded an $f_p(T,0)$ value 0.048, and the slope gave $\beta(T) = 0.05$. The $\beta(T)$ value obtained is reasonable and comparable in magnitude to that ($\beta(T) = 0.07$) for the coalescing aid trimethylpentanediol monoisobutyrate (Texanol) in PBMA latex films.[4]
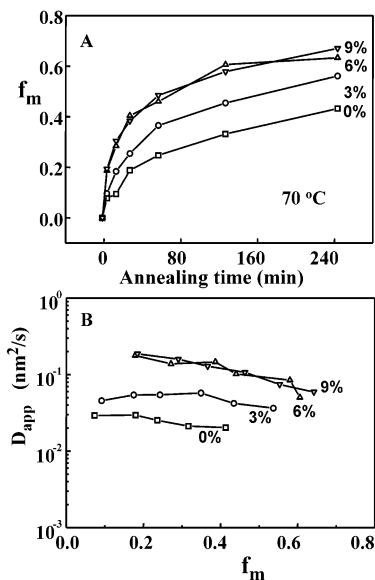

Figure 3. Comparison of the diffusion rates for PBMA at 70 °C with and without the addition of PEO–PPO–PEO. The amounts present in wt % are indicated adjacent to each curve. Plots show (A) the extent of mixing (f_m) vs time and (B) D_{app} vs f_m.

In Figure 3, we show corresponding plots of f_m vs time and D_{app} vs f_m at four films of the same PBMA latex, here formed in the presence of PEO–PPO–PEO. The presence of small amounts (3, 6 wt %) of this substance in the film enhances the PBMA diffusion rate, but the effect appears to saturate. The film containing 9 wt % additive undergoes intercellular polymer diffusion at the same rate as that containing 6 wt %. We conclude that PEO–PPO–PEO has limited miscibility in PBMA films at 70 °C.

As a test of the plasticizing influence of the two triblock copolymers, we examined three samples by differential scanning calorimetry: the PBMA polymer itself and this polymer to which 9 wt % PEO–PPO–PEO or PPO–PEO–PPO was added. The glass transition temperatures for these samples were determined to be 34.5, 31.1, and 26.7 °C, respectively. We attribute the smaller influence of PEO–PPO–PEO on the T_g of PBMA to its lower solubility in PBMA. This result is consistent with well-documented experience in films formed from nonpolar latex like SBR (styrene–butadiene rubber),[21] where nonionic surfactants with lower HLB values are more miscible than those with higher HLB values. The HLB value for PEO–PPO–PEO ($M_n \approx 1900$ g/mol, 50 wt % EO) is significantly higher than that for PPO–PEO–PPO ($M_n \approx 2000$ g/mol, 50 wt % EO).[22]

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