Effect of Gel Content on Polymer Diffusion in Poly(vinyl acetate-*co*-dibutyl maleate) Latex Films

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ABSTRACT: We used energy transfer experiments to examine the rates of polymer diffusion in latex films of two P(VAc−DBM) copolymer samples: one of nominal $M_w = 250\,000$ (by GPC, M_{250K}) and the other, the high-M sample, with a substantial (50%) gel content. An important feature of this sample is that its sol fraction had a similar molecular weight distribution (similar GPC curves) to that of the M_{250K} sample. Films of both samples exhibited the viscoelastic response at high frequencies expected for entangled polymers. At low frequencies, the G' and G'' values for the high-M sample were comparable in magnitude over a wide range of frequencies and were proportional to $\omega^{0.5}$. This type of behavior is often seen as a signature of a critical gel but appears here for a mixture of gel and randomly branched polymer. Our most important finding is that the rates of intercellular polymer diffusion were very similar in latex films of the two polymers. This result indicates that the diffusion rate depends primarily on the molecular weight and degree of branching of the diffusing species and is much less sensitive to the cross-linked nature of the matrix present in one of the samples.

Introduction

While latex coatings normally display excellent performance in many application areas, they generally have poorer chemical and solvent resistance and lower tensile strength and hardness than solvent-borne coatings. Introducing cross-links into a latex coating is necessary to improve certain properties.[1−3] For example, film toughness is strongly enhanced by polymer chains that are anchored by cross-links on both sides and span the boundary between individual cells in a latex coating.[4] For rather different reasons, waterborne polymers intended for adhesive applications often require partial cross-linking, with a gel content on the order of 50%. Films of these polymers are prepared from latex in which the cross-links were introduced during the emulsion polymerization reaction, either by introducing multifunctional monomers or through grafting and coupling reactions of very reactive radicals. This type of synthesis limits the characteristic length scale of the cross-linked networks to the diameter of the latex particles. Thus, the networks represent a microgel contribution to the overall composition of the polymer. The presence of these cross-links has an important effect on the rheological properties of the films formed from these latex particles, and it is this rheological response that plays an important role in the adhesive behavior of the polymer.[5−7]

We are interested in understanding how the presence of cross-links in latex particles affects their coalescence into latex films. Classic experiments from the Gent group[8] have shown that when two cross-linked polymers are brought together at a temperature above their glass transition temperature T_g, the strength of adhesion decreases with increasing cross-link density. This result implies that polymer diffusion across the interface to generate adhesion is restricted to chain segments dangling from the network, and the longer the length of these dangling ends, the stronger the adhesion. We have shown that the same considerations apply to films formed from fully cross-linked latex particles. If the annealing temperature for these films is well above the glass transition temperature (T_g) of the polymer, the extent to which the dangling ends can diffuse across the interparticle boundaries is limited by the cross-link density in the polymer.[9] Nevertheless, even when the poly(butyl methacrylate-*co*-butyl acrylate) latex particles were synthesized in the presence of 4 mol % of a bifunctional monomer (ethylene glycol dimethacrylate), their films showed considerable toughness, with an extension-to-break of nearly 150%. These films had very poor solvent resistance.

This paper is part of a series in which we investigate the effect of gel content and chain architecture on polymer diffusion across intercellular boundaries in poly(vinyl acetate-*co*-dibutyl maleate) latex films. These types of latex have been used both in interior latex paints and in adhesives. PVAc and its copolymers are known to be branched or partially cross-linked polymers. The intrinsic branching of PVAc itself is due to the chain transfer of the highly reactive PVAc radical to the methyl side group on another polymer chain.[10] In the case of PVAc copolymers with more reactive C−H bonds in the backbone, branching can arise as a consequence of intra- and intermolecular hydrogen abstraction by the PVAc radical. In these polymers, branching is normally accompanied by gel formation. Several authors have argued that the branching mechanism itself is not able to create gels and that cross-linking occurs as a consequence of termination by recombination.[11−13] More recently, Iedema et al.[14] used a mathematical analysis based on population balance

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Table 1. Characteristics of P(VAc−DBM) Latex Particles

	M_w	gel content (%)	main T_g (°C)	minor T_g (°C)
Phe-high-*M* P(VAc−DBM)		ca. 50	24	33
NBen-high-*M* P(VAc−DBM)		ca. 50	24	34
Phe-M_{250K} P(VAc−DBM)	2.2×10^5	0	18	27
NBen-M_{250K} P(VAc−DBM)	2.3×10^5	0	18	28
high-*M* P(VAc−DBM)		ca. 50	24	34
M_{250K} P(VAc−DBM)	2.4×10^5	0	18	29
high-*M*, sol fraction	2.8×10^5		10[a]	

[a] The sol fraction has only one T_g.

modeling to examine the molecular weight distribution (MWD) of VAc radical polymerization. They found that for a system with transfer to polymer only long molecular weight tails can form without recombination, but the model system remains free of gel.

In a previous report, we described the synthesis of dye-labeled P(VAc−DBM) copolymers for ET experiments. One of the characteristics of batch emulsion polymerization of VAc−DBM is that under our experimental conditions polymer composition is independent of monomer conversion.[15] We have studied the effect of temperature on the rate of polymer interdiffusion in latex films formed from these P(VAc−DBM) copolymers. Two pairs of dye-labeled latex particles were prepared. One sample (the M_{250K} latex) had a negligible gel content and a nominal molecular weight (gel permeation chromatography, polystyrene standards) of $M_w = 2.3 \times 10^5$. The other sample (the high-*M* latex) had a significant gel content (ca. 50%). From analysis of the apparent diffusion coefficients (D_{app}) obtained from experiments at different temperatures, we calculated the effective activation energy for diffusion to be ca. 45 kcal/mol for the M_{250K} P(VAc−DBM) sample and a somewhat lower value (37 kcal/mol) for the high-*M* P(VAc−DBM) sample.[16] These differences were explained in part by the different glass transition temperatures (T_g) of the two samples. The polymer diffusion experiments for the high-*M* sample were carried out at higher temperatures than for the M_{250K} sample. More important, the range of temperatures for the diffusion experiments for the M_{250K} sample was closer to T_g than those for the high-*M* sample. From the perspective of the Williams, Landol, Ferry (WLF) expression,[17] this result is consistent with the prediction of higher effective activation energies for experiments performed at temperatures closer to T_g.

To help us gain further insight about the influence of gel content on the polymer diffusion step in latex films, we have reanalyzed the diffusion data reported in ref 16. In addition, we describe new experiments carried out at a higher temperature. To serve as a basis for this data reanalysis, we have measured the linear viscoelastic response of our samples as a function of the frequency. The presence of gel in our samples affects the rheological properties of these polymers. We use this information to help understand how this microstructure affects polymer diffusion in gel-containing latex films.

Experimental Section

Materials. The synthesis and characterization of the polymer samples employed here were described in ref 15. Absolute molecular weights were unavailable. Nominal molecular weights were obtained by gel permeation chromatography (GPC) based upon polystyrene standards. These properties as well as the gel content and glass transition temperatures of the samples as determined by differential scanning calorimetry are collected in Table 1. A PVAc homopolymer sample for rheology measurements was purchased from Aldrich ($M_w = 83$ kg/mol).

Rheology Measurements. The following procedure was used to prepare the samples for the measurements of viscoelastic properties. First, the latex samples were dried under vacuum at 60 °C for 12 h to eliminate any trace of volatiles. Then, the samples were molded in a two-step procedure. In the first step a known amount of sample was pressed between metal plates in a Carver press at 88 °C for 2−4 min. Dust-free poly(ethylene terephthalate) sheets (3M, 100 μm thick) were used to prevent direct contact between the sample and the plates. In the second step, the material free of air bubbles was remolded at the same temperature to its final dimensions (25 mm in diameter and approximately 0.8 mm thick).

The viscoelastic response of P(VAc−DBM) copolymers was studied with a Rheometrics RAA instrument in the oscillatory shear mode (parallel plates, 25 mm diameter). The mechanical response was measured over a range of frequencies from 10^{-2} to 70 Hz at several temperatures ranging from 60 to 140 °C. Small strains (0.01−0.05) were applied in order to obtain viscoelastic response in the linear regime. When the same sample was used for measurements at different temperatures, corrections for the change in the distance between the plates with temperature were made.

Fluorescence Decay Measurements and Data Analysis. For energy transfer experiments, films were formed from dispersions containing a 1:1 mixture of donor- and acceptor-labeled particles or solutions containing an equal mixture of the two polymers. Donor fluorescence decay curves were measured at room temperature on the newly formed films and on films subjected to various annealing protocols. Individual donor fluorescence decay profiles [$I_{DA}(t)$] were fitted to a stretched exponential function,[18] which was then integrated to obtain the area under the decay curve. The details for all of these steps are described in ref 16. Analysis of the data from these energy transfer experiments is developed in terms of the quantum efficiency of energy transfer $\Phi_{ET}(t_n)$

$$\Phi_{ET}(t_n) = 1 - \frac{\int_0^\infty I_{DA}(t)\,dt}{\int_0^\infty I_D(t)\,dt} = 1 - \frac{\text{area}(t_n)}{\tau_D} \qquad (1)$$

In eq 1, $\int I_D(t)\,dt$ (equal to the unquenched donor lifetime τ_D) is the area under the donor decay profile of a film containing only donor. The term $\int I_{DA}(t)\,dt$ describes the area under the donor decay profile of a film containing both donor and acceptor, and t_n refers to the time that a given sample was annealed prior to the fluorescence decay measurements.

As a measure of polymer diffusion in latex films, we calculate the "extent of mixing" parameter f_m.

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

This parameter measures the fractional growth of Φ_{ET} from its initial value in a newly formed film to the value expected for full randomization (due to diffusion) of donor and acceptor dyes in the polymer film.

Results and Discussion

The syntheses and characterization of the P(VAc−DBM) polymers examined here were reported previously.[15,16] The polymers were synthesized from a 4:1 wt ratio (10.6:1 mole ratio) of VAc−DBM via batch emulsion polymerization. As discussed in ref 15, as monitored by ^{1}H NMR, the composition of the copolymer under these reaction conditions remains constant throughout the reaction with a monomer ratio comparable to that in the feed. This result is likely due to the fact that the reactivity ratios ($r_1 = 0.171$, $r_2 = 0.040$[19]) for these monomers promote formation of an alternating copoly-

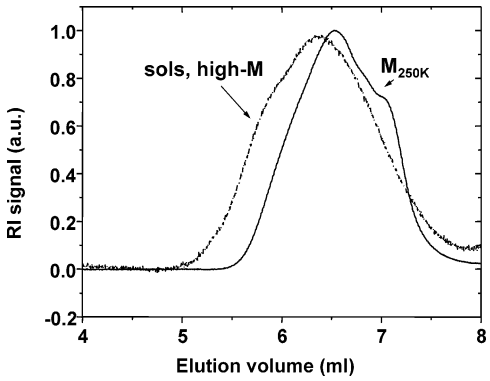

Figure 1. Comparison of GPC traces of the M_{250K} P(VAc−DBM) and the sol fraction of the high-M P(VAc−DBM). Based on polystyrene standards, the M_{250K} sample is characterized by $M_w = 230\,000$, $M_n = 96\,000$, and $M_{peak} = 184\,000$; for the sol fraction of the high-M sample, $M_w = 280\,000$, $M_n = 107\,000$, and $M_{peak} = 204\,000$.

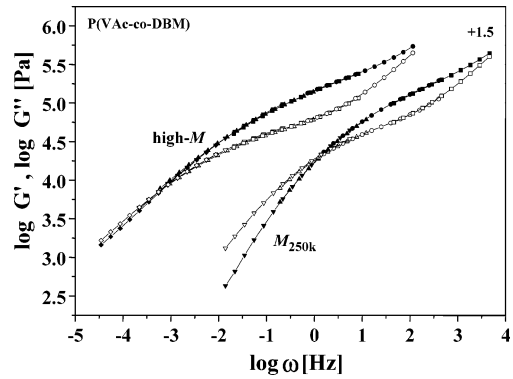

Figure 2. Master curves for the storage and loss shear moduli as a function of frequency for M_{250K} and high-M P(VAc−DBM).

mer, and the less water-soluble monomer undergoes the slower reaction. The presence of DBM in the reaction mixture slows the polymerization reaction to such an extent that one cannot carry out the reaction under monomer-starved conditions. In absence of a chain transfer agent, the syntheses of the Phe- and NBen-labeled and unlabeled high-M samples gave polymers with a gel content of ca. 50%. The high-M P(VAc−DBM) copolymer had a major glass transition, determined by differential scanning calorimetry (DSC), at ca. 24 °C and a minor glass transition at ca. 34 °C. The M_{250K} P(VAc−DBM) dye-labeled copolymer samples for diffusion measurements and the unlabeled sample for rheology measurements were synthesized in the presence of the chain transfer agent, dodecyl mercaptan, giving M_w of ca. 2.3×10^5 and no detectable gel.[20] These polymers had a major glass transition at ca. 18 °C and a minor glass transition at ca. 28 °C. We have attributed the presence of two glass transitions to the presence of polymers having different degrees of branching.[15]

To help us understand the factors affecting the evolution of film properties in latex films of the high-M polymer, samples of this polymer were fractionated to separate the sol and gel components. The sol fraction of the high-M sample has a molecular weight comparable to that of the M_{250K} P(VAc−DBM). The GPC traces of the two samples are very similar (Figure 1). As can be seen from Figure 1, the GPC trace of the sol extract of the high-M latex strongly overlaps the GPC peak of the M_{250K} sample. We see that the M_{250K} sample had a peak molecular weight (1.8×10^5) slightly lower than that (2.0×10^5) of the sol fraction of the high-M sample. It is this similarity in the mean molecular weight and the molecular weight distribution for the two samples that allows us to draw our most important conclusions about polymer diffusion in their respective latex films.

Viscoelastic Measurements. Storage (G') and loss (G'') shear moduli were measured as a function of frequency (ω), for several temperatures above T_g, for both M_{250K} and high-M samples. The time−temperature superposition principle was applied to extend the experimental frequency window. In this way, data from frequency sweeps acquired at each temperature (60, 80, 100, 120, and 140 °C) were horizontally shifted in a log−log scale plot with respect to a reference temperature to obtain master curves. Figure 2 shows G' and G'' master curves for both M_{250K} and the high-M P(VAc−DBM), built by choosing a reference temperature of 80 °C. For clarity, the G' and G'' master curves corresponding to the M_{250K} copolymers have been shifted along the horizontal scale by 1.5 log units.

Features corresponding to the rubbery and the terminal region are clearly observed in both samples. In the rubbery region, delimited by two G' and G'' crossovers, G' is higher than G'', which indicates elastic behavior due to the contribution of entanglements. The frequency interval between crossovers is larger in the high-M copolymer, consistent with its gel content. The G' values in this region are higher for the high-M sample than for the M_{250K} sample, suggesting that chemical cross-links in addition to physical entanglements make a contribution to the magnitude of G'. We also note that certain features in this region [i.e., no local maximum in $G''(\omega)$ can be observed] are completely smeared out due to the combined effects of polydispersity in molecular weights and branching. It is difficult to separate the effect of molecular weight distribution from branching and to infer meaningful conclusions in terms of differences in sample microstructure because both structural features have a similar influence on the viscoelastic response.

The most remarkable difference between the samples is observed in the terminal region, at frequencies lower than the first G' and G'' crossover. In the M_{250K} sample, the G' and G'' plots are divergent in the terminal region, exhibiting different slopes close to the expected limiting values for liquid flow (2 and 1, respectively). We can conclude that the sample exhibits liquidlike behavior at low frequencies, with no influence from any microgel present in the sample that might limit its flow. This result is consistent with the results of the solubility experiments, in which no significant amount of gel could be detected.

For the gel-containing high-M sample, the behavior in the terminal region is very far from liquidlike. We observe that the G' and G'' curves are almost coincident in this region, with the same frequency dependence. The behavior observed is very similar to that reported about the characteristic G' and G'' frequency dependence in the terminal zone for "critical gels".[21,22] This phenomenon was first observed by Chambon and Winter,[21] who found that G' and G'' exhibited self-similar behavior in systems close to the gel point, following a frequency dependence proportional to $\omega^{0.5}$. In their experiments, changes in the G' and G'' frequency dependences were monitored during cross-linking reactions as a function of the reaction time. Before the gel point, the systems exhibited liquidlike behavior ($G' \sim \omega^2$; $G'' \sim \omega$). As the extent of reaction increased to the gel point, the slopes

of G' and G'' frequency plots decreased to ca. 0.5. After that, the system behaved as a solid due to the cross-linked network, showing the behavior of a fully cross-linked system ($G' = \text{const} > G''$ and $G'' \sim \omega$). In their experiments, Chambon and Winter employed prepolymers with molecular weights below the critical molecular weights for entanglements. In this way they avoided a contribution to their signal of the rubbery region due to physical entanglements. Later, Derosa and Winter[22] published an extension of this work to prepolymers of molecular weight high enough to be entangled. As in our system, they observed rubberlike behavior due to physical entanglements in addition to the self-similar behavior close to the gel point with a $\omega^{0.5}$ dependence in the terminal zone.

For our gel-containing sample, we find that G' and G'' slopes in the terminal zone are very close to 0.5 (see Figure 2), even though the polymer architecture is rather different from that expected for a critical gel. In a critical gel, a small number of chains form a macroscopic network that spans the dimensions of the sample, and most of the polymer is unconnected to the network. In our sample, domains of microgel with dimensions no larger than the original latex particles coexist with an approximately equal weight fraction of branched polymer. We conclude that this mixture of branched and microgel-containing polymer has a rheological response in the terminal zone essentially identical to that expected for a critical gel. In this context, it is worth noting that Zosel and Ley[6] found a similar rheological behavior for films prepared from microgel-containing poly(butyl methacrylate) latex particles. Their latex was synthesized by emulsion polymerization of butyl methacrylate in the presence of small amounts methallyl methacrylate, a cross-linking agent. For one monomer mixture, they reported critical-gel-like rheological behavior and inferred from this result that the sample must be near the gel point. In our system, we see that a mixture of branched and microgel containing sample can give a similar terminal response.

Polymer Diffusion in P(VAc−DBM) Films Containing Different Amount of Gels. In films prepared from the Phe-labeled latex, the fluorescence decay profiles were exponential with a lifetime of 44.6 ns for high-M P(VAc−DBM) and 43.0 ns for M_{250K} P(VAc−DBM). Figure 3 shows a comparison of the donor fluorescence decay profiles in high-M and M_{250K} P(VAc−DBM) latex films annealed at 55 °C for 75 min. Curve (1) represents the decay with Phe-labeled P(VAc−DBM) only. The film with donor only is exponential. There is a small curvature in the decay curve labeled (2) from a newly formed film from 1:1 mixture of Phe- and NBen-labeled high-M latex. When this film was annealed at 55 °C for 75 min, the curvature became more pronounced (curve (3)). Curve (4) in Figure 3 presents the decays for an M_{250K} sample also annealed at 55 °C for 75 min. It is obvious from the plots that the decay (4) gives a larger curvature than that in the decay (3), which means that the M_{250K} sample undergoes a larger degree of energy transfer or polymer diffusion under the same annealing conditions. The lowermost trace (curve (5)) in Figure 3 is for a solvent-cast film from 1:1 mixture of Phe- and NBen-labeled sol fraction of the high-M P(VAc−DBM), which represents the minimum value the system may reach.

To quantify the extent of polymer diffusion in latex films by means of eq 2, we determined independently

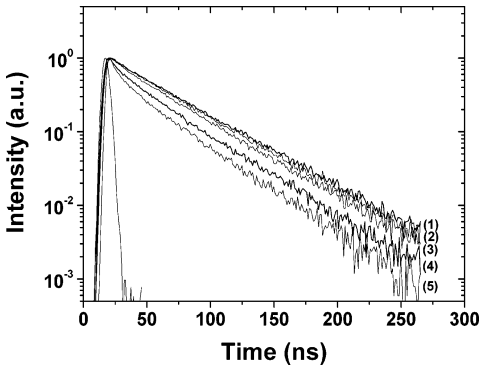

Figure 3. Donor fluorescence decay profiles for P(VAc−DBM) latex films from (1) high-M P(VAc−DBM) containing only phenanthrene (Phe) (1 mol %) as a fluorescent dye; (2) a freshly formed high-M P(VAc−DBM) film containing Phe as the donor (1 mol %) and NBen (0.3 mol %) as the acceptor with a ratio of Phe/NBen = 10:3; (3) the same film in (2) but annealed at 55 °C for 75 min; (4) the M_{250K} P(VAc−DBM) film containing Phe (1 mol %) as the donor and NBen (0.3 mol %) as the acceptor with a ratio of Phe/NBen = 10:3 annealed at 55 °C for 75 min; (5) sol fraction of high-M P(VAc−DBM).

the values of the two parameters $\Phi_{ET}(0)$ and $\Phi_{ET}(\infty)$. In the newly formed films, we found values of $\Phi_{ET}(0)$ on the order of 0.06−0.09 for the M_{250K} and high-M samples, consistent with little or no polymer diffusion accompanying film drying. Determination of $\Phi_{ET}(\infty)$ for branched polymers is more delicate. This value, representing full mixing of donor- and acceptor-labeled polymer, should correspond to random mixing of donor and acceptor groups in the film. For branched polymers it is possible that correlation effects can limit the extent to which donor dyes attached to donor-labeled molecules can penetrate the coil dimensions of acceptor-labeled polymer molecules. Here we are fortunate that two experiments to model the value for $\Phi_{ET}(\infty)$ gave identical results. For the high-M polymer, we used the sol fraction as a model for a polymer capable of complete mixing of the donor- and acceptor-labeled polymer molecules. A solvent-cast film containing equal amounts of the two labeled polymers gives a value of $\Phi_{ET}(\infty) = 0.52$. As a test of the random distribution of dyes in the system, we showed[15] that the decay profiles measured for these samples fit well to the Förster equation.[23] This expression is appropriate for randomly distributed donors and acceptors in rigid media. To obtain an alternative value for $\Phi_{ET}(\infty)$, we examined a solvent-cast film of the M_{250K} polymer. This film was prepared from a 1:1 mixture of the D- and A-labeled M_{250K} samples. Here we also obtained $\Phi_{ET}(\infty) = 0.52$. The donor decay profile for this measurement also fit the Förster equation. These experiments provide a value for $\Phi_{ET}(\infty)$ and support for the idea that the D and A dyes are randomly distributed in the model films from which this value was determined.

In Figure 4A, we plot values of Φ_{ET} as a function of annealing time for films containing M_{250K} and high-M P(VAc−DBM) annealed at 55 °C. In both polymer films, Φ_{ET} increases with annealing time. For both samples, the initial growth in Φ_{ET} is rapid, with a much slower increase after several hundred minutes annealing. In both experiments, Φ_{ET} appears to level off at long times, reaching a much higher value (0.4) for the M_{250K} sample than that (0.25) for the high-M sample. In Figure 4B, we replot these data as f_m vs annealing time. These f_m values increase with the annealing time, indicating that the PheMMA-labeled polymers diffuse into the regions

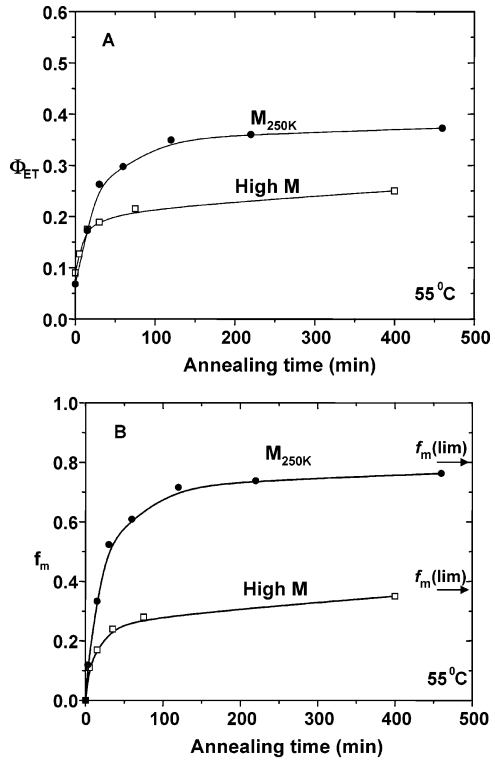

Figure 4. (A) Efficiency of energy transfer Φ_{ET} of P(VAc−DBM) films upon annealing at 55 °C: top curve, M_{250K}; bottom curve, high-M. (B) Degree of mixing f_m of P(VAc−DBM) films upon annealing at 55 °C: top curve, M_{250K}; bottom curve, high-M.

containing the NBen-labeled polymers and the NBen-labeled polymers diffuse into the regions containing PheMMA-labeled polymers. From the shape of the curves, we see that the largest increase in f_m occurs at early times, followed by smaller increases at longer times. The extent of polymer diffusion in M_{250K} P(VAc−DBM) is much higher than that in high-M P(VAc−DBM) sample.

At long times, the values of f_m for both M_{250K} P(VAc−DBM) and the high-M sample appear to level off, and the limiting value for the M_{250K} sample is less than the expected value of 1.0. One expects a limiting value of f_m [f_m(lim)] less than 1.0 for the high-M polymer because the gel component will undergo little or no diffusion, and D- and A-labeled microgel can mix only through their dangling ends.

To test whether this value of $f_m = 0.8$ is in fact a limiting value for the M_{250K} polymer, we carried out a further series of experiments with these samples. For example, the lower curves in parts A and B of Figure 5 describe the growth in Φ_{ET} and f_m, respectively, for a film of the M_{250K} polymer annealed at 100 °C. At this higher temperature, polymer diffusion is rapid, and the system evolves to limiting values of Φ_{ET} and f_m. The value for f_m(lim) (0.8) obtained for the sample annealed at 100 °C is identical to that inferred from experiments carried out at 55 °C.

To gain further insights into the origin of the limiting value of f_m, we examined the influence of annealing on solvent-cast films containing a 1:1 mixture of D- and A-labeled M_{250K} polymer. As one can see in the upper curves in Figure 5, heating these films leads to partial demixing of the D- and A-labeled polymer, accompanied by a decrease in both Φ_{ET} and f_m. When we combine this result with that described above about the random

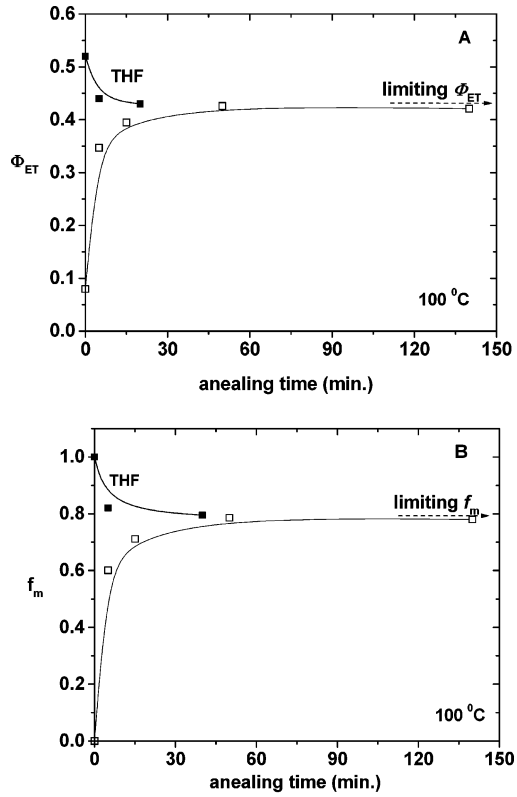

Figure 5. (A) Evolution of the efficiency of energy transfer Φ_{ET} after annealing at 100 °C in P(VAc−DBM) films (M_{250K}) consisting of a 1:1 by weight mixture of donor- and acceptor-labeled polymer: open squares, latex film; filled squares, solvent (THF)-cast film. (B) The same data in (A) transformed into the extent of mixing f_m.

distribution of D- and A-chromophores in the freshly dried solvent-cast film, we learn that solvent casting leads to a film, which is trapped in a nonequilibrium state. This type of behavior is never seen for comparable experiments on linear polymers. To us, this result indicates that there is more interpenetration of polymer, presumably highly branched polymer in the film formed immediately upon solvent drying than at equilibrium. Annealing this film provides the polymer mobility for the film to evolve toward the equilibrium composition.

Effect of Gel on the Rate of Sol Diffusion. In this section, we compare the rate of polymer diffusion in the two sets of samples described above. This comparison is meaningful because the molecular weight distribution of the sol component of the high-M polymer is similar to overall molecular weight distribution of the M_{250K} polymer. To make this comparison, we normalize the individual f_m values by the limiting values f_m(lim) found for the two respective polymers. These results are plotted in Figure 6. The remarkable result is that these two sets of polymers diffuse at very similar rates.

Another way of looking at these results is to calculate apparent diffusion coefficients D_{app} from the f_m values. This type of calculation involves making rather severe assumptions about the diffusion process. While these assumptions are not fully justified, this type of calculation does provide a measure related to the diffusivity of the polymer molecules in the system. As we have shown for a variety of systems,[24,25] including the P(VAc−DBM) polymer under consideration here,[16] the temperature dependence of these D_{app} values provides an excellent estimate of the effective activation energy for polymer diffusion in the system. For both polymers

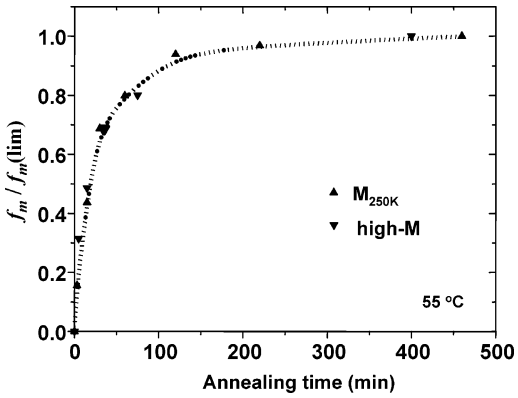

Figure 6. Comparison of the rates of polymer diffusion for the mobile components of the M_{250K} and high-M samples. The rate of the polymer diffusion is represented by overall extent of mixing f_m in Figure 4B normalized by their respective limiting values [f_m(lim)] of the extent of mixing.

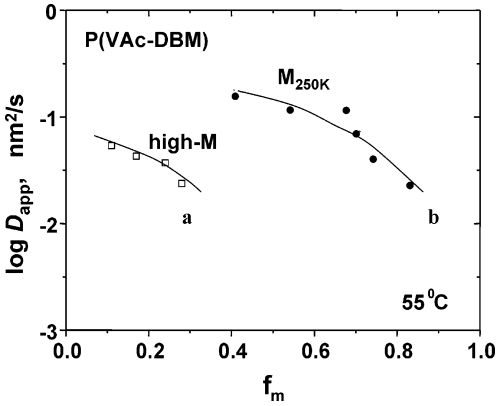

Figure 7. Comparison of apparent diffusion coefficient (D_{app}) values plotted against f_m for P(VAc−DBM) samples at 55 °C: (a) high-M; (b) M_{250K}.

under consideration here (Figure 7), the D_{app} values decrease by about an order of magnitude over the accessible range of the experiment. These D_{app} values describe the mean cumulative diffusion in the system that leads to mixing of donor and acceptor chromophores. The evolution of these values is an indication of the complex composition of the system, which contains polymers with a broad range of diffusivities. The most mobile species are likely the lowest M and possibly linear components of the mixture, whereas the slowest moving species have a much higher molecular weight and contain long-chain branches.

The main result of this analysis (Figure 7) is that the D_{app} values for the mobile component of the high-M polymer are of very similar magnitude to those of the gel-free M_{250K} polymer, even though this diffusion corresponds to very different extents of mixing. In the case of the M_{250K} polymer, all of the polymers present in the sample are mobile, and the extent of diffusion is limited only by correlation effects that limit the interpenetration of coils of the most highly branched polymers in the system. For the high-M polymer, we imagine that the gel component is unable to undergo large-amplitude diffusion. Mixing of D- and A-labeled polymers occurs by diffusion of the mobile sol polymers into adjacent cells in the latex film. In this way, mobile D-labeled polymer can diffuse into the microgel network of the A-labeled cells, replacing polymer that has diffused out of this network. The interesting feature of this result is that the mobility of polymers diffusing into adjacent cells in the film is not significantly affected by the presence of the cross-linked network.

This result recalls important experiments published nearly 20 years ago by Antonietti and Sillescu,[26] who studied the diffusion of linear polystyrene (PS) chains into model PS networks using a holographic grating technique. The molecular weights of the linear chains studied ranged from M_e to $5M_e$ (where M_e is the entanglement molecular weight, ca. 18 000 g/mol for PS). In the networks, the average degree of polymerization between cross-links varied from 16 to 400. The most important result from these experiments was that the diffusion coefficients for the diffusion of the linear chains into the networks were not severely affected by the restriction of the cross-links. The authors found only a small reduction in the values of the diffusion coefficients compared with those obtained from diffusion experiments into linear entangled matrices (M_w = 110 000).

In our system, as in the polystyrene system just described, the composition of the mobile component is the same as that of the cross-linked network. There are no strong interactions between the gel and the sol component of the mixture. The rate of polymer diffusion is not significantly affected by the presence of gel in the network. To the extent that this effect is general, we expect that it represent a common feature of postcoalescence polymer diffusion in all waterborne adhesives that contain a significant gel content.

Summary

We compared the rates of polymer diffusion in latex films of two samples of P(VAc−DBM) copolymer: one of nominal M_w = 250 000 (by GPC, M_{250K}) prepared in the presence of a chain transfer agent and one (the high-M sample) prepared without the chain transfer agent. The M_{250K} sample had no detectable gel content. It exhibited a linear viscoelastic behavior consistent with an entangled polymer with normal behavior in the terminal region, with G' proportional to ω^2 and G'' proportional to ω. The high-M sample had a measured gel content of ca. 50%. It is important to note that this is not a macroscopic gel in the classic sense, since the gel component was formed within individual latex particles and had a characteristic length scale no larger than the diameter (120 nm) of the latex particles. Its rheological behavior was unusual in that G' and G'' were comparable in magnitude over a wide range of frequencies and were proportional to $\omega^{0.5}$. This type of behavior is often seen as a signature of a critical gel but appears here for a mixture of gel and randomly branched polymer.

When this sample was fractionated into its gel and sol components, the sol fraction was found to have a GPC trace similar to that of the M_{250K} sample. Thus, the two samples share in common a similar molecular weight distribution for the mobile component of the material.

Polymer diffusion in these latex films was studied by energy transfer. The two samples differ strikingly in the limiting extent of polymer diffusion. For the high-M polymer, the limiting value of f_m is 0.4, whereas for the M_{250K} polymer f_m reaches 0.8. It is interesting that in this polymer full mixing is found for newly dried solvent-cast films containing a 1:1 mixture of D- and A-labeled polymer, but this polymer undergoes limited demixing [consistent with f_m(lim) = 0.8] when the solvent-cast film

is annealed. We interpret this result to indicate that there are prominent correlation effects for the highest molecular weight and most branched components of the P(VAc−DBM) copolymer. These prevent complete penetration of D-labeled molecules into corresponding A-labeled molecules.

One of our most important findings is that the rates of polymer diffusion for the two polymer samples are similar. Each sample is characterized by a distribution of diffusion rates, which presumably vary with the molecular weight and degree of branching of the mobile species. This distribution is similar in both samples, despite the cross-linked networks present in films of the high-*M* sample. In this rather complex system, which is a model for waterborne adhesives, the polymer diffusion rate has a characteristic first identified by Antonietti and Sillescu[26] for diffusion of polystyrene. They found that the diffusion rate of linear polystyrene molecules into a polystyrene network had a similar magnitude with the diffusion of these molecules in a high molecular weight entangled matrix.

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