Temperature Dependence of Polymer Diffusion in Poly(vinyl acetate-*co*-dibutyl maleate) Latex Films

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ABSTRACT: We describe polymer diffusion and its temperature dependence in poly(vinyl acetate-*co*-dibutyl maleate) [P(VAc−DBM)] latex films prepared from 4:1 w/w ratio of VAc:DBM. Two sets of polymers were investigated: one set containing 50% gel (high-*M*); the other set, with $M_w \approx 250\,000$ (M_{250K}), free of a measurable gel content. Despite their similar chemical compositions, as determined by ^{1}H NMR, these two sets of samples exhibited different glass transition temperatures (T_g). Latex particles were labeled with 9-methacryloxymethylphenanthrene as the donor dye and 2′-acryloxy-4′-methyl-4-(*N,N*-dimethylamino)benzophenone as the acceptor. Polymer diffusion was monitored by nonradiative energy transfer (ET), and apparent diffusion coefficients (D_{app}) were calculated from the ET data using a simple diffusion model. These values increased with temperature and were characterized by an apparent activation energy (E_a) of 37 ± 2 kcal/mol for the high-*M* polymer and 45 ± 2 kcal/mol for the M_{250K} sample. Rheology measurements at different fixed temperatures were carried out to follow the response of the dynamic moduli (G', G'') with respect to frequency (ω). A master curve based on the Williams−Landel−Ferry (WLF) equation could be constructed as a plot of shift factors vs $1/T$, and shift factors for D_{app} for both sets of polymers as well as for the G', G'' values fell on the same curve. Thus, the difference in E_a values for the polymer diffusion can be ascribed to changes in the microscopic friction coefficient and the differences in T_g of the two sets of samples.

Introduction

Environmental concerns are driving changes in the coatings industry. Prominent among them is the drive to remove volatile organic compounds (VOC) from the formulations.[1] A typical solvent-based coating contains 60−70 wt % of volatile solvents. These VOCs are used to control the coating viscosity at various stages of drying after the coating has been applied to a substrate. Several alternatives have been considered. These include reactive solvents, powder coatings, high-solids coatings, radiation-cured coatings, and water-based coatings.

Water-based coatings offer advantages of low odor, low combustibility, quick drying, and inexpensive manufacturing costs. Most waterborne coatings are based on dispersions of latex particles prepared by emulsion polymerization. When a latex dispersion is cast on a substrate and water is allowed to evaporate, a continuous latex film is formed under appropriate conditions. It is well-known that, during the drying process, latex particles deform above the glass transition temperature (T_g) of polymer to form a void-free solid composed of polyhedral cells. The newly formed film often has poor mechanical properties, but these evolve and improve over time. During this stage the film loses its initial cellular structure and finally forms a continuous polymer matrix. We now understand that during this maturation process polymer molecules diffuse across the intercellular boundaries. This is a key step for the buildup of mechanical properties of a latex film because entanglements formed during diffusion provide mechanical strength to the film.

Theories of polymer diffusion in melts describe the motion of polymer chain in terms of a diffusion coefficient that depends on chain length and is inversely proportional to the monomeric friction coefficient (ζ_0). This coefficient (ζ_0) represents the average drag force that surroundings exert on each monomer unit when the polymer chain is diffusing. Among the factors that affect this parameter are temperature and the chemical structure of the repeat unit. Temperature effects operate through the thermal expansion of the polymer matrix. Thus, changes in ζ_0 with temperature can be effectively described by the Williams−Landel−Ferry (WLF) equation.[2] For polymers of a given chemical structure, changes in microstructure or in the architecture of the polymer can affect the magnitude of monomeric friction coefficient. This effect normally operates through changes in the glass transition temperature (T_g) so that similar values of ζ_0 are found at comparable values of $T - T_g$. For example, Klopffer et al.[3] explored the influence of polymer microstructure on ζ_0 for a series of polybutadienes and polyisoprenes with different vinyl content. The isothermal storage and loss moduli, G' and G'', were measured, and ζ_0 values were calculated. They found that although an increase of vinyl content does increase the magnitude of ζ_0 at a fixed temperature, it is a unique function of $(T - T_g)$ independent of the chain microstructure. One might also expect that the diffusion rates of these polymers would respond similarly to changes in temperature.

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

	$C_{12}-SH^a$ (mL)	M_w	PDI[b]	gel content (%)	main T_g (°C)
Phe-high-M P(VAc−DBM)	0			50	24
NBen-high-M P(VAc−DBM)	0			50	24
Phe-M_{250K} P(VAc−DBM)	0.24	2.2×10^5	3.0	0	18
NBen-M_{250K} P(VAc−DBM)	0.04	2.3×10^5	2.5	0	18
high-M P(VAc−DBM)	0			50	24
M_{250K} P(VAc−DBM)	0.1	2.4×10^5	2.5	0	18
sol fraction of the high-M		2.8×10^5	2.6		10[c]

[a] Dodecyl mercaptan; for the amount of other ingredients, please refer to ref 10. [b] Polydispersity index (M_w/M_n). [c] The sol fraction has only one T_g.

In this report, we describe the influence of branching on the diffusion rate in latex films consisting of copolymers of vinyl acetate (VAc) with dibutyl maleate (DBM). Homopolymers of vinyl acetate and its copolymers are normally extensively branched.[4] The branching occurs during the polymerization reaction, caused by the highly reactive PVAc radical. When VAc is the only monomer, branching is due primarily to hydrogen abstraction from the acetate methyl group. For copolymers, the comonomer is often the source of reactive hydrogens along the polymer backbone. These copolymers are often more branched than PVAc itself. While intra- and intermolecular hydrogen abstraction can lead to branching, it does not by itself lead to gel formation. The gel fraction commonly found in these polymers arises through termination involving coupling of two growing chains.

The latex particles we examine are prepared from a 4:1 w/w ratio of VAc:DBM via conventional batch emulsion polymerization. The VAc−DBM copolymerization under our experimental conditions behaves differently from those prepared by batch emulsion copolymerization of VAc with other monomers such as butyl acrylate (BA). In the case of VAc-BA copolymerizations, a strong mismatch in reactivity ratios promotes early conversion of the acrylate comonomer, leading to phase separation. Phase separation can be avoided (or at least minimized) only if the emulsion polymerization reaction is carried out under monomer-starved conditions.[5] In the case of VAc−DBM, the reactivity ratios ($r_1 = 0.171$, $r_2 = 0.040$[6,10]) promote formation of an alternating copolymer. 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. Under bulk emulsion polymerization conditions, the chemical composition of P(VAc−DBM), as monitored by ^{1}H NMR, is independent of conversion. Thus, the polymer obtained in the copolymerization of VAc with DBM is fundamentally different from that obtained in its copolymerization with BA.

Here we compare two sets of samples of P(VAc−DBM). The high-M P(VAc−DBM) samples were synthesized in the absence of any chain transfer agent. These samples have a gel content of ca. 50%. The lower M samples were prepared in the presence of dodecyl mercaptan (C_{12}-SH) as a chain transfer agent. These samples are free of gel as detected under our experimental protocol, and the amount of C_{12}-SH added was chosen to give a molecular weight similar to that of the sol fraction of the high-M samples. Since the nominal M_w of these samples (determined by gel permeation chromatography) is ca. 250 000, we refer to these samples as M_{250K}. The feature of this system that recalls the experiments of Klopffer et al. is that the glass transition temperature of P(VAc−DBM) appears to depend on the extent of branching and the gel content. Samples that show different thermal response by different scanning calorimetry (DSC) show similar composition by ^{1}H NMR. This behavior prompts the question of how differences in T_g affect the diffusion rate of polymers in P(VAc−DBM) latex films.

The technique we use for diffusion measurements is fluorescence resonance energy transfer (ET). This technique requires the synthesis of polymers labeled randomly with fluorescent dyes. Two sets of essentially identical latex particles were prepared: one labeled with a donor dye (phenanthrene, Phe) and the other with an acceptor dye 4-(*N,N*-dimethylamino)benzophenone, NBen). The dye comonomers used in the synthesis were 9-methacryloxymethylphenanthrene (PheMMA) and 2′-acryloxy-4′-methyl-4-(*N,N*-dimethylamino)benzophenone (NBenA).[7,8] When a dispersion containing donor- and acceptor-labeled particles dries to form a film, some of the boundaries separate donor- and acceptor-labeled polymers. As these polymers diffuse across the boundaries, they bring donor and acceptor dyes into proximity, accompanied by an increase in the extent of energy transfer.

A reviewer asked us to comment on whether the dyes attached to the polymer have a significant effect on the polymer diffusion rate. This effect is likely to be small. For example, Ye in our group compared polymer diffusion rates in films formed from two sets of donor- and acceptor-labeled samples of poly(butyl methacrylate) (PBMA) latex particles of similar molecular weight, in which the acceptor-labeled particles had different dye contents (0.3 and 0.5 mol % NBen, respectively).[9] Although the higher concentration of acceptor groups led to a higher efficiency of energy transfer (Φ_{ET}), the rates of polymer diffusion, as inferred from our data analysis methodology, did not depend on the dye content of the polymers.

Experimental Section

Materials and Instrumentation. THF (spectral grade, Aldrich) and 1,4-dioxane (Aldrich) were used as received. Deionized water was collected from a Milli-Q water system. The syntheses of PheMMA- and NBen-labeled high-M P(VAc−DBM) latex particles were described elsewhere.[10] The recipes used for the other samples used in this report differ only in the amount of dodecyl mercaptan−C_{12}-SH employed in the synthesis. Because rheology measurements require larger amounts of sample, we also prepared unlabeled samples of the high-M and M_{250K} latex by omitting the dye comonomer from the recipes. These samples had gel contents and molecular weights similar to those of the corresponding high-M and M_{250K} dye-labeled P(VAc−DBM). In Table 1 we list the samples prepared and their key characteristics. For details about the synthesis of the P(VAc−DBM) latex particles, refer to ref 10.

Particle sizes and particle size distribution were recorded with a Brookhaven BI-90 particle sizer. Molecular weights and molecular weight distribution were measured by gel permeation chromatography (GPC) at 22 °C, based on a Waters

model 515 pump, Styragel columns HR-1 and HR-5E, and a Waters R10 differential refractometer detector. Reagent grade THF was used as eluent at a rate of 0.8 mL/min. The columns were calibrated with linear poly(methyl methacrylate) (PMMA) standards.

Film Preparation. A few drops (3−5 drops) of a latex dispersion (containing 1:1 wt ratio of mixed Phe- and NBen-labeled particles, 20 wt % solids) were spread on a small quartz plate (20 mm × 10 mm). The film was allowed to dry at room temperature (22 °C) in the open air and was dry within 2 h. The films were then moved to a cold room (4 °C) to prevent further polymer interdiffusion. The films prepared in this way were transparent and have a thickness of ca. 100 μm. Solvent-cast films were prepared from the same dispersion [1:1 wt ratio of Phe- and NBen-labeled P(VAc−DBM)]. A latex film was allowed to dry, and the dry film was dissolved in a minimum amount of tetrahydrofuran (THF). The solution was cast onto a quartz plate and allowed to dry at room temperature for 24 h. The solvent-cast films have a typical thickness of ca. 50 μm.

The films on quartz plates were placed directly on a high mass (2 cm thick) aluminum plate in an oven preheated to the annealing temperature and then annealed for various periods of time. The annealed films were taken out of oven and placed directly on another high mass aluminum plate at room temperature for 3−5 min before carrying out fluorescence decay measurements.

Polymer Characterization. *Gel Content Determination.* An unpurified latex sample (4.0 g) was dried to a constant weight W_0. The dried polymer was subsequently immersed in 1,4-dioxane (10 mL). The mixture was agitated gently at room temperature for 72 h. The resulting solution was then centrifuged at 20 000 rpm for 20 min, and the top transparent layer was poured off and saved. The precipitate was washed three more times with excess 1,4-dioxane to remove residual sols from the gel. All the dioxane solutions were combined and dried for GPC and DSC analysis. The remaining sample (the gel fraction) was dried and weighed (W_1). The gel content (%) was calculated from the expression

$$\text{gel content (\%)} = (W_1/W_0) \times 100 \tag{1}$$

DSC Measurements. The glass transition temperatures T_g of the VAc−DBM copolymer samples were determined by differential scanning calorimetry (DSC) experiments with a Universal V2.6D TA Instruments on 5 ± 1 mg samples under N_2 at a heating and cooling rate of 10 °C/min. For most samples two or three heat−cool cycles were run: heating from −20 to 60 °C followed by cooling back to −20 °C. A complete measurement took about 1 h. The T_g values were obtained as the inflection point on the second heating curves. The characteristics of all of the latex particles considered in this paper are listed in Table 1.

Fluorescence Decay Measurements and Data Analysis. For fluorescence decay measurements, each labeled film was placed in a quartz tube and degassed with flowing N_2 for 3−5 min before each measurement. Fluorescence decay profiles were measured by the time-correlated single photon counting technique. The excitation wavelength was 300 nm, and emission from the sample was detected through a combination of a band-pass filter (310−400 nm) and a cutoff filter (335 nm) to minimize the amount of scattered sample excitation light (300 nm) from reaching the detector. In the absence of benzophenone as an energy transfer acceptor, for samples containing 1 mol % donor, the Phe decay profiles were exponential, with $\tau_D = 44.6$ ns for the high-M P(VAc−DBM) and $\tau_D = 43.0$ for the M_{250K} P(VAc−DBM). Each measurement was continued until there were 5000 counts in the maximum channel. This requires 10 min for the newly formed films and 12−15 min for films annealed for longer times.

$$\Phi_{ET}(t_n) = 1 - \frac{\int_0^\infty I_{DA}(t)\,dt}{\int_0^\infty I_D(t)\,dt} = 1 - \frac{\text{area}(t_n)}{\tau_D} \tag{2}$$

The quantum efficiency of energy transfer $\Phi_{ET}(t_n)$ is defined in eq 2, where $I_{DA}(t)$ and $I_D(t)$ represent the decay functions of donor fluorescence intensity in the presence and absence of acceptor, respectively; t_n refers to the time that a given sample was annealed prior to the fluorescence decay measurements. $\int I_D(t)\,dt$ is the area under the donor decay profile of a film containing only donor. Since the unquenched donor decay profiles for the phenanthrene derivatives employed here are exponential, the value of the integral [area(D)] equals the unquenched donor lifetime τ_D. The term $\int I_{DA}(t)\,dt$ describes the area under the donor decay profile of a film containing both donor and acceptor. These areas have the dimension of time. To obtain an accurate area for each decay profile, we fitted each decay curve to the empirical eq 3 and then evaluated the integral analytically from the magnitude of the fitting parameters. Φ_{ET} values were then calculated from the areas with eq 2.

$$I_D(t') = A_1 \exp[-t/\tau_0 - P(t/\tau_D)^{1/2}] + A_2 \exp(-t/\tau_D) \tag{3}$$

Some samples, especially the gel-containing samples, lead to a significant scattering of the excitation light, which could not be eliminated by sample alignment. A signature of a good fluorescence decay profile is that the fitting parameters from eq 3 remain the same with or without a light scattering correction in the data analysis. To test our measurements, when we fitted experimental decay profiles with a light scattering correction, the first channel of fitting was set to be five channels before the maximum of the lamp profile. When the same decay profile was fitted without the light scattering correction, the first channel of fitting was set to be five channels after the lamp maximum. If we found a significant discrepancy between the fitting parameters of the two analyses, the fit was discarded, and the sample was remeasured.

Our measure of polymer diffusion in latex films is the "extent of mixing" parameter f_m

$$f_m(t_n) = \frac{\Phi_{ET}(t_n) - \Phi_{ET}(0)}{\Phi_{ET}(\infty) - \Phi_{ET}(0)} = \frac{\text{area}(0) - \text{area}(t_n)}{\text{area}(0) - \text{area}(\infty)} \tag{4}$$

which is defined as the fractional growth of the quantum efficiency in the system. $\Phi_{ET}(0)$ represents the extent of ET across the interfaces in the newly formed film, whereas $\Phi_{ET}(\infty)$ refers to ET efficiency in a film in which the donors and acceptors have been fully randomized. $\Phi_{ET}(t_n)$ represents the degree of energy transfer in a film annealed for time t_n. According to eq 2, the $f_m(t_n)$ can be calculated from the corresponding areas under the fitted donor decay profiles.

Rheology Measurements. The viscoelastic response of P(VAc−DBM) copolymers was studied at several temperatures above T_g with a Rheometrics AA instrument in the oscillatory shear mode. We employed a cone and plate geometry (25 mm diameter, 0.04 rad cone angle, and 0.048 mm gap height). The frequency was scanned between 10^{-2} and 80 Hz at a constant temperature. The rheometer motor limits the highest frequency. The lowest frequency was set to keep acquisition times to be less than 20−30 min. After testing the linear viscoelastic response at all frequencies, small strains, between 0.02 and 0.05, were imposed. The range of temperatures studied was selected to be as close as possible to the range of temperatures used in the ET diffusion experiments. However, the lower temperatures used were limited by the high relaxation times of the samples at temperatures close to T_g.

The following procedure was used to prepare the samples for the measurements of viscoelastic properties. First, latex samples were allowed to evaporate in a beaker, followed by further drying 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 90 °C to eliminate bubbles of air. Clean PET sheets were used to prevent contact between the sample and the plates. In a second step, the material, free of air bubbles, was remolded at the same temperature, but now the thickness of the samples was

controlled by separators between the plates of the press. In this way, samples were obtained free of bubbles, approximately 25 mm in diameter and 0.5 mm thick.

Some precautions were taken to ensure that the instrumental conditions were the same during the entire experiment. Before and after running each material, the instrument response was checked by running standard samples at selected temperatures. The standard commonly used for checking the calibration of this instrument is PDMS at 35 °C. We also checked the instrument response at higher temperatures (100 °C) by using a PVAc homopolymer sample as a standard.

Results and Discussion

Polymer Characterization. The syntheses of the PheMMA- and NBen-labeled high-M P(VAc−DBM) latex particles examined here were reported previously.[10] The polymers were synthesized from a 4:1 wt ratio (10.6:1 molar ratio) of VAc−DBM in absence of chain transfer agent via batch emulsion polymerization. The high-M polymer, prepared without chain transfer agent, had a substantial gel content. Despite the constant composition as a function of conversion for this sample, we found two distinct glass transition temperatures (T_g) by differential scanning calorimetry (DSC), a pronounced transition at 24 °C, and a much weaker transition at ca. 34 °C. Since samples collected at different extents of conversion showed similar DSC signals, these observations point either to a consistent formation of small high-T_g (PVAc-rich) domains throughout the polymerization or to a DSC response that depends on the distribution of branch points or crosslink junctions.

We fractionated this polymer into sol (50 wt %) and gel (50 wt %) components. ^{1}H NMR experiments showed that the sol and gel components had similar compositions. The glass transitions determined by DSC were different. The sol fraction exhibited only one T_g at 8 °C, whereas the gel showed a large-amplitude T_g at 28 °C and a minor T_g at 35 °C. The expected difference between sol and gel fractions in P(VAc−DBM) polymer is the degree of branching. According to Lovell et al.,[4] branching in VAc polymerization is primarily an interpolymer process. In a complementary experiment, we synthesized a very low molar mass copolymer with $M_w \approx 5 \times 10^4$. The degree of branching was suppressed by introducing a larger amount of C_{12}-SH (1 mL) based on the recipe in ref 10. By DSC, this sample showed a strong T_g at ca. 12 °C with no transition at higher temperature. We conclude that differences in the degree of branching lead to phase separation, with separate branch-rich and branch-poor domains.

The lower M P(VAc−DBM) copolymer (M_{250K}) latex particles that we examine here were synthesized in the presence of a smaller amount of C_{12}-SH. These samples had no detectable gel as measured by the protocol described in the Experimental Section. By GPC (PMMA standards), we calculated $M_w = 2.4 \times 10^5$ (PDI ≈ 3). We did note, however, that for a constant amount of C_{12}-SH added to the recipe the mean molecular weights of the Phe-labeled, NBen-labeled, and unlabeled M_{250K} P(VAc−DBM) samples were different. To make meaningful comparisons among the samples, we varied the amount of chain transfer agent added to the recipe until we found conditions that gave virtually superimposable GPC traces for these lower M samples. To simplify our notation, we refer to these various samples prepared to exhibit a nominal $M_w \approx 2.5 \times 10^5$ as M_{250K}. We list the amount of C_{12}-SH added to each recipe in Table 1. These
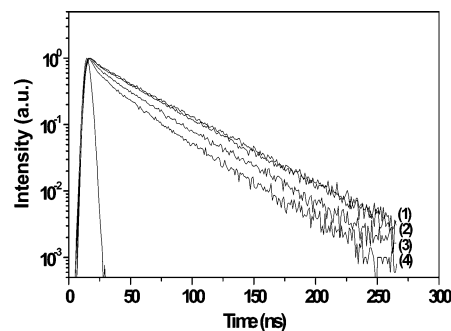

Figure 1. Donor fluorescence decay profiles of (1) a M_{250K} P(VAc−DBM) film labeled with donor PheMMA (1 mol %) only; (2) a nascent film formed at room temperature, prepared from a 1:1 ratio of PheMMA-labeled M_{250K} P(VAc−DBM) (PheMMA, 1 mol %) and NBen-labeled M_{250K} P(VAc−DBM) (NBen, 0.3 mol %) latex particles; (3) a similar film annealed at 55 °C for 75 min; and (4) a film formed from a THF solution of a mixture with the same composition as the film in (2).

M_{250K} latex polymers also show two T_g's by DSC: a major transition at ca. 18 °C and a minor (much weaker) transition at ca. 28 °C.

Polymer Diffusion in Films of the Gel-Free M_{250K} P(VAc−DBM) Latex. Films were prepared by casting aliquots of a latex dispersion onto glass substrates and allowing it to dry in the open air at room temperature, 22 °C. These films were transparent and crack-free after drying.[11] Figure 1 shows typical donor fluorescence decay profiles in these latex films. The decay profile for a film containing only donor is exponential with a lifetime of 43 ns. In the newly formed film from a 1:1 mixture of Phe- and NBen-labeled particles, the $I_{DA}(t)$ profile (curve 2) is not exponential. From the shape of the normalized decay curve for a series of similar samples, we calculate an ET efficiency (Φ_{ET}) of 0.06−0.10. While the lower value is appropriate for a film in which intimate contact between donor- and acceptor-labeled cells, the higher value of $\Phi_{ET}(0)$ in the newly formed films points to a small extent of polymer diffusion at room temperature during the drying process. Curve 3 in Figure 1 shows the result of 75 min annealing at 55 °C. This film shows a more pronounced curvature in the donor fluorescence decay profile. Polymer diffusion in this sample has led to an increase in Φ_{ET}. Curve 4 in Figure 1 represents the decay profile for a film of the M_{250K} sample cast from a THF solution. For this sample, we assume that complete mixing of the donor and acceptor chromophores has occurred. The area under this normalized decay profile represents the smallest area and the largest extent of energy transfer possible for this polymer.

To assess how much diffusion can occur in these M_{250K} films allowed to age at room temperature, we monitored the increase in Φ_{ET} over time. These results are plotted in Figure 2. In the experiments described in Figure 2, the film was dried 2 h before the first point defining t_n = 0 was measured. Over the next 20 h, Φ_{ET} increased from 0.08 to 0.14. For the corresponding high-M latex film, Φ_{ET} increased from 0.08 to 0.10 over 16 h. We conclude that polymer diffusion in both the M_{250K} and high-M P(VAc−DBM) latex films at 22 °C is slow, but not negligible. To avoid any complications associated with room temperature diffusion, we stored samples at 4 °C except during annealing or during fluorescence decay measurements.

To determine the extent of polymer diffusion in latex films by means of eq 4, we need to determine indepen-
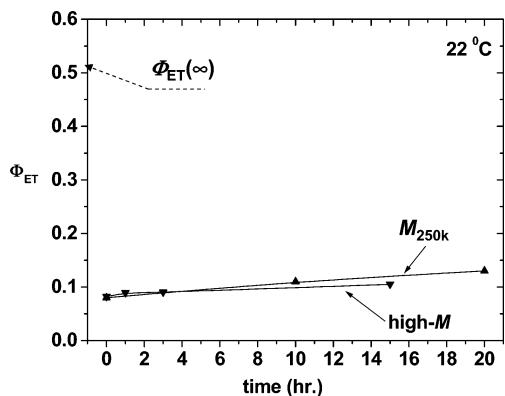
Figure 2. Plot of the quantum efficiencies of energy transfer (Φ_{ET}) for films from a 1:1 ratio of PheMMA-labeled P(VAc−DBM) (PheMMA, 1 mol %) and NBen-labeled P(VAc−DBM) (NBen, 0.3 mol %) latex particles but allowed evolving for various periods of time at 22 °C: (▲) M_{250K}, (▼) high-*M*.

dently the values of two parameters $\Phi_{ET}(0)$ and $\Phi_{ET}(\infty)$. In the newly formed films, we found $\Phi_{ET}(0)$ values of ca. 0.08. We use this value to calculate the extent of polymer mixing, f_m. In our experience, for films formed from 100 nm diameter latex particles, the presence of sharp interfaces with ET arising only from donor and acceptor groups on opposite side of this interface would lead to a $\Phi_{ET}(0)$ value on the order of 0.05−0.07.[12] Our result here is consistent with a small amount of polymer diffusion accompanying film drying, possibly as a result of the plasticizing effect of water on PVAc copolymers.

$\Phi_{ET}(\infty)$ represents the extent of energy transfer corresponding to the fully mixed state. For systems containing gel, one cannot obtain a value for $\Phi_{ET}(\infty)$ by examining a solvent cast film. The microgel present in donor- and acceptor-labeled cells does not diffuse. It makes only a limited contribution to the increase in energy transfer as the un-cross-linked polymer diffuses across cell boundaries. In a previous publication,[10] we discussed the problem of selecting a proper value of $\Phi_{ET}(\infty)$. We showed that there are two ways to approximate a $\Phi_{ET}(\infty)$ value for P(VAc−DBM) latex films. First, we prepared from a doubly labeled latex containing the Phe and NBen concentrations expected from a fully mixed latex film. Here we obtained $\Phi_{ET} = 0.52$. We also separated the high-*M* polymer into its sol and gel fractions. Solvent-cast films from a 1:1 mixture of the donor- and acceptor-labeled sol fractions also gave a value of $\Phi_{ET} = 0.52$. In both instances, the shapes of the donor fluorescence decay profiles were consistent with a random distribution of donors and acceptors in the films.[13] Thus, to calculate f_m values, we set $\Phi_{ET}(\infty) = 0.52$.[14]

In Figure 3 we plot values of Φ_{ET} and f_m as a function of annealing time for films of the M_{250K} polymer annealed at different temperatures. The data in Figures 3 show that Φ_{ET} and f_m increase with annealing time. From the shapes of the curves, we observe that a large increase in Φ_{ET} values occurs at early times, followed by a smaller increase at longer times. In Figure 3B, we see that rate of growth of f_m depends strongly on the annealing temperature. The increases of Φ_{ET} and f_m values track the diffusive mixing of the PheMMA-labeled polymers and the NBen-labeled polymers. We explain the rapid growth in ET at early times in terms of the more rapid diffusion of the lower molar mass components of the latex polymer. Larger chains and
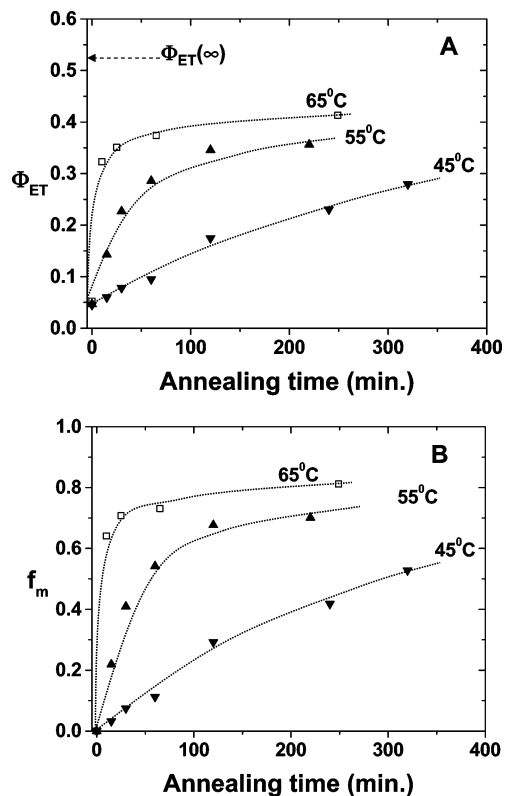

Figure 3. Plots of Φ_{ET} (A) and f_m (B) vs annealing time for the M_{250K} P(VAc−DBM) latex films annealed at 45, 55, and 65 °C.

branched polymer, which diffuse more slowly, contribute at longer times to the growth of ET in the sample.

To compare polymer diffusion at different temperatures, we need a measure of the polymer diffusion rate. For this purpose, we calculate values of the apparent mean diffusion coefficient D_{app}. This calculation makes a number of strong assumptions about the nature of the diffusion process that, strictly speaking, do not apply to polymers with complex mixtures of architectures such as those found in PVAc copolymers. Thus, the values of D_{app} are different from the actual diffusion coefficients of the polymers that contribute to the growth in ET signal at various times in the experiment. Despite this problem, we have shown that these D_{app} values allow one to assess changes in the rates of diffusion as influenced by changes in temperature as long as one is careful to compare D_{app} values at similar extents of mixing f_m.[15] Values of D_{app} calculated in this way for the M_{250K} sample at 65, 55, and 45 °C are plotted as a function of f_m in Figure 4. For each sample, these D_{app} values decrease with increasing extent of mixing as slower diffusing species make their contribution to the growth in ET. We also see that the diffusion rate is faster at higher temperature.

An Arrhenius plot (ln D_{app} vs 1/*T*) of the data in Figure 4 plotted for D_{app} values at $f_m = 0.68$ is shown in Figure 5 (curve A). From the slope of this plot, we calculate an activation energy of ca. 45 kcal/mol that characterizes the diffusion process in the range of temperature between 45 and 65 °C. Since temperature affects the rate of diffusion by a change in the microscopic friction coefficient, the magnitude of E_a should be independent of f_m. We test this idea by using the value of $E_a = 45$ kcal/mol as a shift factor to create a master curve of D_{app} values at 45 °C. The shifted values calculated in this way are also shown in curve C of
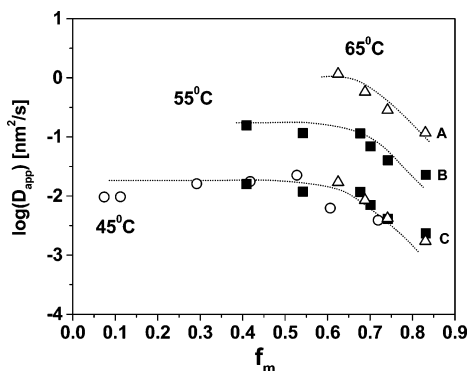
Figure 4. Values of the apparent diffusion coefficient D_{app} calculated from the data in Figure 3 plotted vs the extent of mixing f_m. The $\triangle$ and $\blacksquare$ on curve C refer to data obtained at 65 and 55 °C recalculated for 45 °C using $E_a = 45$ kcal/mol, respectively.
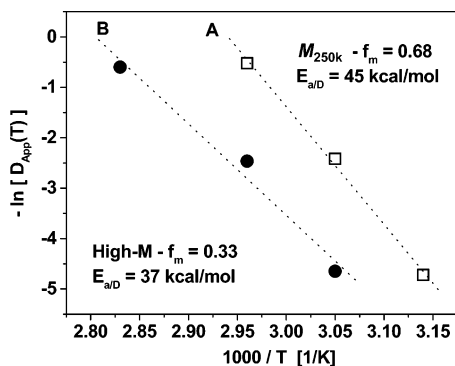

Figure 5. Plots of ln D_{app} vs $1/T$ over the temperature range for diffusion measurements: (A) M_{250K} P(VAc−DBM); (B) high-M P(VAc−DBM).

Figure 4. We take the success in generating the master curve as support for the validity of our analysis to obtain D_{app} values. From these data, we conclude that the diffusion of the polymer in the M_{250K} sample, with a mole ratio of VAc:DBM = 10.6:1, is characterized by an effective activation energy of 45 kcal/mol in the range 45−65 °C.

Polymer Diffusion in Films of the Gel-Containing High-M P(VAc−DBM) Latex. In Figure 6, we plot values of Φ_{ET} and f_m as a function of annealing time for the high-M P(VAc−DBM) films annealed at different temperatures. From the shape of the curves, we see that there is a large increase in Φ_{ET} values at early times, followed by a smaller increase at longer times. The limiting value of Φ_{ET} in this sample is much lower than $\Phi_{ET}(\infty)$, and the limiting value of f_m is much less than 1.0. This is a consequence of the gel content of the sample, which limits the extent of diffusive mixing of polymers in adjacent cells in the film.

D_{app} values for these experiments were calculated as described above. These values are plotted against f_m in Figure 7 for experiments carried out at 55, 65, and 80 °C. For each sample, these D_{app} values decrease with increasing extent of mixing, and the rate of diffusion increases with increasing temperature. An Arrhenius plot of the D_{app} values at $f_m = 0.33$ is shown in Figure 5. This plot yields an apparent activation 37 kcal/mol over the range of 55−80 °C. This value is appropriate for this polymer at all values of f_m, as shown by the fact that we can use this value as a shift factor to construct a master curve for polymer diffusion at 55 °C, as shown in Figure 7.
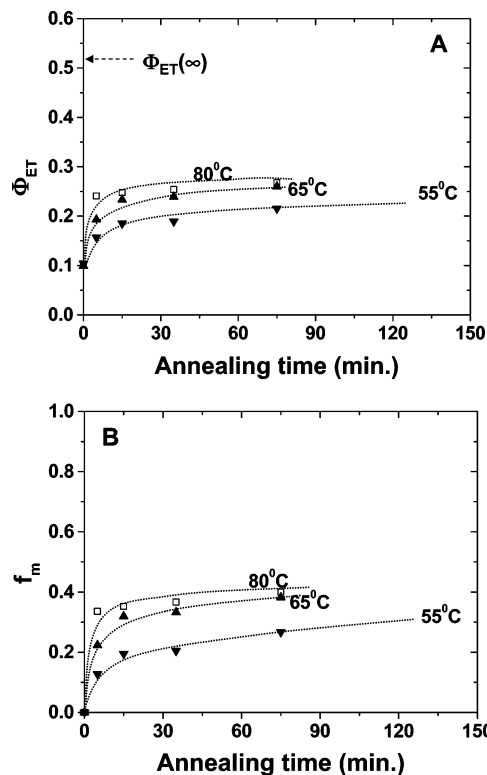

Figure 6. Plots of Φ_{ET} (A) and f_m (B) vs annealing time of the high-M P(VAc−DBM) latex films annealed at 55, 65, and 80 °C.
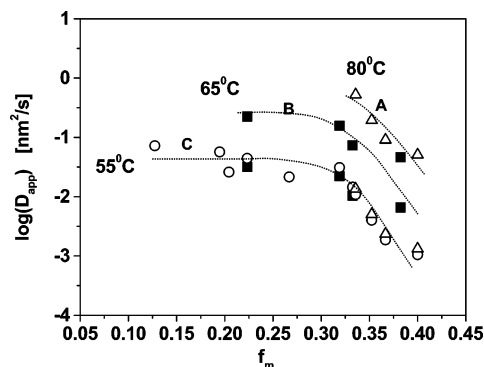

Figure 7. Values of the apparent diffusion coefficient D_{app} calculated from the data in Figure 6 plotted vs the extent of mixing f_m. The $\triangle$ and $\blacksquare$ on curve C refer to data obtained at 80 and 65 °C recalculated for 55 °C using $E_a = 37$ kcal/mol, respectively.

One of the most interesting features of the data in Figures 4, 5, and 7 is that the activation energy found for the high-M polymer is lower (37 kcal/mol) than that found for the M_{250K} polymer (45 kcal/mol). This difference is well outside experimental error. We next turn our attention to understand the origin of this difference.

Flow Activation Energy by Rheology Measurements. The temperature dependence of polymer diffusion and viscoelastic properties of polymers reflects the temperature dependence of large-amplitude motions of the polymer backbone. It is normally described in models where the temperature dependence derives from the free volume increase due to the thermal expansion of the polymer matrix.[2] The WLF equation (5) is widely employed to describe this kind of dependence

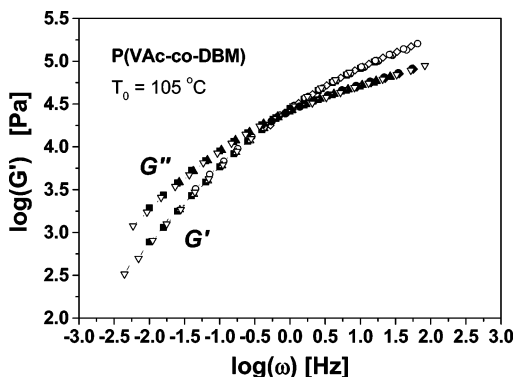$$\log(a_T) = \log \frac{DT_0}{D_0 T} = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \quad (5)$$

Figure 8. Plots of master curves of G' and G'' for P(VAc−DBM) latex films at $T_0 = 105$ °C.

where C_1 and C_2 are parameters that depend basically on the choice of the reference temperature (T_0). Another important parameter that characterizes the temperature dependence is the activation energy associated with the motions of polymer backbone. It can be obtained by plotting the data in Arrhenius fashion [ln(a_T) vs $1/T$]. This plot is usually curved, but when one has limited data over a relatively narrow range of temperatures, the plot can appear linear. The activation energy E_a for viscoleastic relaxation can be calculated from the slope of this plot, whose magnitude will increase as the measurement temperature approaches T_g.

To test the validity of the data analysis described for polymer diffusion, we performed independent oscillatory shear measurements as a function of frequency over a range of temperature close to that of the diffusion experiments. For viscoelastic measurements we used an unlabeled sample, with a molecular weight similar to the M_{250K} sample (see Table 1). We measured the storage and loss moduli (G', G'') vs frequency for several temperatures that ranged from 52 to 115 °C (not shown). The time−temperature superposition (TTS) principle is usually applied to superimpose log−log plots of viscoelastic properties vs frequency in order to obtain the temperature dependence of the shift factors (a_T). The TTS principle is only applicable if the various relaxation times belonging to a given relaxation process have the same temperature dependence, as occurs in linear amorphous polymers above T_g. Our sample is composed of polymer chains with various degrees of branching, which eventually leads to phase separation between branch-rich and branch-poor components.[10] It is well-known that branching may affect slightly the temperature sensitivity of the viscoelastic response, but TTS basically holds.[16] A second important issue is that, although the DSC traces of the latexes show a main T_g, a second minor transition, observed as a small shoulder, reveals some inhomogeneities in the sample. In the case of heterogeneous polymeric materials, as immiscible polymer blends, one can find in the literature examples in which TTS holds,[17] especially when the WLF parameters or the activation energies of the components are not too far apart, as well as examples in which TTS dramatically fails.[18] In Figure 8, we show the G' and G'' master curves after applying TTS, by choosing $T_0 = 105$ °C as the reference temperature. Only shifts in the horizontal scale were applied. We found that the shifts factors corresponding to G' and G'' were practically the same. The crossover observed corresponds to the transition between the terminal zone and the rubbery region, indicating that the molecular weight of the sample is high enough to form entanglements. As observed in this
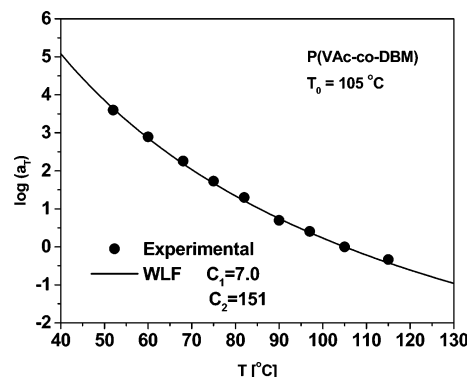

Figure 9. Plot of log(a_T) against temperature ranging from 52 to 105 °C. From the curve, we obtained $C_1 = 7.0$ and $C_2 = 151$ at $T_0 = 105$ °C.
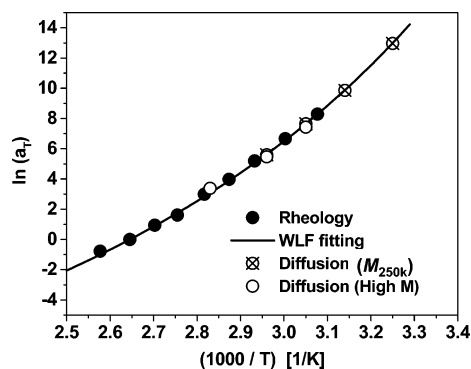

Figure 10. Plots of shifted D_{app} and a_T vs the inverse of the absolute temperatures.

figure, good matching between curves is obtained, even if we extended the range of frequencies analyzed.[19] Similar results in terms of goodness of superposition were obtained from the high-M gel-containing sample.[19] We conclude that in this case the presence of a second minor T_g does not produce observable failure of TTS, which we can safely apply to calculate the activation energies from viscoelastic measurements. The reasons might be the minor contribution of the second T_g and the close proximity between them (10 °C difference).

Values of log(a_T) obtained from TTS can be plotted in WLF fashion against the temperature (Figure 9). These data can be nicely fitted to the WLF equation to obtain the C_1 and C_2 parameters. We obtained $C_1 = 7.0$ and $C_2 = 151$ using $T_0 = 105$ °C. Values of the apparent activation energy in the range of temperatures studied can be obtained by plotting ln(a_T) in Arrhenius fashion against the inverse of the absolute temperature. The results are presented in Figure 10 as filled circles. From the slope of the linear regression we obtained an average value of $E_{a/v}$ of 35.0 kcal/mol, in the range of temperature from 50 to 130 °C.

Comparison between Different Experiments. We can compare parameters that characterize the temperature dependence of the viscoelastic relaxation (WLF parameters and apparent activation energies) of our P(VAc−DBM) copolymers with those obtained from materials chemically similar. Proper comparisons should be done in similar ranges of temperatures with respect to T_g. We will employ the WLF constants previously obtained ($C_1 = 7.0$ and $C_2 = 151$), and we will assume that the main T_g (18 °C) controls the viscoelastic relaxation.

For PVAc copolymers, with butyl acrylate as comonomer ($T_g = 11$ °C), we obtained $C_1 = 6.67$ and $C_2 = 143.0$

at the same $T_0 - T_g$.[20] We also measured the WLF constants for pure PVAc. We obtained $C_1 = 7.24$ and $C_2 = 140.0$ for a commercial PVAc sample with $T_g = 25$ °C. These results indicate that, independently of the different microstructures, the temperature dependence obtained from rheological measurements can be characterized by similar WLF parameters, which, as expected, are close to those of pure PVAc.

Similar conclusions can be drawn when we compare values of the apparent activation energy obtained from Arrhenius plots. For the M_{250K} sample we obtained an average value of $E_{a/v}$ of 35.0 kcal/mol, in the range of temperature from 50 to 130 °C. Similar results were obtained from the high-M gel-containing sample. By plotting the $\ln(a_T)$ in Arrhenius fashion, we obtained activation energy of 35.9 kcal/mol in the range 60–120 °C. We can compare these values with that obtained for pure PVAc in the same $T - T_g$ temperature range (36 kcal/mol). We can conclude that, from the point of view of viscoelastic relaxation, the temperature dependence does not reflect changes in polymer microstructure (i.e., degree of branching, gels, or chemical composition).

To compare these results with those results obtained from the diffusion experiments, we have to take into account the clear WLF curvature in Figure 9 due to the proximity to the glass transition temperature and to the relatively wide range of temperatures analyzed. For a proper comparison, we recalculate E_a from viscoelastic measurements using an interval of temperatures closer to the diffusion experiments. Thus, we obtained a value of 41 kcal/mol in the range of temperature between 75 and 52 °C (34–57 °C above T_g). This value is in good agreement with the results obtained from diffusion measurements (45 kcal/mol), taking into account that the range of temperatures in diffusion experiments is slightly closer to T_g.

A direct comparison between data obtained from rheology and from diffusion experiment can be made by plotting both data in the same graph, Figure 10, where shift factors obtained from rheology (filled circles) and diffusion experiments (open circles) are shown together. The data diffusion were taken from Figure 5A,B (Arrhenius plots) and then shifted vertically to compensate for the different reference temperatures used in each plot. The full line represents the WLF fitting, calculated by using the C_1 and C_2 values described above. It can be observed how well the diffusion data follow the tendency given by WLF equation prediction obtained from rheology, within the experimental error. This plot is also useful to show that the temperature dependence is independent of polymer microstructure and that the main T_g of the polymers controls the viscoelastic properties. From this result, we can infer that both the temperature dependences of the friction coefficients and diffusion coefficients are not affected by the presence of gels, which is consistent with the results by Klopffer et al.[3] They showed that friction coefficient is a unique function of $(T - T_g)$ regardless of chain microstructure in polyolefins with various vinyl contents.

Summary

We employed the fluorescence resonance energy transfer (ET) technique to study the effect of temperature on the rate of polymer interdiffusion in latex films containing gel-free and gel-containing P(VAc–DBM) copolymers. Analysis of the apparent diffusion coefficients (D_{app}) at different temperature gives an apparent activation energy for diffusion of ca. 45 kcal/mol for M_{250K} P(VAc–DBM). The presence of gel has little effect on the temperature dependence of the polymer diffusion rate in the high-M P(VAc–DBM) sample, which is characterized by an E_a of ca. 37 kcal/mol. These results were confirmed by rheology measurements, in which we followed dynamic moduli (G', G'') with respect to frequency (ω) at fixed temperatures. A plot of shift factors against the inverse of temperature gives apparent activation energy for P(VAc–DBM) system to be 41 kcal/mol, which is in good agreement with that from diffusion measurements.

References and Notes

(1) Bezinski, J. J. Regulation of Volatile Organic Compound Emission from Paints and Coatings. In *Paint and Coating Testing Manual*, 14th ed. of the *Gardner-Sward Handbook*; Koleske, J. V., Ed.; 1995; Chapter 1.

(2) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.

(3) Klopffer, M. H.; Bokobza, L.; Monnerie, L. *Polymer* **1998**, *39*, 3445.

(4) Britton, D.; Heatley, F.; Lovell, P. A. *Macromolecules* **1998**, *31*, 2828.

(5) Misra, S. C.; Pichot, C.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Part C: Polym. Lett.* **1979**, *17*, 567.

(6) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.

(7) Oh, J. K.; Wu, J.; Winnik, M. A.; Craun, G. P.; Rademacher, J.; Farwaha, R. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1594.

(8) Oh, J. K.; Wu, J.; Winnik, M. A.; Craun, G. P.; Rademacher, J.; Farwaha, R. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3001.

(9) Ye, X. D.; Farinha, J. P. S.; Oh, J. K.; Winnik, M. A.; Wu, C. *Macromolecules* **2003**, *36*, 8749.

(10) Wu, J.; Oh, J. K.; Yang, J.; Winnik, M. A.; Farwaha, R.; Rademacher, J. *Macromolecules* **2003**, *36*, 8139.

(11) Attempts to form films at 4 °C to minimize polymer diffusion during the drying step led to cracked films.

(12) Farinha, J. P. S.; Vorobyova, O.; Winnik, M. A. *Macromolecules* **2000**, *33*, 5863.

(13) (a) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7. (b) Baumann, J.; Fayer, M. D. *J. Chem. Phys.* **1986**, *85*, 4087. (c) For a review of the use of energy transfer to study polymers, see: Morawetz, H. *Science* **1988**, *240*, 172.

(14) In P(VAc–BA) latex films containing very similar dye concentrations, Φ_{ET} values reach 0.6. This result is suggestive of a higher value of R_0 for Phe–NBen in this matrix than in P(VAc–DBM). Oh, J. K.; Yang, J.; Tomba, J. P.; Rademacher, J.; Farwaha, R.; Winnik, M. A. *Macromolecules* **2003**, *36*, 8836.

(15) Liu, R. H.; Winnik, M. A.; Di Stefano, F.; Vanketessan, J. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1495.

(16) (a) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2702. (b) Carella, J. M.; Gotro, J. T.; Graessley, W. W. *Macromolecules* **1986**, *19*, 659.

(17) (a) Watanabe, H.; Kotaka, T. *Macromolecules* **1983**, *16*, 769. (b) Wang, K. J.; Lee, L. J. *J. Appl. Polym. Sci.* **1987**, *33*, 431. (c) Cassagnau, P.; Espinasse, I.; Michel. A. *J. Appl. Polym. Sci.* **1995**, *58*, 1393. (d) Lipatov, Y. S.; Shumsky, V. F.; Gorbatenko, A. N.; Panov, Y. N.; Bolotnikova, L. S. *J. Appl. Polym. Sci.* **1981**, *26*, 499.

(18) (a) Han, C. D.; Kim, J. K. *Polymer* **1993**, *34*, 2533. (b) Bazuin, C. G.; Eisenberg, A. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1021.

(19) Wu, J.; Tomba, J. P.; Winnik, M. A.; Farwaha, R.; Rademacher, J. *Macromolecules*, submitted.

(20) Oh, J. K.; Tomba, J. P.; Ye, X. D.; Eley, R.; Rademacher, J.; Farwaha, R.; Winnik, M. A. *Macromolecules* **2003**, *36*, 5804.