Interdiffusion in Cellular Latex Films[†]

M. Joanicot,[‡] K. Wong,[‡] and B. Cabane*,[§]

Rhône Poulenc, 93308 Aubervilliers, France, and Equipe mixte CEA-RP,
Service de Chimie Moléculaire, CEA-Saclay, 91191 Gif sur Yvette, France

Received July 25, 1995[⊗]

ABSTRACT: Latex films have been produced through evaporation of aqueous dispersions containing polymeric particles. These films have a cellular structure: The cell cores are made of hydrophobic polymers, and the cell walls are made of carboxylic monomers that are copolymerized with the core polymers. The mechanical properties of these films are determined by the state of the cell walls. In humid environments, the cell walls take up water and lose their cohesive strength; consequently the films become brittle. The possibility of reinforcing the films through interdiffusion of core polymers across the cell walls was examined. Annealing the films at temperatures where these polymers are mobile produced extensive interdiffusion of low molar mass polymers across the cell walls. This had no effect on the mechanical properties of the films. Annealing at temperatures that caused fragmentation of cell walls produced interdiffusion of high molar mass polymers. At this stage the films became resistant to humidity.

Introduction

A latex is an aqueous dispersion of polymeric particles, with cores made of hydrophobic, rubbery polymers and protected by cell walls made of hydrophilic molecules. Polymer films can be made by spreading a latex onto a substrate and then evaporating water until the particles come into contact and fuse together. Ideally, the process of film formation may be viewed as a succession of four steps (Figure 1): (a) concentration—as water is removed, the particles are packed into a smaller volume where they must order to minimize their repulsions;[1] (b) film formation—neighboring particles are forced into contact, and they are deformed by capillary and surface forces in order to fill all volumes left by the removal of water;[2−7] (c) coalescence—the hydrophilic cell walls break up, allowing direct contact between the cores of neighboring particles;[5,8] (d) interdiffusion—the core polymers are released from their original confinement and diffuse through the film, forming a continuous matrix of core polymers. In this last step all trace of the original particles is lost.[9−17]

It is extremely important to find out whether this division into four separate stages is realistic. Indeed, control of film properties depends on understanding and manipulating the processes involved in film formation. For instance, resistance to water penetration is not achieved until the hydrophilic array of cell walls has been fragmented into isolated lumps immersed in a continuous hydrophobic matrix.[5,8] Moreover, a good cohesion of the film is not reached until the polymers from neighboring particles have interdiffused acrosss the particle boundaries.[13,14]

In many cases these steps have not been clearly identified, or there has been some confusion between them. For instance, in the technical litterature, coalescence has often been meant to designate the compression of particles into a film (step b), whereas in the scientific litterature, droplet coalescence means fusion of the cores (step c).

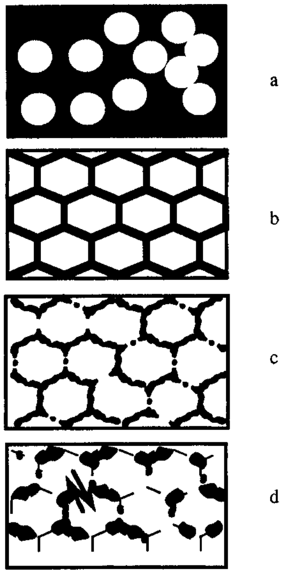

Figure 1. Structural transformations of a latex film upon drying: (a) concentration of the initial dispersion by evaporation of water, (b) film formation through complete removal of water—the particles are deformed into polyhedral cells, (c) coalescence of the particles through fragmentation of the hydrophilic cell walls, and (d) interdiffusion of core polymers and expulsion of cell wall polymers to isolated hydrophilic lumps.

This confusion stems from the fact that many studies have dealt with latex dispersions where the particle cell walls are made of surfactant monolayers. In this case, step c is not limiting (the cell walls break up during step b), and the final properties of the material are determined only by step d. Interdiffusion of core polymers could then be induced by annealing the samples at temperatures where the core polymers become mobile. The extent of interdiffusion was measured by Hahn et al.[9,10] and Winnik et al.[11,12] and was related to the self-diffusion coefficient of the macromolecules. Later, Yoo et al.[13] demonstrated that the interdiffusion of polymers across the particle boundaries was also affected by the density of chain ends near the particle surfaces and by the initial confinement of the macromolecules within the particles. Their central result was that the material reached a full tensile strength when the penetration

---

[†] This work used neutron beams of ILL in Grenoble and LLB in Saclay.
[‡] Rhône Poulenc.
[§] CEA-Saclay.
[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

S0024-9297(95)01080-1 CCC: $12.00 © 1996 American Chemical Society

depth was ca. 4 nm, comparable to the radius of gyration of the "critical entanglement molecular weight".

In most applications of latex films, however, the particle cell walls are made of hydrophilic polymers that have been copolymerized with the core polymers. These strong cell walls prevent aggregation and coalescence during the removal of water.[5,8] Cellular films are obtained at the end of the drying stage (step b); in these films the array of cell walls forms a continuous network which separates the cell cores from each other; the thickness of these cell walls is of the order of 2 nm. Fragmentation of the cell walls (step c) can be induced by annealing the films at higher temperatures.[8] After fragmentation occurs, the hydrophilic cell wall material is expelled to large lumps immersed in a continuous latex matrix.

In the present work we focus on the *interdiffusion of core polymers* (step d) in such cellular films. There are two extreme possibilities and a range of intermediate situations between them. Either the cell walls are *permeable* to the core polymers; in this case interdiffusion does not require fragmentation of the cell walls. Then the films would spontaneously acquire good mechanical properties upon aging at room temperature. Or the cell walls are *impermeable* to core polymers, and interdiffusion will not occur until they have been fragmented by thermal treatments. In this case films which have not been annealed at elevated temperatures would remain weak and susceptible to reswelling by water. The intermediate situations correspond to cell walls which are permeable to low molecular weight core polymers but not to the larger ones.

This problem has already been studied by Winnik et al.[16,17] They have observed that the copolymerization of hydrophilic polymer around the particle cores limits the interdiffusion of core polymers. The materials that they have studied appear to show the intermediate behavior described above, where the low molecular weight polymers diffuse first and other polymers diffuse later, either because they are of higher molecular weight or because they are copolymerized with some cell wall polymers. However they had no direct characterization of the particle cell walls in the material; therefore it was difficult to relate the observed interdiffusion to a particular state of the cell walls.

In the present work, we have determined for each latex film the state of the cell walls and the extent of interdiffusion of core polymers. Small angle neutron scattering (SANS) was used in both cases. The structure of the array of cell walls was determined by labeling the cell walls with D_2O, as we did in previous work.[1,5,8] The extent of interdiffusion was measured through the particle-labeling method pioneered by Hahn and coworkers.[9,10] This method measures the size of the volume in which the polymers from one particle have diffused after they have escaped their initial confinement. This method is good at measuring interdiffusion over distances comparable with the particle size; it is not good at much shorter distances, for which the fluorescence energy transfer is better.[11,12,16,17]

These techniques were used to compare the extent of interdiffusion and the state of the cell walls in films that had been submitted to different *thermal treatments*. The effect of such annealing processes on interdiffusion can be direct or indirect: They may increase the mobility of core polymers and allow them to pass through the cell walls, or they may break up the cell walls and allow core polymers to interdiffuse freely.

Table 1. Dispersions of Latex Particles in Water

label[a]	core[b]	surface groups[c]	pH[d]	surface density[e]	TEM diam[f]
L-AA, pH 3	S-BA	AA SO_4	3	3 0.3	120
L-AA, pH 9	S-BA	AA SO_4	9 NaOH	3 0.3	120

[a] Name of the dispersion. First letter: cross-linking in the core, L = linear polymer. Second group of letters: cell wall (see below). Third group: pH of the original latex dispersion. [b] Particle cores. S-BA is a statistical copolymer of styrene and butylacrylate which is linear and uncrosslinked. [c] Cell wall groups. AA stands for acrylic acid monomers which are copolymerized with core monomers. SO_4 are sulfate groups bound to core polymers. [d] pH of the original latex dispersion. At pH 3 the AA groups of the cell walls are in the acid form; at pH 9 they are bound to sodium or ammonium counterions. [e] Densities of surface groups, in numbers of groups/nm^2. [f] Particle diameters according to pictures from transmission electron microscopy, in nm.

Having determined the extent of interdiffusion, we have also examined its consequences on film properties. The properties of interest are the mechanical properties, the resistance to swelling by water and, most important, the combination of both, i.e., *mechanical properties in wet environments*. It is well known that cellular films with hydrophilic walls separating hydrophobic cells are quite susceptible to the penetration of water: Under prolonged exposure to water, the volume of the film may double and its mechanical properties become extremely weak. This susceptibility to water may be altered by thermal treatments, in two ways. (i) The increased mobility of hydrophilic and hydrophobic macromolecules may allow some core polymers to diffuse through the cell walls into the neighboring cells. (ii) The increased mobility of hydrophilic polymers may cause the cell walls to break up, allowing the fusion of the cores and the expulsion of hydrophilic macromolecules. Both processes would reduce the swelling and improve the mechanical properties, although in a more dramatic way for the latter one. Thus the results of mechanical measurements may determine whether (i) or (ii) is operating during the thermal treatments applied to the films; this conclusion may then be compared with the information from neutron scattering on fragmentation and interdiffusion.

Materials and Methods

Latex Particles. Our films were made from aqueous dispersions of polymer latex particles, which are widely used for paper coating, paints, and adhesives. The particles had diameters of 120 nm. They contained a hydrophobic core made of a statistical copolymer of butyl acrylate (BA) and styrene (S), with equal amounts of butyl acrylate and styrene. The glass transition temperature of this copolymer is around 15 °C; hence at room temperature it is a viscoelastic, amorphous material. This core was surrounded by a hydrophilic layer, the cell wall, made of hydrophilic monomers copolymerized with the core polymers. The hydrophilic monomers carried electrical charges which generated repulsions between dispersed particles, thereby stabilizing the dispersion. A list of the latex dispersions with the natures of particle cores and cell walls is given in Table 1. The synthesis of the particles and the compositions of the cores and the cell walls are indicated below.

Synthesis of Particles. The particles were made through a semicontinuous procedure where monomers were continuously added to an initial start-up load until the total volume fraction of monomers in the reaction miwture was 0.5, in a process similar to that described in ref 17; the polymerization temperature was 80 °C. The composition of the reaction mixture was: styrene, 45.7%; butyl acrylate, 50%; acrylic acid, 4.3%; and initiator, ammonium persulfate. A small amount of anionic surfactant (≤0.5% of the monomer weight) was added in order to control the number and size of the growing particles. The overall conversion rate was at least 95%, including 84% of the original acrylic acid groups. The molar mass of the core polymers was measured through gel permeation chromatography; the weight-average mass was M_w = 330 000, and the polydispersity index was $M_w/M_n = 5$.

Deuterated core–shell particles were also synthesized for the neutron-scattering measurements. The deuterated monomer was styrene, and it was mixed with protonated butyl acrylate to give polymers with the same composition as above. Because of the small amount of deuterated monomer available, the synthesis was made through a two-step polymerization procedure using protonated seed particles which were made separately. A batch of protonated monomer mixture (50%) was polymerized to provide the primary protonated seed latex. It was polymerized further with 50% of the deuterated monomer mixture added continuously and slowly into the reactor. As a result, these particles may have a core–shell structure, with protonated polymer in the central core and deuterated polymer in a shell around this core.

Composition of Particle Cell Walls. Since the cell walls have a strong influence on the film properties, it is important to know their exact composition. As explained above, these cell walls were made of acrylic acid (AA) sequences which were copolymerized with core polymers. The cell wall contained 5% of the particle mass; its composition was estimated as S (22%)/BA (35%)/AA (42%). The surface concentrations of AA and SO_4 groups were determined through titration with detection through conductimetry, on a latex dispersion where the aqueous phase had been washed with water. The measured concentration of AA groups was 260 μequiv/g, or 3 AA groups/nm^2; it corresponds to a monolayer coverage of the particle. If the latex was neutralized at pH ≥7, then some of the AA were charged and generated long range repulsions between particles. The surface density of sulfate groups was 0.3 SO_4/nm^2; these groups also contributed to long range repulsions between particles.

Film Formation. The final latex dispersions were prepared by adding 1% or 2% (by wt) of deuterated latex in a dispersion of the corresponding protonated latex; the pH of the aqueaous phase was set. Films were made by dehydration of these dispersions according to the following procedure. First the dispersions were degassed and concentrated to a volume fraction $\phi = 0.59$ by distillation at room temperature under a moderate vacuum. Then they were cast by spreading a thick layer (2 mm) of a concentrated dispersion on a smooth substrate with a nonstick coating made of siloxane elastomer. These liquid films were then dried in an oven at high humidity; the drying temperature was room temperature. They were subsequently removed from the molds and annealed at temperatures of 50, 100, or 140 °C for periods of 1, 5, or 24 h.

Neutron Scattering. Our aim was to study the interdiffusion of polymers in the film. Of course macromolecules in a bulk polymer sample do not travel very fast: We are interested in distances comparable with the cell size and travel times of a few hours. This problem requires the use of a technique which can measure displacements of a few tens of nanometers; moreover some of the polymers must be tagged and recognized as they diffuse through all others. There are at present two techniques which are capable of this: fluorescent dye tagging[11,12] and isotopic labeling in neutron scattering.[8,9] Of these, fluorescence is better at measuring displacements on the order of 1 nm and neutron scattering for displacements on the order of 10 nm.

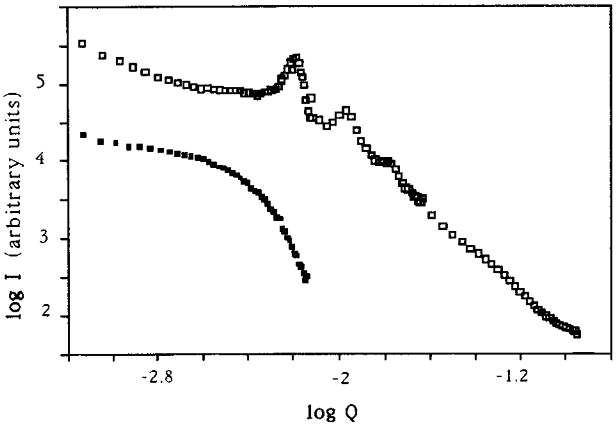

Figure 2. Scattering curves of latex films with the same composition but different contrasts. Horizontal scale: scattering vector Q in Å^{-1}, decimal log scale. Vertical scale: radially averaged intensity in arbitrary units, decimal log scale. Open squares: the cell walls that separate the particles have been rehydrated with D_2O; the peaks are produced by the regular ordering of these cell walls in the film. Filled squares: a fraction (1%) of the latex particles contain deuterated core polymers; the film is dry.

In an elastic scattering event, a neutron of wave vector $\mathbf{k_0}$ is scattered at an angle θ, which determines the wave vector $\mathbf{k_1}$ of the outgoing neutron. In scattering experiments, neutrons scattered at the same $\mathbf{k_1}$ by all nuclei in the sample interfere with each other and are collected in one point of the detector.[18,19] Thus the relative locations of nuclei in the sample are measured through the phase differences of scattered neutrons. For a pair of nuclei separated by a vector $\mathbf{r}$, the phase difference is $\mathbf{Qr}$, where $\mathbf{Q} = \mathbf{k_1} - \mathbf{k_0}$ is the scattering vector. All data in neutron scattering are collected as functions of $\mathbf{Q}$ or, if the sample is isotropic, of its magnitude Q which is determined by the wavelength λ of incident neutrons and the scattering angle θ:

$$Q = (4\pi/\lambda)\sin(\theta/2) \tag{1}$$

For a homogeneous sample, all these interferences cancel exactly and there is no scattering outside the beam. Scattering is visible when the sample is heterogeneous for the incoming radiation. In this work we created heterogeneities for neutrons in the sample by introducing deuterated particles in the protonated latex film.

Scattering of Deuterated Particles in a Protonated Film. Deuterated latex particles in a matrix of protonated latex give a strong scattering at very small Q values.[9,10] If there are few deuterated particles, their scattering may be described according to the laws for isolated objects immersed in a uniform matrix. Thus, for a collection of identical, homogeneous particles, the intensity is highest at low Q and its limit at $Q \to 0$ is proportional to the square of the "content" of a particle:

$$I_0 = KN\,(v\delta\rho)^2 \tag{2}$$

where K is an instrumental constant, N the number of particles, v the volume of a particle, and $\Delta\rho$ the difference in scattering length density between the particles and the matrix. This difference is caused by the presence of the deuterated polymers in the particles, and their absence in the matrix. At higher Q values the rays scattered by nuclei located at opposite ends of the particle interfere destructively, and the intensity decays according to the Guinier law:

$$I = I_0(1 - Q^2 R_g^{\,2}/3) \tag{3}$$

where R_g is the radius of gyration of the particle. At still higher Q values, the destructive interferences are so strong that only scattering centers near the surface of the particle contribute to the intensity; then the intensity decay follows Porod's law, $I \approx AQ^{-4}$, where A is the surface area of the particle.

The scattering from these samples was measured on the instruments PACE of LLB and D11 of ILL as explained in a previous paper.[8] The data from each sample were normalized by the sample thickness, which allowed meaningful comparisons to be made between the magnitudes of intensities scattered by different samples. Figure 2 shows the measured scattering curve for a latex film which contained 1% deuterated latex particles.

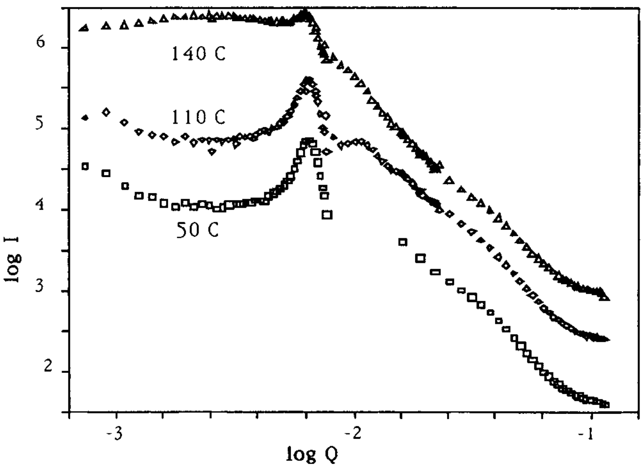

Figure 3. Scattering curves of latex films (L-AA, pH3) annealed at different temperatures for 24 h and rehydrated with D_2O. The decrease in the peak intensity reflects loss of order caused by fragmentation of the cell walls. The rise toward $Q \rightarrow 0$ reflects the expulsion of cell wall materials to large lumps immersed in the hydrophobic matrix.

If deuterated and protonated polymers interdiffuse, then the sizes of regions containing deuterated polymers expand accordingly. In the early stages of interdiffusion, these deuterated regions are still well separated, and their "content" ($v\Delta\rho$) remains unchanged since the volume and the difference in scattering density vary inversely. Consequently the intensity will remain the same at low Q but decay faster according to (3). The extent of interdiffusion can then be determined from the variation of the radius R_g. In the late stages of interdiffusion, deuterated polymers will permeate in the whole volume of latex. Then the difference in scattering density $\Delta\rho$ vanishes, and so does the intensity scattered at low Q. For a material containing 1% deuterated particles, this state of uniform mixing will be reached after the macromolecules have traveled distances on the order of two particle diameters. In this uniformly mixed state, the particle intensity has collapsed; there remains a contribution at higher Q from the differences between individual deuterated and protonated macromolecules, but this is much smaller.

Scattering of Samples Reswollen with D_2O. In order to interpret the results of interdiffusion experiments, it was necessary to check whether the films had retained or lost their cellular structure. This was done by reswelling the hydrophilic cell walls with D_2O. In previous work[1,5,8] we have demonstrated that the array of D_2O-swollen cell walls in a protonated matrix acts as a grating which diffracts the incoming neutrons. The radially averaged diffraction pattern shows a peak at the distance between reticular planes, which is the signature of a periodic array of cell walls; the scattering curve of a latex film with cell walls reswollen with D_2O is shown in Figure 2. Thermal treatments of the films may cause fragmentation of the cell walls, and this is recognized by the collapse of the diffraction peak[8] (Figure 3). Thus identical thermal treatments were performed on samples which were used for interdiffusion experiments and samples which were used for checking the state of the array of cell walls. Comparison of both types of experiments indicated whether interdiffusion was the result of cell wall fragmentation.

Mechanical Experiments. The effect of interdiffusion of polymers on the mechanical properties of films was investigated through measurements of the stress caused by a stretching deformation. Samples were submitted to standard thermal treatments, i.e., annealed at 50, 100, or 140 °C and then stored at room temperature (23 °C) in dry air (55% relative humidity). Sections of the latex samples, 1 mm thick and 20 mm long, were clamped in a traction instrument and stretched at a rate of 50 mm/min. The measurement gave the stress, expressed as a force/initial cross section, according to deformation, expressed as stretching relative to the initial length. The stretching was continued until the samples tore apart, and the stress level reached before tearing was recorded.

The effect of humidity on the mechanical properties was examined by submerging the samples in water for 5 min before performing the mechanical measurements. Some samples gave an extremely weak mechanical response after exposure to water, and others were almost unaffected; this was related to the effects of thermal treatments, i.e., fragmentation of cell walls or interdiffusion of core polymers.

Fragmentation of Cell Walls

The effect of thermal annealing on the structure of cell walls was examined in the following way. Films were rehydrated with D_2O, either before annealing or after annealing at 140 °C for 24 h. Then they were examined through SANS. As explained in the Methods section, the D_2O swells the hydrophilic polymers that form the cell walls. Therefore the neutron-scattering spectra reflect the organization of these polymers in the latex films.

The spectra taken *before annealing* show a deep depression of intensity at low Q followed by a peak located at $Q = 0.0065$ Å^{-1} (Figure 3). Both features indicate that the polymer cell walls form an ordered array with a peak that matches the spacings of latex particles in the film.

The spectra taken *after annealing* depend on the nature of the cell walls. For cell walls made of PAA in the acid form (L-AA, pH 3), the depression fills up and the peak collapses, indicating that the cell walls have been randomly displaced throughout the film. As explained earlier,[8] these displacements are made possible by the fragmentation of the acid cell walls. For cell walls made of neutralized PAA (L-AA, pH 9), the depression and peak are unchanged, indicating that the cell walls have not been fragmented.

Interdiffusion of Polymers

The effect of thermal annealing on the interdiffusion of core polymers was examined in the following way. Films containing a small fraction of deuterated particles were examined through SANS before and after annealing. As the deuterated polymers interdiffuse with the protonated ones, the size and the composition of the regions containing deuterated polymers may change. Both changes can be measured through SANS. As explained in the Methods section, the magnitude of the scattered intensity is proportional to the content of the deuterated regions according to eq 2. Moreover, the Q dependence of the intensity measures the sizes of these regions according to eq 3.

Radii of Gyration. The spectra taken *before annealing* show a linear decay of $\ln(I)$ according to Q^2, as expected from eq 3 (Figure 4). The measured radius of gyration is $R_g = 50$ nm; it is slightly larger than the value expected for a homogeneous particle with a diameter of 120 nm. This is because the deuterated polymers are localized in the external region of the latex particle; for a localization in a thin shell, the radius of gyration equals the shell radius, as observed here.

The spectra taken *after annealing* show similar decays in the $\ln(I)$ vs Q^2 plot, but the slopes are generally not as steep, corresponding to *smaller* radii (Figure 4). The evolution of the radius of gyration with annealing time is presented in Figure 5. In films annealed at 50 °C, this evolution is insignificant. In films annealed at 140 °C, the radii decrease by 10% over a period of 1 h, then remain constant. The final radius is close to that expected for a homogeneous distribution of the deuterated polymers in the original particle.

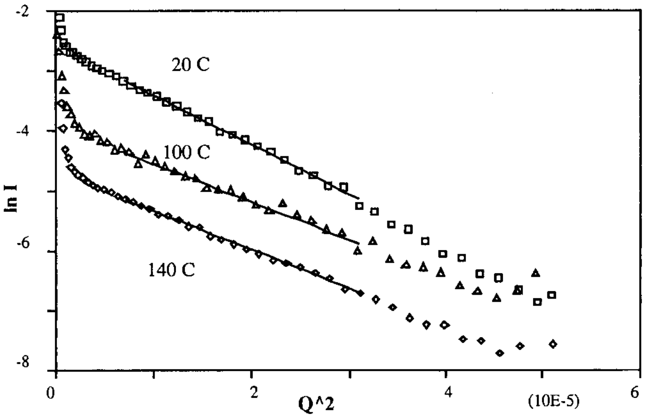

Figure 4. Scattering curves of latex films (L-AA, pH 3) containing a fraction (1%) of deuterated particles. Vertical scale: natural log of intensity. Horizontal scale: square of scattering vector Q. In this representation the slope of the curve measures the radius of gyration of the deuterated particles. The curves obtained after annealing at 100 and 140 °C show lower intensities but similar radii as the curve of the film kept at 20 °C.

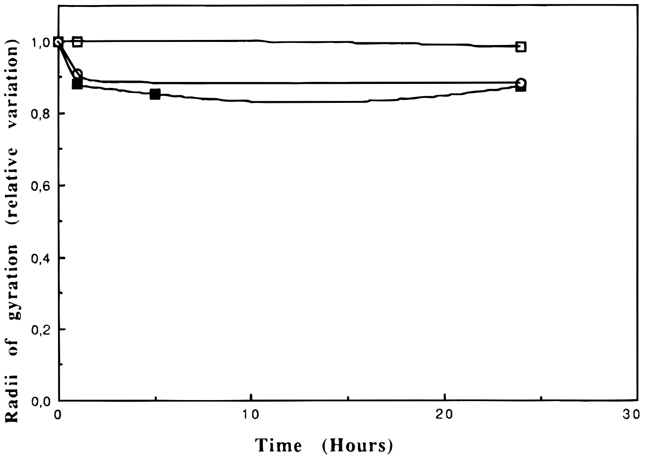

Figure 5. Relative variation of the radii of gyration of the deuterated particles in films that have been annealed for different times. Open squares: film made from a latex dispersion at pH 3 (L-AA, pH 3) and annealed at 50 °C. Filled squares: film made from a latex dispersion at pH 3 (L-AA, pH 3) and annealed at 140 °C. Circles: film made from a latex dispersion at pH 9 (L-AA, pH 9) and annealed at 140 °C. Unlimited interdiffusion of the core polymers would have resulted in a steady increase of the radii with annealing time.

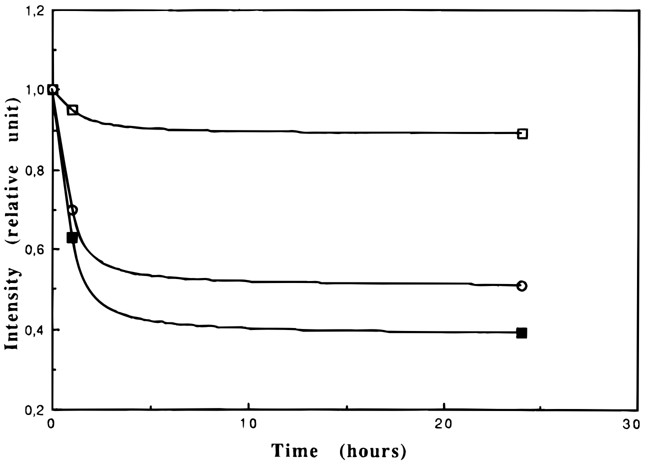

Figure 6. Relative variation of the intensity scattered from the deuterated particles in films that have been annealed for different times. Open squares: film made from a latex dispersion at pH 3 (L-AA, pH 3) and annealed at 50 °C. Filled squares: film made from a latex dispersion at pH 3 (L-AA, pH 3) and annealed at 140 °C. Circles: film made from a latex dispersion at pH 9 (L-AA, pH 9) and annealed at 140 °C. Unlimited interdiffusion of the core polymers would have resulted in a steady decrease of the intensity with annealing time.

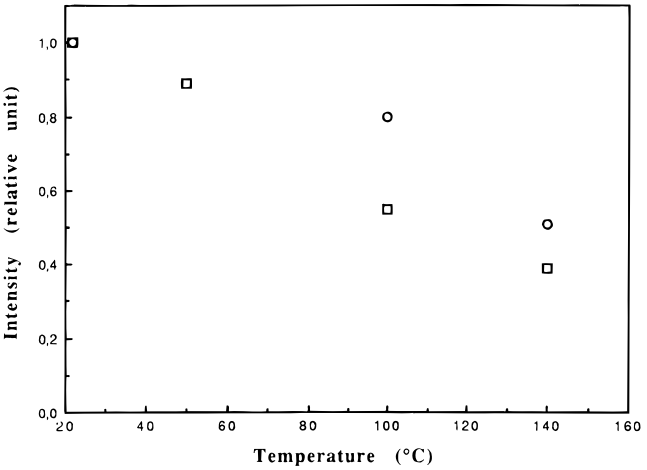

Figure 7. Relative variation of the intensity scattered from the deuterated particles in films that have been annealed for 24 h at different temperatures. Squares: film made from a latex dispersion at pH 3 (L-AA, pH 3). Circles: film made from a latex dispersion at pH 9 (L-AA, pH 9).

Intensities. *Films that have been annealed give smaller intensities* at all Q values. Figure 6 presents the evolution of the scattered intensities with annealing time for different temperatures of annealing or different pH. In each case, the intensity decreases for a few hours and then stabilizes at a constant level. This level is determined by the temperature of annealing and the nature of the cell walls, as shown in the figure.

This residual intensity decreases regularly with the temperature of annealing, as shown in Figure 7. *These variations show no obvious relation to the structural evolution of the films.* For all films, the intensity has dropped by a factor of 2 after annealing at temperatures that are below the threshold for fragmentation of the cell walls.

Mechanical Properties

The effect of thermal annealing on the mechanical properties of the films was examined for two types of films: dry films and films that had been immersed in water for 5 min before mechanical testing. This comparison is important, since humidity is known to have a drastic effect on the mechanical properties of latex films. Generally, dry films have a mechanical response which is elastic at small stress and plastic at large stress; humid films stretched at low temperatures suffer brittle failure before reaching the plastic range. This brittle failure results from the rehydration of the hydrophilic cell walls, which causes them to lose cohesive strength while the cell cores remain comparatively strong. In view of the effectcts of thermal annealing on cell wall structure and interdiffusion of cell cores, it is of interest to find out what their consequences are for the mechanical properties of the films.

Films Tested before Annealing. The stress/strain responses a dry film and for the corresponding humid film are shown in Figure 8. The curve for the dry film is typical of the response of polymer films stretched at temperatures *near their glass transition temperature* T_g. It is characterized by a stiff elastic response at

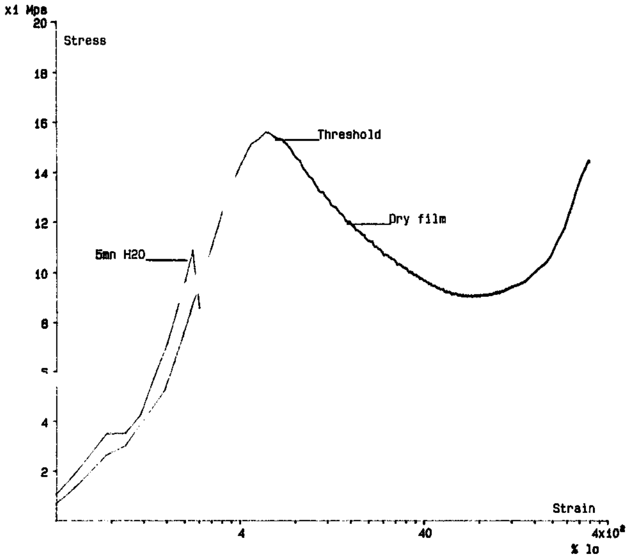

Figure 8. Stress/strain response for a dry film and the corresponding humid film. Dry film: a plastic deformation typical of polymer film stretched near T_g. Humid film: failure occurs at very low strain.

stresses below a yield stress σ_T followed by a plastic response after σ_T has been reached. At large strains the stress rises again, and the film breaks when the deformation is on the order of 300%.

The curve for the humid film shows the same initial elastic rise, with the same elastic modulus, but failure occurs at very low strains, of the order of 2−3%, before the plastic range is reached (Figure 8). Comparison with the response of the dry film shows that the modulus is determined by the stiffness of the cell cores, while the maximal strain is controlled by the state of the cell walls.

Effect of Annealing. Similar films, made of latex with acid cell walls, were annealed for 24 h at temperatures ranging from 50 to 140 °C, and then tested in the same conditions. Annealing at temperatures up to 100 °C had very little effect on the stress/strain response of the film. In particular, films rehydrated immediately before stretching kept breaking at very low strains. Annealing at 140 °C removed the fragility of the rehydrated films: These annealed films could be deformed into the plastic regime and failed only at large strains, of the order of 100% (Figure 9).

Films made of latex with neutralized cell walls had similar stress/strain curves in the dry state. Upon contact with water they took up more water and became weaker than the films with acid cell walls; the failure of these rehydrated films occurred at very low strains, of the order of 1%. Annealing at 140 °C did not have the same effect as for the films made of latex with acid cell walls: The rehydrated films remained fragile and failed at low strains, much below the plastic range (Figure 10).

Discussion

The aim of this work was 2-fold: (i) measure the extent of interdiffusion of core polymers originating from cells separated by cell walls and (ii) examine the consequences of this interdiffusion on the mechanical properties of the latex films.

Extent of Interdiffusion. Concerning the extent of interdiffusion, two extreme possibilities were considered in the Introduction: Either the cell walls are permeable to all core polymers, and the extent of interdiffusion is determined only by their diffusion coefficients, or the cell walls are impermeable to all core polymers, and interdiffusion occurs only after the cell walls have been fragmented.

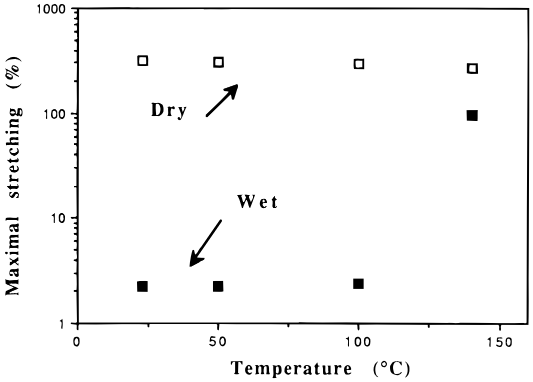

Figure 9. Cohesion of films made from latex at pH 3 (L-AA, pH 3) and annealed at different temperatures. Vertical scale: maximal stretching before rupture. Horizontal scale: temperature of annealing. Open squares: dry films. Filled squares: rehydrated films. The wet films break at very low stretching because their cell walls are weakened by rehydration; annealing at 140 °C causes fragmentation of the cell walls and restores the cohesion of these films.

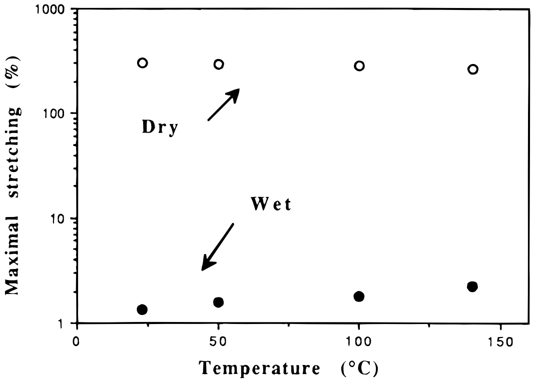

Figure 10. Cohesion of films made from latex at pH 9 and annealed at different temperatures. Vertical scale: maximal stretching before rupture. Horizontal scale: temperature of annealing. Open circles: dry films. Filled circles: rehydrated films. The cell walls of these films are not fragmented by annealing at 140 °C . The cohesion of the wet films is not restored by annealing because only low molecular weight core polymers can interdiffuse across the cell walls.

First consider the former option, i.e., free diffusion of all polymers across the cells. In this case the deuterated polymers from one cell would spread progressively into the neighboring cells. As a result, the size of the deuterated region would expand, but its content would remain the same because the variations of v and $\Delta\rho$ in eq 2 would cancel each other. In fact the opposite behavior is observed, as the measured radii remain essentially the same, while the scattered intensities decrease sharply.

Then consider the latter option, i.e., complete inhibition of diffusion by the cell walls. In this case the deuterated polymers from one cell will mix only with the protonated polymers of the seed particle in the interior of the cell. This homogeneization will cause a limited decrease in the radius of gyration of the deuterated regions, as some deuterated polymers move from their location in a shell around the seed to a location closer to the center of the cell. This decrease has indeed been observed, as shown in Figure 5.

However, this model also predicts that the content of each cell should remain the same, whereas the measured intensity was found to be lower in annealed samples (Figures 6 and 7). Moreover, this modification also predicts a complete collapse of the intensities when the cell walls are fragmented because the deuterated polymers would then mix uniformly with the protonated ones; this is not observed either.

These comparisons indicate that interdiffusion is actually limited by the cell cell walls but not in the "all or nothing" mode described in the last model. In this respect, the critical information is the drop in the magnitude of the scattered intensity, which was shown in Figures 6 and 7. According to eq 2, the $Q \to 0$ limit of the scattered intensity yields the amount of deuterated material that is correlated with each of the N original deuterated particles; the geometrical nature of the correlation (expansion, contraction, or any other deformation) is irrelevant in the $Q \to 0$ limit. Consequently, a loss of scattered intensity implies that some species have lost all correlation with the original deuterated particles. Indeed, if some types of deuterated polymers are able to cross freely through the cell walls and mix uniformly with the matrix, they no longer contribute to the structural scattering, and the residual intensity measures the amount of polymers that are still unable to cross the cell walls. This selection explains the fast drop and subsequent stabilization of the intensity that are shown in Figure 6.

The selection of species that cross the cell walls is determined by the annealing temperature. Indeed, as the temperature of annealing is raised, the residual intensity is decreased, indicating that fractions that are less mobile become able to cross the cell walls as well. Accordingly, the selection of species that can cross the cell walls is according to their molar mass. Thus, the cell walls act as a chromatography barrier for the passage of core polymers from one cell to the next (Figure 11).

Comparison with Previous Work. This selective diffusion of polymers that cross the cell walls has already been observed by two other groups. Cohen-Addad et al.[20] have compared the polymers that are extracted from different latex films by organic solvents. With toluene as an extractant, they found that films with a high amount of acid groups in their cell walls released smaller amounts of latex polymers and that these polymers were of lower molecular weight. Using a polar solvent that also dissolved the cell wall polymers, they found that all latex polymers were extracted. These results confirm the hypothesis that the diffusion of core polymers across cell walls is limited only by the their molecular weight and the presence of cell wall polymers; moreover, they demonstrate that the saturation of interdiffusion, observed in Figure 6, is not caused by the existence of a "gel fraction" that would be unable to diffuse.

Similarly, Winnik et al.[16,17] used the fluorescence energy transfer technique to measure the extent of intermixing and the corresponding diffusion coefficient of polymers in different latex films. Again, they found that in films with high amounts of acid groups the interdiffusion of polymers was sharply reduced. From these results alone it could not be concluded whether the very low diffusion coefficients were from core polymers that were slowly diffusing across the cell walls or from cell wall polymers that were slowly dissociating from each other. Our experiments on labeled core polymers confirm that the former interpretation is correct.

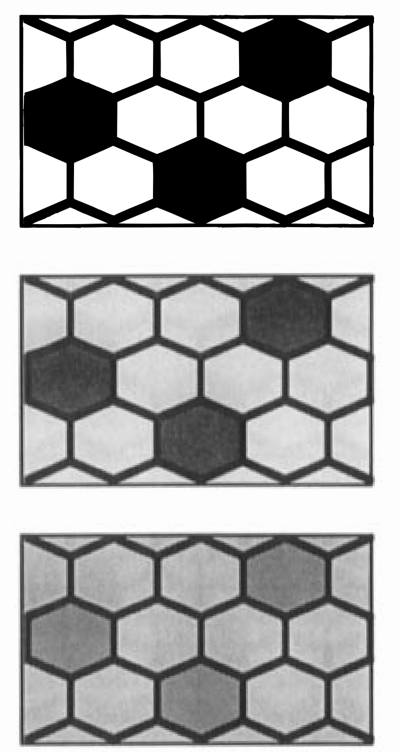

Figure 11. Interdiffusion of core polymers across the cell walls. The latex film is represented as a hexagonal array of cells separated by cell walls (in black). Some of the cells (in black) contain labeled core polymers. Top: the labeled polymers are confined in the particles. Middle: the lower molecular weight labeled polymers have diffused across the cell walls. Bottom: higher molecular weight fractions are also able to diffuse freely across the cell walls. The diffusing polymers are uniformly distributed in the film; therefore the apparent size of the deuterated regions does not change, while their contrast vanishes.

Model for Interdiffusion across a Cell Wall. A theory for the diffusion of polymers across a polymeric cell wall has been proposed by de Gennes.[21] This theory calculates the range of interpenetration of a diffusing polymer (A) into an incompatible cell wall polymer (B).

Initially, the A/B interface is sharp. Then macromolecules of polymer A diffuse across the interface into the B region. After equilibrium has been reached, the average number m of monomers of an A macromolecule that are in the B region is such that the free energy of transfer is of the order of the thermal energy kT. Let χ be the Flory interaction parameter, $v = a^3$ the volume per monomer, and δ_A and δ_B the solubility parameters of A and B. Then:

$$m = \chi^{-1} = (kT/v)[\delta_A - \delta_B]^2 \qquad (4)$$

In the case where $\chi \ll 1$, the thickness e of the diffuse boundary is

$$e = a(m)^{1/2} = a\chi^{-1/2} \qquad (5)$$

According to this analysis, two limiting cases may be defined.

(a) If the thickness of the cell walls is much larger than the length e, then core polymers of polymerization degree $p > m$ that would cross the cell walls would need to bring all their monomers into the cell wall. The cost of bringing these p monomers into the cell walls would, according to eq 4, be larger than kT per macromolecule; therefore they are excluded. In this case, the cell wall selects macromolecules according to their molecular weights, by letting through only those polymers with polymerization degrees p such that:

$$p < \chi^{-1} \tag{6}$$

(b) If the thickness *h* of the cell walls is smaller than the length *e*, then large macromolecules (polymerization degree $p > m$) may still cross the cell wall if they do not have to keep too many monomers within the cell wall at any time. The number of monomers of a crossing macromolecule that must be located in the cell wall is $(h/a)^2$. The cost of bringing these monomers into the cell wall is below kT if the limit set by eq 4 is not exceeded for this number of monomers:

$$(h/a)^2 < \chi^{-1} \tag{7}$$

In this case, the cell wall selects macromolecules according to their affinity, by letting through only those macromolecules which have a monomer composition close to that of the cell wall, such that their interaction parameter χ with the cell wall polymers is below the limit set by eq 7.

In the latex films that we have used, the cell walls contained 5% of the film weight; therefore the half-thickness of the cell walls is $h = 20$ Å. The thickness of the diffuse boundary where core polymers may penetrate the cell walls may be calculated by estimating the value of χ. Indeed, for hydrophilic cell wall polymers and the hydrophobic core polymers, the values of χ are of the order of 10^{-1}; according to eq 5, and taking a monomer size of 5 Å, we get $e = 1.6$ Å. Therefore the cell wall thickness is much larger than the average penetration depth *e*, as in case (a) above. Consequently, the macromolecules that cross the cell walls are selected according to their degree of polymerization, which must be below the limit set by eq 6. Since the interaction parameter χ decreases with temperature (eq 5), the limiting molecular weight of the crossing macromolecules must increase with temperature. This rise may explain the observed decrease of the scattered intensity for samples annealed at increasing temperatures. A more quantitative comparison would require a knowledge of the χ values of the latex polymers or the addition to the latex of labeled polymers with known χ values.

Consequences of Interdiffusion. Even though substantial interdiffusion of core polymers has been observed, the effects on the mechanical properties of the films have not been as spectacular as anticipated. The aim was to reinforce the cohesive strength of the films through interpenetration of core polymers initially located in neighboring cells. Indeed, previous work on PS latex films has shown that tensile strength develops as a result of interpenetration of core polymers.[13,14] However, for the cellular films studied here, the mechanical properties are quite different.

Comparison of dry films and rehydrated films shows that these properties are controlled by the state of the cell walls (Figures 9 and 10). Dry films have a high modulus, even without annealing, and they can withstand large plastic deformations. This is because their cell walls have a high cohesive strength, either through H-bonds (in the acid state) or through ion pairs (in the neutralized state). The mechanical properties of these films are not changed by interdiffusion of core polymers nor by fragmentation of the cell walls; therefore these properties are the same as those of a homogeneous film of the core polymers. Thus, through chemical bonds with core polymers and internal ionic bonds, the cell walls make proper mechanical connections between neighboring cells.

Rehydrated films are brittle at temperatures near T_g because their cell walls lose their cohesive strength through solvation of the ion pairs. A major result of the present work is that interdiffusion of core polymers does not remove this brittleness (Figure 10). Therefore the polymers that interdiffuse across the cell walls are not long enough to act as connectors between neighboring cells. Conversely, fragmentation of the cell walls brings the properties back to the level of the continuous film of core polymers.

Yet the additional mixing that occurs upon fragmentation of the cell walls involves only a small fraction of the core polymers. This fraction may be estimated by comparing the residual intensity obtained in conditions where the cell walls are fragmented (acid cell walls, annealing at 140 °C) with that obtained after the same annealing but with cell walls that are not fragmented (neutralized cell walls). These intensities are respectively 40% and 50% of the initial intensity (Figure 7). Accordingly, the fraction of core polymers that causes the improvement in the mechanical resistance after fragmentation of the cell walls is only 10% of the total polymer mass.

Conclusions

Polymer films can be made by evaporation of aqueous dispersions containing polymeric particles (latex). If the particles are obtained through copolymerization of hydrophobic and hydrophilic monomers, the resulting film is an array of hydrophobic cells separated by hydrophilic cell walls. The mechanical resistance of these cellular films is determined by the state of the cell walls. In the dry state, the cell walls have a strong cohesion and the films do not fail until the cell cores themselves fail. In a humid environment, the cell walls take up water and lose their cohesive strength while the cell cores remain comparatively strong; consequently the rehydrated films are brittle.

We have examined the possibility of reinforcing these cellular films through interdiffusion of core polymers across the cell walls. We have measured the extent of interdiffusion obtained after annealing the films at temperatures where the core polymers are mobile. We found that the cell walls act as a size selective barrier, letting through the low molar mass polymers only. Substantial intermixing is achieved in this way, without any effect on the mechanical properties of the film. Therefore, these polymers are too short to act as connectors across the cell walls. The polymers that are long enough to create mechanical connections between cells do not interdiffuse until the cell walls are fragmented through high-temperature annealing.

We conclude that these cellular films cannot be reinforced through interdiffusion of polymers across the cell walls. Fragmentation of the cell walls may yield the desired protection against humidity; however it requires high temperatures unless the cell walls are very fragile to start with. With cell walls that cannot be fragmented, like the standard cell walls of neutralized polyacrylic acid, other methods of reinforcing the films and protecting them against humidity must be sought.

Acknowledgment. Some of the ideas presented in this work originated from discussions with M. Winnik. We thank him for bringing to our attention some features of the interdiffusion processes. We thank L. Léger for useful discussion on diffusion of polymers. We also thank D. Charmot for the synthesis of the deuterated latex dispersions and the staff of LLB and ILL for providing us with guidance and support during neutron scattering experiments.

References and Notes

(1) Joanicot, M.; Wong, K.; Maquet, J.; Chevalier, Y.; Pichot, C.; Graillat, C.; Lindner, P.; Rios, L.; Cabane, B. *Prog. Colloid Polym. Sci.* **1990**, *81*, 175.
(2) (a) Dobler, F.; Pith, T.; Lambla, M.; Holl, Y. *J. Colloid Interface Sci.* **1992**, *152*, 1. (b) Dobler, F.; Pith, T.; Lambla, M.; Holl, Y. *J. Colloid Interface Sci.* **1992**, *152*, 12.
(3) Wang, Y.; Kats, A.; Juhué, D.; Winnik, M. A. *Langmuir* **1992**, *8*, 1435.
(4) Distler, D.; Kanig, G. *Colloid Polym. Sci.* **1978**, *256*, 1052.
(5) Chevalier, Y.; Pichot, C.; Graillat, C.; Joanicot, M.; Wong, K.; Maquet, J.; Lindner, P.; Cabane, B. *Colloid Polym. Sci.* **1992**, *270*, 806.
(6) Rieger, J.; Dippel, O.; Hadicke, E.; Ley, G.; Lindner, P. In *Colloidal Polymer Particles;* Goodwin, J. W., Buscale, R., Eds.; Academic Press, London, 1995.
(7) Sperry, P. R.; Snyder, B. S.; O'Dowd, M. L.; Lesko, P. M. *Langmuir* **1994,** 10, 2619.
(8) Wong, K.; Joanicot, M.; Richard, J.; Maquet, J.; Cabane, B., *Macromolecules* **1993**, *26,* 3168.
(9) Hahn, K.; Ley, G.; Schuller, H.; Oberthür, R. *Colloid Polym. Sci.* **1986**, *264*, 1092.
(10) Hahn, K.; Ley, G.; Oberthür, R. *Colloid Polym. Sci.* **1988**, *266*, 631.
(11) Winnik, M. A.; Wang, Y. *J. Coat. Technol.* **1992**, *64*, 51.
(12) Zhao, C. L.; Wang, Y.; Hruska, Z.; Winnik, M. A. *Macromolecules* **1990**, *23,* 4082.
(13) Yoo, J. N.; Sperling, L. H.; Glinka, C. J.; Klein, A. *Macromolecules* **1990**, *23*, 3962.
(14) Daniels, E. S.; Klein, A. *Proc. Org. Coat.* **1991**, *19*, 359.
(15) Goh, C. M.; Juhué, D.; Leung, O.; Wang, Y.; Winnik, M. A. *Langmuir* **1993**, *9*, 1319.
(16) Kim, H.-B.; Winnik, M. A. *Macromolecules* **1994**, *27*, 1007.
(17) Kim, H.-B.; Winnik, M. A. *Macromolecules* **1995**, *28*, 2033.
(18) Jacrot, B. *Rep. Progr. Phys.* **1976**, *39*, 911.
(19) Cabane, B. In *Surfactant Solutions: New Methods of Investigation*; Zana, R., Ed.; Marcel Dekker: New York, 1987.
(20) Cohen-Addad, J. P.; Bogonuck, C.; Granier, V. *Macromolecules* **1994**, *27*, 5032.
(21) de Gennes, P. G. *C. R. Acad. Sci. Paris* **1989**, *308* (II), 1401.

MA9510808