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Ripening of Cellular Latex Films[†]

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ABSTRACT: Cellular films have been produced through evaporation of aqueous dispersions containing latex particles. The membranes of the cells are made of hydrophilic species which originate from the surfaces of the particles; they form a periodic structure which separates the cell cores from each other. Thermal treatments have been applied to induce the fragmentation of membranes. The resulting structural changes have been observed through small-angle neutron scattering and electron microscopy. It has been found that the fragmentation of membranes is controlled by three parameters: the mobility of membrane polymers, the anchoring of these polymers on the core, and the mobility of the core. After fragmentation occurs, the hydrophilic membrane material is expelled to large lumps immersed in a continuous latex matrix.

Introduction

Latex particles can be synthesized and kept in aqueous dispersions, provided that repulsive interactions keep particles away from each other. These repulsions are generated by hydrophilic layers which we call the membranes.[1,2] The membranes may be made of either surfactants adsorbed on the polymer cores or hydrophilic polymers copolymerized with the hydrophobic core polymers. Surfactant membranes tend to break up when the particles are forced into contact; this results in coalescence of the dispersion upon drying.[3] Polymeric membranes prevent coalescence; then upon compression the dispersions turn into cellular structures where the particle cores form polyhedral cells (rhombic dodecahedra) while the hydrophilic membranes form the walls of these cells[1–5] (Figure 1).

These arrays of membranes have a profound influence on film properties such as permeability to water vapor,[6–8] reswelling,[9] mechanical properties,[6,9–14] and the adhesion to substrates. At room temperature they can be preserved for indefinitely long times.[1–4] However, there must be limits to their stability, depending on the storage conditions and, more likely, the thermal events they can encounter; this leads to the following questions: (1) Which force ensures the permanence of the membranes? (2) What processes can induce their fragmentation? (3) What happens to the hydrophilic material after its fragmentation: does it remain dispersed in the latex matrix or is it expelled?

In this work we have submitted latex films to thermal treatments to induce fragmentation of the membranes, and we have observed the resulting structural changes through small angle neutron scattering (SANS) and transmission electron microscopy (TEM).[15]

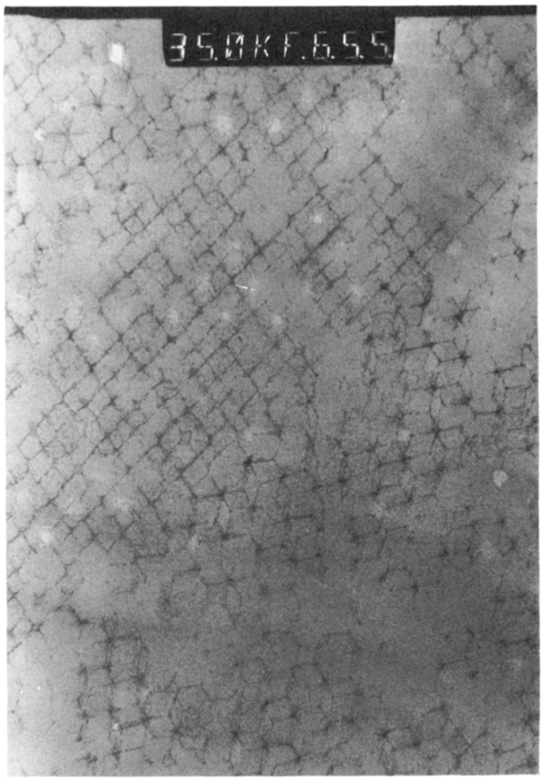

Figure 1. Electron microscopy picture of a stained film. The initial dispersion was made of latex particles coated with hydrophilic membranes and dispersed in water. When water was removed the particles deformed into polyhedral cells, with the membranes acting as cell walls (foam structure). The two types of tilings observed on the upper left and lower right of the figure correspond to different orientations of fcc crystals.[1,3]

Materials

Our films were made from aqueous dispersions of polymer latex particles, which are widely used for paper coating, paints, and adhesives. The particles are spherical droplets with diameters in the 1000–1500-Å range; they consist of a hydrophobic core protected by a hydrophilic membrane.

Emulsion Polymerization. The particles were made through a semicontinuous procedure where monomers were continuously added to an initial start-up load. For the S–BA latex the composition of the reaction mixture was as follows: styrene(S), 45.7%, butyl acrylate (BA), 50%; acrylic acid (AA), 4.3%; initiator, ammonium persulfate. A small amount of anionic surfactant was added to control the number and size of the growing particles. The important feature of this polymerization reaction is that the pH must be low; indeed if the AA sequences are neutralized, they tend to remain in the serum instead of binding to the core.[16] The overall conversion rate was at least 95%, including 84% of the original AA groups.

A similar procedure was followed for the S–B particles. The composition was 69% styrene, 27% butadiene(B), and a small amount of an acrylic acid type monomer.[14]

A complete list of the latex dispersions with the compositions of the particle cores and membranes is given in Table I.

Particle Cores. In most of our films the particle cores were made of a statistical copolymer of butyl acrylate and styrene,

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Table I. Dispersions of Latex Particles in Water

label[a]	core[b]	surface groups[c]	surface density[e]	pH[d]	TEM diam[f]	gel fraction[g]
L-AA-3	S–BA	AA SO_4	3 0.3	3	1200	
L-AA-9	S–BA	AA SO_4	3 0.3	9 NaOH	1200	
L-CE-3	S–BA	CEA SO_4	3 0.3	3	1200	
C-AA-4.5	S–B cross-linked	AA SO_4	3 0.3	4.5 NH_4OH	1700	0.975
T-AA-4.5	S–B CTA	AA SO_4	3 0.3	4.5 NH_4OH	1800	0.14
C-SDS	S–B cross-linked	SDS SO_4	1.6 0.3	4.5 NH_4OH	1600	0.84
T-SDS	S–B–CTA	SDS SO_4	1.6 0.3	4.5 NH_4OH	1600	0.1
T-AA-9	S–B–CTA	AA SO_4	3 0.3	9 NH_4OH	1800	0.14

[a] Name of the dispersion. First letter: refers to cross-linking in the core; L = linear polymer; C = cross-linked; T = cross-linking inhibited by chain transfer agent. Second group of letters: membrane (see below). Third group: pH of the original latex dispersion. [b] Particle cores. S–BA is a statistical copolymer of styrene and butyl acrylate which is linear and un-cross-linked; S–B is a statistical copolymer of styrene and butadiene which is strongly cross-linked. S–B–CTA is the same copolymer, but a chain transfer agent (CTA) has been added to control the formation of cross-links. [c] Membrane group. AA stands for acrylic acid monomers which are copolymerized with core monomers. SO_4 are sulfate groups bound to core polymers. SDS are sodium dodecyl sulfate molecules which are adsorbed on the core. [d] pH of the original latex dispersion. At pH 2 or 3 the AA groups of the membranes 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 per nm^2. [f] Particle diameters according to pictures from transmission electron microscopy. [g] Fraction of cross-linked polymer in the core.

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.

In some films the cores were made of a copolymer of butadiene and styrene with 70% styrene and 30% butadiene; this material is also viscoelastic (glass transition temperature at 19 °C), but it is cross-linked; hence it includes a gel fraction which is immobilized by the cross-links. The amount of the gel fraction was measured through dissolution in $CHCl_3$;[14] it was controlled with a chain transfer agent (CTA) which reduces the length of all growing chains during polymerization.[14]

Particle Membranes. The membranes were made of electrically charged species which generate repulsions between dispersed particles, thereby stabilizing the dispersion. In most films the membranes were made of acrylic acid (AA) sequences which were copolymerized with core polymers. For the S–BA latex the membrane contained 5% of the particle mass; its composition was estimated as 22% S/35% BA/42% AA. The number of AA groups at the surface resulted in a monolayer coverage of the particle; their surface density was 3 AA groups/nm^2. If the latex was neutralized at pH ≥ 6, then some of the AA were charged and generated long-range repulsions between particles. In addition, there were also a few sulfate groups originating from the initiator decomposition; their surface density was 0.3 SO_4/nm^2. For the S–B latex the membranes had a similar density of surface groups, but their exact composition was not known.

In some films the membranes were made of surfactant molecules adsorbed on the core, together with sulfate groups originating from the initiator decomposition and chemically bound to the core. The surfactant molecules were sodium dodecyl sulfate (SDS); their surface density was 1.6 molecules/nm^2. Together with the sulfate groups (0.3 SO_4/nm^2) they generate long-range electrostatic repulsions between particles when the ionic strength is low. In a previous work, we have shown that surfactant membranes may break and allow particle coalescence when the particles are forced into direct contact.[1,3]

Film Formation. Films were made by dehydration of the 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 for 6 h; the drying temperature was either room temperature or 50 °C. They were subsequently removed from the molds and annealed at temperatures ranging from 50 to 180 °C for periods ranging from 1 to 24 h.

Methods

Our aim was to study how a periodic array of hydrophobic cells with hydrophilic membranes turns into a continuous polymeric film. This required the use of techniques which provide a good contrast between hydrophilic and hydrophobic species. In electron microscopy, this contrast was obtained by staining the membranes with heavy-atom salts. In neutron scattering, contrast was provided by swelling the membranes with D_2O. We have checked that the structures of our latex samples are not affected by the rehydration processes which are used to obtain contrast. This was done by examining rehydrated samples at various time intervals and also samples which had been stretched and then rehydrated. There is no problem there as long as the samples are stored, after rehydration, below the glass transition of the core polymers, which was always the case.

Observation of Dry Films through Electron Microscopy. For transmission electron microscopy the samples must be thin (ca. 1000 Å thick), dry, and stained to reveal the edges of the particles by enhanced electron scattering. They are prepared through cryoultramicrotomy. First a small piece of dry film is cut with a razor blade and glued on a stand. Then it is cooled to −35 °C and sliced to 0.1-μm thickness with an ultramicrotome apparatus. Finally, this slice is mounted on a copper grid and stained by contact with an aqueous solution of 1% uranyl acetate; excess salt is eliminated by contact with drops of pure water. The uranyl acetate stains the hydrophilic material in the film, in particular the acrylic acid groups which form the hydrophilic membranes of the original latex particles.

Observation of Wet Films through Neutron Scattering. Neutrons are scattered by the nuclei of atoms in the sample. For small-angle scattering, the scattering is controlled by the local density of the scattering length. It is possible through isotopic substitution to achieve very different densities of scattering length for two hydrogenated materials, e.g., latex vs heavy water. Then small-angle scattering is produced, reflecting the distribution of deuterated material in a protonated matrix or vice versa.[17,18]

In this work we used protonated latex with protonated membranes swollen by D_2O. This contrast was obtained through rehydration of the film with D_2O; we found that this rehydration was easy when the membranes were not fragmented. After 24–48 h of exposure to water vapor, the films were placed in the neutron beam of a SANS instrument. We used the instruments PACE of LLB and D11 of ILL as explained in a previous paper.[3,19,20]

Scattering of Samples Reswollen with D_2O. When the array of membranes is swollen with D_2O, it forms a grating which diffracts incoming neutrons;[1,3] the diffracted intensities are collected according to the scattering vector $\mathbf{Q}$, and they are determined by the structure of the sample. The diffraction pattern is made of spots if the film was made as a single crystal of particles ordered along fixed directions; it is made of rings if the film is polycrystalline, i.e., made of domains with different orientations. In our experiments such diffraction patterns were radially averaged to yield scattering curves where the intensities are measured according to the magnitude Q; this is related to the wavelength λ of incident neutrons and to the scattering angle θ by

$$Q = (4\pi/\lambda)\sin(\theta/2) \qquad (1)$$

The values of Q for the diffraction peaks yield the spacings of planes of particles.[21] For a face centered cubic (fcc) packing

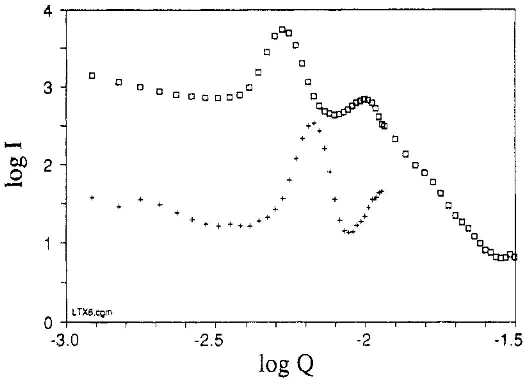

Figure 2. Small-angle neutron scattering of latex films reswollen with D_2O. In this case the content in hydrophilic monomers was quite high (7.5% AA) and they were neutralized at high pH (8). Consequently, the uptake of water by the films was quite substantial ($\phi = 0.48$), resulting in a large shift of the diffraction peak. Squares, $\phi = 0.98$; crosses, $\phi = 0.48$.

with unit cell a the first diffraction peak corresponds to the distance between 111 planes; the spacing of these planes is $d_{111} = a/\sqrt{3}$, and the peak position is at $Q = 2\pi/d_{111}$. There are 4 particles per unit cell, and the closest distance between their centers is $d = a/\sqrt{2}$; they occupy a volume fraction $\phi = (2\pi/3)(D/a)^3$, where D is the particle diameter. Since the size a of the unit cell may be determined from the positions of diffraction peaks, the volume fraction may be calculated as well:

$$\phi = (2\pi/9\sqrt{3})(D/d_{111})^3 \qquad (2)$$

For hard spheres at contact, $d = D$ and then $\phi = \pi/3\sqrt{2} = 0.74$; for soft spheres the volume fractions may exceed this value and go all the way up to unity;[1,3] then $d_{111} = 0.739D$ and $d = 0.905D$.

In films exposed to vapor or liquid D_2O the variation of d_{111} measures the swelling of the membranes. *In most films the water uptake was low, just enough to provide contrast; hence the swelling was very slight* (1–5% water in the sample); then the peak position is given by eq 2 with $\phi = 1$. In the case of the L-AA-9 dispersion the water uptake was pushed much further, and from the peak position we found that the interparticle distance had risen from 1140 to 1460 Å (Figure 2). According to eq 2, this increase corresponds to decrease in ϕ from unity to 0.48. Beyond this point the films made at pH 9 may break apart into lumps of aggregated particles; however, complete redispersion into the original particles is never obtained.

In some films the diffraction peak had vanished, indicating that the array of membranes had been destroyed.[3] Uptake of water in these films was much slower; after a prolonged exposure to water vapor, diffuse scattering near the beam could be observed; this scattering corresponds to isolated objects, presumably pools of expelled hydrophilic material. For a single object the $Q \rightarrow 0$ limit of the scattered intensity measures its content and the curvature at higher Q measures its size; for a collection of independent objects the intensities from each just add up.

A practical conclusion from these reswelling experiments is that the permeability of the films to water vapor appears to be related to the permanence of an array of membranes. Hence experiments which determine the thresholds for the destruction of this array may explain the variations of this permeability with the nature of the film and with its thermal history.

Fragmentation of Membranes

In this section the effects of thermal annealing on films made with different membranes are presented and compared with each other. The comparison shows that some factors in the internal structure of the membranes are critical for their stability.

Observation through Neutron Scattering. A typical effect of thermal annealing is shown in Figure 3. In this case the films were made from a S–BA latex, where the membranes contained PAA sequences in the acid form. The films were annealed for 24 h at different temperatures and then rehydrated with D_2O to give contrast between membranes and hydrophobic cores. The neutron scattering spectra of films annealed at 50 and 110 °C show a strong diffraction peak; the peak position at $Q = 0.00652$ Å^{-1} corresponds to a distance $d = 1140$ Å. This corresponds to a slight swelling, since the distance between the centers of polyhedral cells in the unswollen film must be, according to eq 2, $d = 1090$ Å.[1,3] The quality of order is indicated by the depression at low Q, where the intensity is 10 times lower than at the peak. Both observations indicate that the membrane polymers have been unable to move, even though the temperature was such that the cores were in a liquid state. Hence the membranes were still fully connected, and no fragmentation had occurred yet.

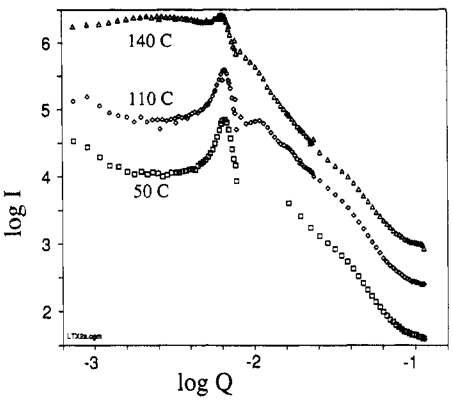

Figure 3. Small-angle neutron scattering from latex films annealed at different temperatures and rehydrated with D_2O. The original latex particles are made of a soft, un-cross-linked S–BA core surrounded by a membrane based on poly(acrylic acid) sequences (Table I); the acrylic acid groups have not been neutralized; hence the cross-links within the membrane are only weak hydrogen bonds.

A major change occurred when such films were annealed at 140 °C: the depression at low Q was filled up by a very broad hump, with a maximum at a Bragg distance of a few interparticle distances (Figure 3). Since scattering reflects the distribution of hydrophilic material, these changes indicate that the membranes had been displaced. In this respect the decrease in the relative peak height reflects a loss of the ordered structure, and the rise at low Q reflects the formation of lumps of fragmented and expelled hydrophilic material.

Electron Microscopy. These heterogeneities were visualized through TEM pictures of stained films. Figure 4a shows a picture of a film kept at room temperature, where the ordered array of membranes is clearly visible. Figure 4b shows a picture of a film with the same composition annealed at 140 °C for 24 h: the array of membranes has been replaced by large, irregular lumps of hydrophilic material. Thus TEM pictures give essentially the same result as neutron diffraction spectra: the array of membranes is stable at all temperatures up to 110 °C, and at 140 °C it undergoes fragmentation and expulsion.

Effects of Annealing Time and Temperature. Systematic investigations of these processes were conducted through neutron scattering, because the experiments are less time-consuming and require less transformations of the samples. In a first stage, the effects of annealing time were investigated (Figure 5).

The unannealed film shows very good order, as indicated by the sharp diffraction peak (notice that logarithmic scales are used) and the deep depression at low Q. After 6 h of annealing at 140 °C a rise at low Q had developed in the spectrum, corresponding to scattering from large-scale heterogeneities. The average size of these heterogeneities

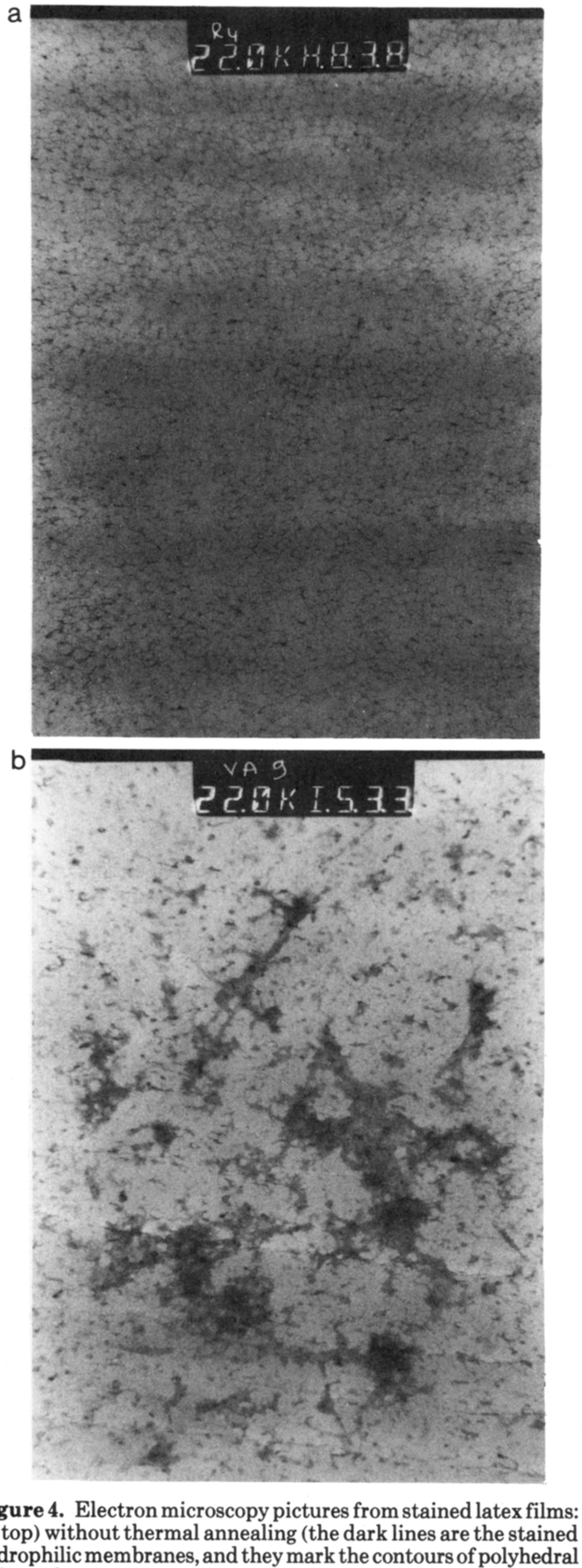

Figure 4. Electron microscopy pictures from stained latex films: (a, top) without thermal annealing (the dark lines are the stained hydrophilic membranes, and they mark the contours of polyhedral cells made through the compression of the original particles); (b, bottom) with annealing for 24 h 140 °C (the hydrophilic membrane material has been fragmented and expelled; some of the resulting lumps are comparable to the original particle size, whereas others are much larger).

can be obtained from the curvature at low Q, which follows Guiner's law; the corresponding diameter is 980 Å. After 24 h at 140 °C the rise had shifted to lower Q values, indicating that the heterogeneities had become much larger.

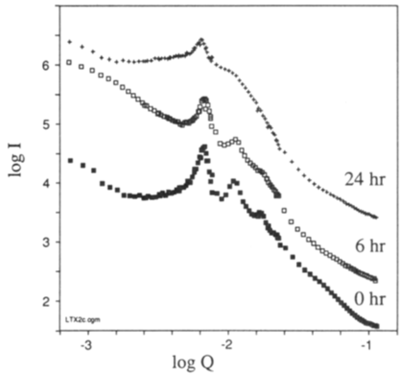

Figure 5. Scattering from films annealed for different times at 140 °C and rehydrated with D_2O. The decrease in the peak intensity reflects loss of order caused by fragmentation of the membranes. The rise toward $Q \rightarrow 0$ reflects the expulsion of membrane materials to large lumps immersed in the hydrophobic matrix.

The kinetics for expulsion of membrane material is better described by the diffusion time of a particle in a viscous medium rather than by the time for the diffusion of a polymer chain in a melt. A typical time for Brownian motion of the excluded polymer particle in a viscous fluid which is the polymer melt is

$$t = \eta_F R^3/kT \tag{3}$$

where η is the viscosity of the polymer melt and R is the particle diameter. According to the neutron scattering spectra, the size of heterogeneities is on the order of 0.15 μm. The viscosity η_F of the polymer melt has been determined through capillary viscometry at 140 °C; it is about 1000 Pa s. The resulting diffusion time is 1 h; it is indeed comparable with the time scale for segregation. However, the observed kinetics may be controlled by a distribution in the rupture times for the membranes of different cells rather than by diffusion of membrane polymers after these ruptures (see the discussion).

Effect of Membrane Composition. Membranes based on poly(acrylic acid) sequences may be rather rigid since the glass transition temperature T_g of pure PAA in the acid form is at 106 °C.[22] This may explain why there is a threshold for fragmentation and expulsion of the membranes between 110 and 140 °C. To investigate this effect we synthesized particles with membranes made by copolymerization of β-CEA. This monomer is a dimer of acrylic acid; the resulting polymers have a very low T_g, about −10 °C. Figure 6 shows the spectrum of a film which was dried at room temperature and then rehydrated. The peak has almost completely vanished, and there is a continuous rise of intensity toward $Q = 0$. The complete loss of order indicates that massive fragmentation of the membranes has taken place; the rise at small Q indicates that the fragments of membrane material have not yet been expelled. Accordingly, the higher mobility of β-CEA lowers the threshold for fragmentation to below room temperature; expulsion is still limited by the mobility of the cores, which is low at room temperature.

Another factor in the preservation of membranes may be the effect of cross-links within the membrane. In membranes made of PAA sequences these cross-links are hydrogen bonds between acid groups; indeed if these cross-links are prevented as in ethyl acrylate, the T_g is much lower (65 °C). In the absence of water much stronger cross-links may be produced if the acid groups have been transformed to the salt form by neutralization with a strong base: the T_g of the sodium salt of PAA is 230 °C. To investigate this effect we neutralized the latex dispersion

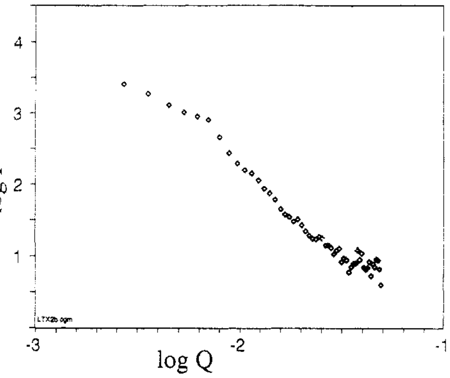

Figure 6. Effect of membrane mobility. In this case the membranes have been made through the polymerization of β-CEA; they have a high mobility at room temperature. The spectrum shows the loss of order for a film kept at room temperature. This is caused by fragmentation and expulsion of the membranes.

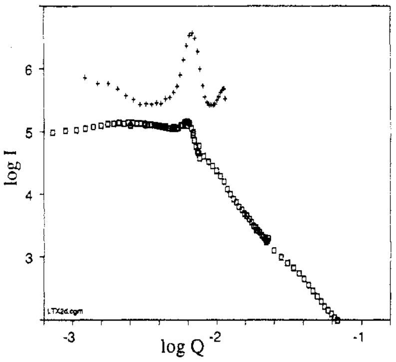

Figure 7. Effect of cross-links within the membrane. Top: the acrylic acid groups in the membranes have been neutralized to pH 9 with NaOH. Bottom: the membranes have been kept in the acid form, at pH 2. In both cases the films were annealed at 140 C; the persistence of the ordered structure in the first film is due to cross-linking by the sodium counterions.

to pH 9 with NaOH; then films were made, annealed for 24 h at 140 °C, and rehydrated as above. Figure 7 shows the spectra of films made from this dispersion and from a dispersion kept at pH 2. The diffraction pattern is preserved in the film at pH 9, and it has vanished in the film at pH 2. Accordingly, metal cations are efficient cross-linking agents for the PAA membranes.[2,12,23]

Effects of Core Composition. In all experiments presented above, the particle cores were made of a styrene–butyl acrylate copolymer (S–BA). This polymer is linear and un-cross-linked, and it has a T_g around 15 °C. In this section we present results of experiments where the particle cores were made of a styrene–butadiene (S–B) copolymer (Table I). This polymer is a strongly cross-linked rubber; however, the cross-linking density can be controlled through the addition of a chain transfer agent.[14] Figure 8 presents the results obtained with different cross-linking densities. The film with a high density of cross-links shows a diffraction by the array of reswollen membranes; remarkably, the second diffraction peak is nearly as high as the first. After annealing at 180 °C, the diffraction pattern is still there, with some broadening caused by disorder. On the other hand, the film where cross-linking was prevented shows a nearly complete loss of the ordered structure after 6 h of annealing at 50 °C.

In this case the relevant comparisons can be made in two steps. First, the film with *un-cross-linked* S–B cores behaves as the films with S–BA cores: in both cases the membranes are made of poly(acrylic acid) sequences, which become mobile and are expelled at high temperature. This was expected, but it was good to verify it. Second, the film with *cross-linked* cores retains the ordered array of membranes at all temperatures. Hence there is something about the cross-linking which prevents fragmentation and expulsion of the hydrophilic material. This could be the restricted mobility of the core or connections between the cores and the membranes.

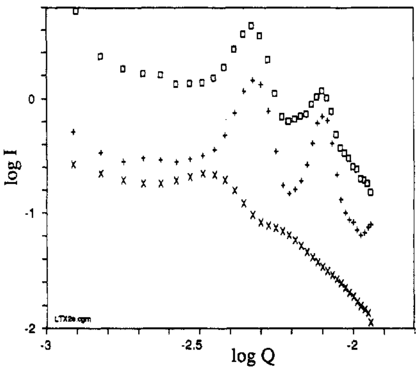

Figure 8. Effect of cross-links within the particle cores. Top: styrene–butadiene cores with a high density of cross-links; films annealed at 180 °C. Middle: same films before annealing. Bottom: a chain transfer agent was added to prevent cross-linking within the cores.

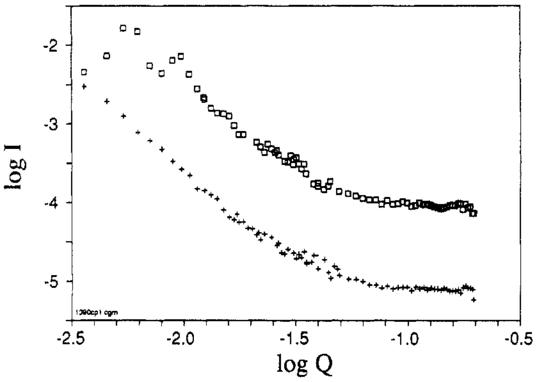

Figure 9. Films with surfactant membranes and different particle cores: (□) strongly cross-linked cores; (+): weakly cross-linked cores.

To isolate the effect of macromolecular mobility from all others we also made latex dispersions where the membranes were made of surfactant molecules. In one case the core was made of a S–B copolymer where 84% of the monomers belonged to the cross-linked network; in the other case this fraction of cross-linked material was less than 10%. The results are presented in Figure 9: the film with cross-linked cores has retained some order despite annealing at 50 °C; the film where cross-linking was avoided shows complete loss of order. Since the only difference between both films was the mobility within particle cores, this mobility must also be a factor in controlling fragmentation and expulsion of hydrophilic membranes.

Discussion

All the latex samples investigated here had the same initial structure: they were periodic arrays of cells containing hydrophobic polymers and separated by hydrophilic membranes. In this initial state the area of interface between hydrophobic and hydrophilic materials was large, on the order of 30 m²/g. Obviously, this is not the state of lowest free energy for the dispersion; consequently, the spontaneous evolution of such dispersions should be to segregate hydrophilic and hydrophobic materials in such a way as to reduce the area of the interface. The evolution of dry latex samples goes in this direction: the stages which we have observed are the loss of periodic structure, which requires fragmentation of the membranes, and the expulsion of hydrophilic materials to large lumps, which requires transport of matter at large scales.

Comparison of "Wet" and "Dry" Coalescence. This evolution is similar to the spontaneous evolution of emulsions, particularly high internal phase ratio emulsions, which have the same cellular structure. In these emulsions, thermal fluctuations of the surfactant monolayers which protect the droplets produce surfactant bridges across the water layers which separate the particles; this recombination allows the oil cores of the particles to fuse together.

However, the *thresholds* for fragmentation and coalescence are not the same in our latex films as in emulsions. Oil-in-water emulsions coalesce spontaneously in the *wet state* when the water films which separate droplets are drained or compressed below a critical thickness;[24] the same behavior occurs for some surfactant-covered latex dispersions.[3] The critical thickness of water layers is determined by the amplitude of thermal fluctuations; typically, water films thinner than 100 Å rupture immediately unless the interfacial tensions are quite low. The latex samples investigated here ripen in the *dry state*, where the hydrophilic membranes which separate particles are no more than 20 Å thick. These arrays of very thin membranes maintain their periodicity unless the thermal treatments applied to the samples go beyond some thresholds which have nothing to do with membrane thickness. Thus a careful analysis of the thresholds is a prerequisite for understanding the transformations of the latex samples.

Thresholds for Fragmentation and Expulsion. Of all the dry films investigated, the ones that behave closest to emulsions are those which are covered with surfactant membranes. These samples show coalescence at room temperature, unless the core is cross-linked. If the core is cross-linked, then the ordered structure is retained even after annealing at 50 °C. These thresholds confirm that (a) very thin surfactant membranes do not resist fragmentation and (b) cross-linked particle cores may prevent transport of mass and therefore segregation of the hydrophilic materials (the membranes may be kept in place by the sulfate groups which are linked to the core polymers).

The other type of latex samples have soft, un-cross-linked cores but polymeric membranes. It was found that membranes with a low T_g (β-CEA) are fragmented and expelled at room temperature, whereas PAA membranes in the acid form resist fragmentation until 140 °C and PAA membranes cross-linked by sodium ions resist fragmentation beyond 140 °C. These thresholds show that (a) very thin (<20 Å) but rigid polymeric membranes resist fragmentation even when the particle cores are fluid; (b) this resistance ceases above the glass transition temperature of the membranes.

Finally, there is the combined case of latex samples with cross-linked cores and polymeric membranes which may also be cross-linked to the core (S–B latex). These samples resist fragmentation and expulsion of the membranes at all temperatures unless the number of cross-links is so reduced that membranes and cores become fully mobile. This result shows that connections between membrane and core polymers are extremely efficient at preventing segregation of membrane polymers.

Taken together, these results demonstrate that the loss of the periodic structure requires mobility in the hydrophilic membranes and in the hydrophobic cores. Conversely, lack of mobility in the membranes will block fragmentation and lack of mobility in the cores will block expulsion.

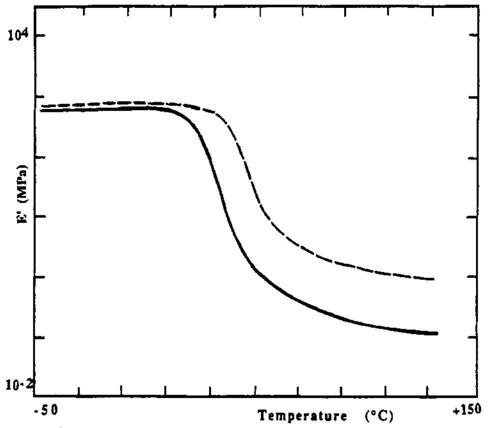

Figure 10. Extension storage modulus E' (f = 1 Hz) of cross-linked (dashed line) and un-cross-linked (full line) S–B latex films versus temperature (from ref 12).

Relation to Mechanical Properties. The information provided by the thresholds is quite clear, but it is of a qualitative rather than quantitative nature. It would be most useful to be able to predict the occurrence of coalescence without having to use neutron scattering or electron microscopy, which are time-consuming and not readily available. Since coalescence appears to depend on mobilities within the membranes and the cores of the particles, it follows that one should use properties which depend on these mobilities. The obvious candidates are the mechanical properties, e.g., elasticity and flow.

Indeed, the same factors which suppress local mobility will also prevent macroscopic flow in the sample. For instance, the effect of cross-links in the core on the shear modulus is demonstrated in Figure 10. At low temperatures the modulus is that of a bulky, glassy polymer; then above the glass transition of the matrix it drops to a rubberlike plateau; the height of this plateau is determined by the extent of cross-linking and intermolecular interactions.[12,14] Similar curves have been obtained for films where the core polymers were not cross-linked but the membrane polymers were cross-linked through ionic pair of cluster formation, using alkali metal cations.[12,13] For each such case where there is a high, well-defined rubberlike plateau in the mechanical response of the films, we have found that segregation of membrane material was prevented. This was expected, since both classes of phenomena originate from features at the molecular level which prevent mass transport.

Still, what is needed is a quantitative prediction. For this purpose it is necessary to estimate local mobilities from the mechanical properties of the sample. In fact, local mobilities can be deduced from the frequencies of relaxation in dynamical measurements of the elasticity of latex samples. Figure 11 shows master curves for dynamical measurements of the storage modulus in samples with different numbers of cross-links. Each curve shows the usual trend with high modulus at high frequency, where the chain segments behave as in a vitreous state, and low modulus at low frequencies, where chain mobility allows complete relaxation of stress. For fully cross-linked latex samples the relaxation frequency is on the order of 1 s. The interesting feature is the effect of different densities of cross-links on this relaxation spectrum: the mechanical spectrum remains the same, but the relaxation frequencies are shifted by 4 orders of magnitude; conversely, for a

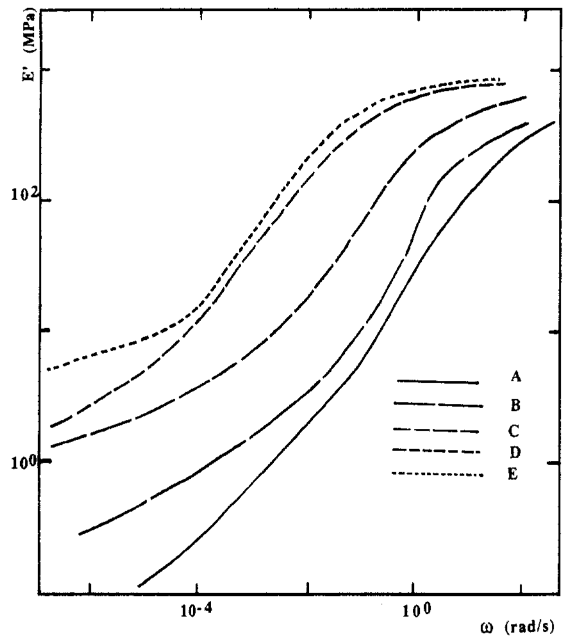

Figure 11. Isothermal master curves of the storage moduli for a series of S–B latex films with various CTA contents (A, 2%; B, 1.25%; C, 0.8%; D, 0.4%; E, 0%). A is sample T-AA-4.5 of Table I, whereas E is sample C-AA-4.5. The location of the transition region is shifted to high frequencies as the cross-linking density decreases.

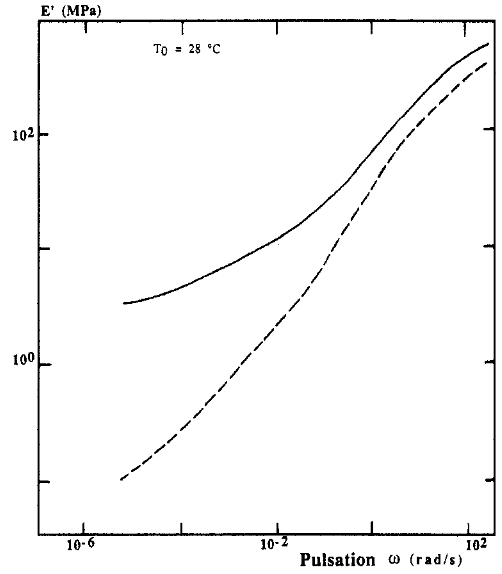

Figure 12. Isothermal master curves of the storage moduli for the nonneutralized S–B latex T-AA (dashed line) and the same S–B latex neutralized with ammonia (full line).

fixed frequency the behavior changes from solidlike to liquidlike. The same changes in cross-link density cause the coalescence of particles to be observed after 6 h of annealing at 50 °C. Therefore coalescence may be expected when the relaxation frequencies in mechanical spectra are in the 10^{-4}–10^{-2} s range.

The effect of cross-links in the membranes on the mechanical properties is not as dramatic, because only a small fraction of the material has restricted mobility. Figure 12 shows master curves for un-cross-linked S–B latex samples with membranes which are either neutralized or in the acid form. The mechanical curve for samples with acid membranes is the same as shown in Figure 11. With neutralized membranes the high-frequency modulus is the same (because there is still local relaxation in most of the sample) but the low-frequency modulus is higher by 3 orders of magnitude, indicating that mechanical relaxation at usual frequencies (0.1–1 s) is incomplete. We do not have neutron scattering spectra for both samples, but for a related series in the S–BA latex system; in these samples cross-links in the membranes prevent coalescence up to 140 °C.

Thus the mechanical property which is best related to the occurrence of coalescence is the low-frequency limit of the dynamic modulus. The proper frequency range is that over which flow and coalescence are observed, i.e., 10^{-6}–10^{-5} s^{-1}. The quantitative criterion is that coalescence is prevented in samples where cross-links, either in membranes or in the particle cores, raise this modulus to above 1 MPa.

Outcome of Segregation: Morphology of Segregated Samples. The pictures of segregated samples show a texture made of large irregular lumps. It is not "a priori" obvious that the result of a segregation process should be so irregular, considering that the original state was quite well ordered. Other possible outcomes for the fragmentation and expulsion of an incompatible phase are known. Going back to high internal phase ratio emulsions, which have a similar geometry, it is found that two types of evolution have been observed: either coalescence of small droplets together or capture of small droplets by much larger ones.[24] The first evolution could be called a homogeneous growth mechanism; it produces a monomodal size distribution with a mean size which grows continuously. The second one could be called a heterogeneous growth mechanism; it results in a distribution containing small droplets and much larger ones.

Our observations on latex samples indicate that the evolution is heterogeneous. Besides the qualitative impression from the electron microscopy images, we can rely on the neutron scattering spectra; indeed, a homogeneous mechanism would result in a continuous shift of the diffraction peak, which is not observed; instead, the spectra show a collapse of the peak accompanied by a rise at very small Q, which reflects the growth of large segregated lumps.

We think that this lack of regularity in the segregation process originates from a broad distribution in the strengths of membranes. Indeed if the surfaces of the original latex particles are somewhat heterogeneous, then the membranes of different cells will be released at different times, and pools of expelled hydrophilic material will form according to where the membranes have been released first. *In this sense the mechanism observed here is a heterogeneous nucleation of defects in the array of membranes.* Conversely, a lack of simultaneity in the segregation process may indicate that the surfaces of the original latex particles were indeed heterogeneous. This would be in agreement with observations on the reswelling of dried films: films can be swollen to a large extent and even broken apart, but complete redispersion into individual particles is never obtained; again this may indicate that the cover of the original latex particles is heterogeneous.

Such heterogeneity in the coverage of latex particles may also be important for the final step of particle coalescence, which is the interdiffusion of the particle cores. Indeed the onset of interdiffusion may be tied to the thresholds for fragmentation of the membranes; hence the interdiffusion processes may follow the same pattern as described in the present work.[26]

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