Low temperature transmission electron microscopy and differential scanning calorimetry characterization of latexes stabilized with surface active block oligomers

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The spatial distribution of a short-chain amphiphilic diblock copolymer (i.e. block oligomer), used as an emulsifier during the preparation of a latex, is determined by low temperature transmission electron microscopy and differential scanning calorimetry (d.s.c.). The main question is whether intermixing of the amphiphilic block oligomer and latex core materials actually takes place to a significant extent. Electron microscopy gives a clear indication that a surfactant-rich layer exists in all latex samples examined. At very high surfactant concentration (> 6%, not typically used in commercial latexes), electron beam radiation damage reveals the presence of a surfactant gradient from the particle surface to its core. These results are in good agreement with our d.s.c. data.

(**Keywords: polymer latex; surface modification; oligomeric surfactants; cryo-TEM; d.s.c.**)

INTRODUCTION

The development of functional or composite latexes is one of the rapidly growing areas in the preparation of novel polymeric materials. Polymerization schemes involving heterogeneous reaction loci, such as emulsion or dispersion polymerizations, provide an excellent opportunity to fabricate intricate composite structures with relative ease and versatility, in a scale ranging from nanometres to micrometres. In recent years, there have been reports on the synthesis of latexes in the presence of water-soluble or water-dispersible polymers, which possess some levels of surface activity[1–4]. Many of these polymers are claimed to adsorb onto the surface of the latex and serve as protective colloids, which enhance the stability of latex particles during synthesis and after preparation.

The possibility of using amphiphilic block or graft copolymers as polymeric surfactants[5] in dispersion[6,7] or emulsion[8–10] polymerization is especially interesting, since these surface-active polymers can function as effective emulsifiers during the preparation stage. Because of their high molecular weight, surface-active polymers may interact with the constituent polymers of latexes in a manner somewhat different from regular low molecular weight surfactants. Thus, latexes prepared with surface-active polymers may be treated as models for microscopic polymer blends or composites, where the extent of intermixing of polymers is strongly influenced by the colloidal nature of the system, characterized by a large surface area and significant interaction with the surrounding medium.

In this paper, the spatial distribution of a short-chain amphiphilic diblock copolymer (i.e. block oligomer), used as an emulsifer during the preparation of a latex, is determined. Several factors are expected to influence the distribution of such surface-active molecules within individual latex particles. Intuitively, amphiphilic oligomers are expected to preferentially accumulate at the surface of the latex because of their surface activity, as do most low molecular weight surfactants. But, it is also conceivable that a large portion of the block segment can intermingle with the polymer molecules comprising the latex core, as long as there is enough affinity between the polymer and oligomer segment. Furthermore, if there is molecular entanglement or partial grafting of surfactants during latex preparation, a substantial amount of surface-active block oligomers may actually be entrappped within the interior of the latex core. We used low temperature transmission electron microscopy (cryo-TEM) and differential scanning calorimetry (d.s.c.) to determine whether such intermixing of the amphiphilic block oligomer and latex core materials actually takes place to a significant extent.

BACKGROUND

Surface-hydrophilic elastomer latex (SHEL)

Recently, a series of elastomer latexes, which have shown some unique properties substantially different from those of ordinary latexes, have been synthesized in the presence of non-ionic amphiphilic diblock oligomers as emulsifiers[11–14]. The most remarkable property of

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these amphiphilic diblock oligomer-containing latexes is that the surface of a rubbery film produced by drying such a latex is highly water wettable[11,12]. The equilibrium contact angles measured on a sessile water drop on the film are well below 10°. The surface hydrophilicity does not disappear even after repeated washing, or exposure to dry air for a prolonged period. The bulk of the rubbery film remains hydrophobic, so that there is no extensive swelling by water. The ability to form such a surface-hydrophilic elastomeric film is not affected even when the latex is extensively dialysed prior to film formation.

The development of very high and apparently permanent hydrophilicity over the surface of a soft elastomer film is somewhat surprising. It is possible to create high-energy surfaces on polymers by incorporating polar functional groups in the vicinity of the surface. But because of the thermodynamic driving force to minimize the surface energy, these groups tend to gradually migrate away from the surface[15,16]. Thus, the effect of conventional surface hydrophilization treatments usually lasts only for a short period of time. The rate of surface-hydrophilicity loss is especially high for rubbers due to the conformational mobility of the polymer chains. Hence, the development of stable surface hydrophilicity at rubber surfaces cannot be easily explained, unless there is a strong molecular interaction to inhibit the free migration of hydrophilic moieties away from the surface.

Another equally remarkable property found in the latexes prepared with the diblock oligomers is their exceptionally high colloidal stability[13,14]. They are resistant to flocculation under extremely harsh conditions, such as high concentration of electrolytes or organic solvents, repeated freezing and thawing, or even a short period of boiling. The level of colloidal stability observed in these latexes, therefore, is well beyond what is expected from steric stabilization effects achieved by normal protective colloids loosely adsorbed to the particle surfaces. The latexes behave as if each particle is surrounded by a very stable hydrophilic layer firmly attached to the surface. These observations, too, suggest a strong interaction between the amphiphilic diblock oligomer and latex core materials. In this study we used polystyrene (PS) latexes as models of SHELs.

Electron microscopy of latex systems

Transmission electron microscopy (TEM) is one of the most suitable methods for the study of latex systems. It provides high-resolution direct images of these particles, which are typically 20–500 nm in diameter. Because latex specimens are fluid, high vapour pressure systems, steps must be taken to make them compatible with the high vacuum in the microscope. Furthermore, all supramolecular motion in the specimen has to be arrested to avoid image blurring due to the high magnifications used, and the relatively long exposures needed to record images on film. The simplest and most commonly used way to 'fix', i.e. to lower vapour pressure and arrest motion, is to apply a drop of the latex on film-covered TEM grid, and let it dry on it. Although suitable for some systems, the technique may strongly affect the microstructure of the latex and introduce structural artifacts by particle collapse, particle aggregation, and even by coating of particles upon drying by solutes present in the suspending medium.

An alternative class of sample preparation techniques are thermal fixation techniques, based on rapid cooling to a temperature where the specimen becomes a low vapour pressure solid. In most latexes of importance the major component is water. Cooling rates of $<10^5$ K s^{-1} produce crystalline, hexagonal ice (I_h); higher cooling rates lead to vitreous ice (I_v); occasionally, cubic ice (I_c) forms at intermediate cooling rates. Vitrification is usually the method of choice, as it assures structural preservation and a featureless solid matrix. Nevertheless in some cases, when electron-beam radiation damage phenomena are applied to elucidate certain microstructural details (see below), a crystalline ice matrix is desirable.

Thermally fixed specimens also known as cryo-specimens, may be examined directly, if they are thin enough (typically <500 nm). Alternatively, the specimen is fractured, a metal–carbon replica of the fracture surface is prepared, and then examined at room temperature. Direct imaging requires special equipment to transfer the specimen into the microscope and to maintain it there at low temperature (<110 K) without excessive heating and frost deposition.

Latex cryo-specimens may be prepared either supported on a single film, sandwiched between two polymer (i.e. polyimide) films, or unsupported, i.e. spanning the holes of a holey carbon film. Our experience has shown that the first method is hard to use. The 'sandwich technique' is best for preparing crystalline samples; it is easy to use, and the two support films suppress the tendency of embedded particles to be ejected from the hexagonal ice matrix. The holey carbon film method is best for achieving the high cooling rates necessary for sample vitrification. More details on preparation techniques are described in the Materials and Methods section.

TEM imaging of thermally fixed latex preparation is relatively simple. Usually it is based on mass–thickness contrast, occasionally enhanced by phase-contrast effects through defocusing of the microscope objective lens. However, to bring out structural details such as different microdomains in a multicomponent system, or to detect an adsorbed layer of surfactant on latex particles, special means are required. One possible technique is preferential staining of a given component. An alternative is to use preferential etching of a latex component by the electron beam[17,18], or the modification of electron beam radiation damage to the latex by an adsorbed surfactant layer on the particle surface, as shown in the present work.

MATERIALS AND METHODS

Latex preparation

Materials. The surfactants used in this study were the non-ionic oligomeric surfactant Volpo-20 (Croda Inc., New York, USA) which is an ethoxylated oleyl alcohol with a degree of ethoxylation of ~20 and a cationic derivative of Volpo-20 in which the terminal hydroxyl group has been replaced by a trimethylammonium bromide group[13]. Distilled water was used in all recipes. Polymerizations were initiated with either potassium persulphate ($K_2S_2O_8$) or V-50, 2,2'-azobis(2-amidinopropane) dihydrochloride (Wako Chemicals, Dallas, USA). The Volpo-20, styrene (Aldrich, Milwaukee, USA) inhibited with 10–15 ppm t-butylcatechol), V-50 and $K_2S_2O_8$ were used as received.

Procedure. The general recipe and reaction conditions used are similar to those used previously[11–14], and are

Table 1 Recipes for latex preparation

Ingredient or condition	Amount used: With surfactant	Amount used: Without surfactant
Styrene (g)	7.3	2.7
Initiator (mM)	1–4[a]	4[a]
Surfactant (%)	2–20[b]	–
Water (ml)	50	70
Temperature (°C)	30–60	85
Time (h)	17–46	20

[a] Based on aqueous phase
[b] Based on weight of monomer
[c] Typically 60°C
[d] Typically 17–20 h

given in *Table 1*. The surfactant, initiator and water were combined in a crown-cap, pressure bottle containing a magnetic stir-bar. The bottle was capped with a rubber gasket and two-holed metal cap, and then purged with argon. Styrene was added by syringe, and the bottle was placed in a constant-temperature bath. After the desired period of time, the bottle was cooled to room temperature and opened. The contents were filtered through a wire screen, and the solids content was determined gravimetrically. Some of the latexes were partially cleaned by dialysis (Spectrapore 2 dialysis tubing in 1–2 l of water for 48 h, changing the water twice). Some latexes were partially cleaned by serum replacement: 20 ml of latex were diluted to 30 ml with water, and this mixture was serum-replaced in a Nucleopore Corporation stirred filtration cell with a 0.1 μm pore size membrane with 100–225 ml of distilled water.

For some of the studies it was important to have one latex series with the same particle size but different levels of surfactant, and another latex series with the same level of surfactant but different particle sizes. The preparation of these latex series was accomplished by the variation of the surfactant concentration and the rate of initiation (initator concentration and reaction temperature) as described by Smith[19].

Electron microscopy

Vitreous specimens were prepared from latex suspensions at concentrations of ~1–10 wt%. Preparation was carried out in a Controlled Environment Vitrification System (CEVS)[20]. Because neither small deviations from the average room temperature of 22°C, nor small changes in sample concentration by water evaporation during specimen preparation were expected to change the observed microstructure, only the plunging mechanism of the CEVS was used (without using temperature or humidity control in the system). Specimens were prepared by applying a drop of the latex onto a holey carbon film-covered electron microscope grid, held by a tweezer attached to the plunging device of the CEVS. A thin liquid film (<0.5 μm) was formed by pressing a piece of filter paper to the grid. The plunger was then triggered, and drove the specimen into a container of liquid ethane at its freezing point, surrounded by liquid N_2. Vitrified specimens were stored under liquid N_2, and subsequently transferred to the Hitachi H-500 TEM using a Gatan cooling holder and transfer station.

Crystalline specimens were prepared by applying a drop of the latex onto a polyimide film-covered grid held with a tweezer. Polyimide films are used because they are relatively radiation damage resistant and are water wettable[21]. The grid with the drop on it was brought at a 45° angle to the edge of second film-covered grid lying on a flat surface. The latter was picked up by the former by capillary forces. The sandwich thus formed was blotted by touching its edge with a filter paper. This reduced the liquid layer thickness to <0.5 μm, the thickness desirable for TEM. Thermal fixation was done by manually plunging the sandwich, still held by the tweezer, into liquid N_2. In this case cooling rates were rather slow, leading to an I_h matrix. Specimen handling after freezing was as described for the I_v specimens. These specimens were examined in JEOL JEM 120CX TEM equipped with a Gatan cooling holder and transfer station.

Specimens were kept in the microscope at −170°C, and examined at an acceleration voltage of 100 kV. Micrographs were recorded on Kodak SO-163 electron image film, and developed in full strength Kodak D-19 developer. Images of vitreous samples were recorded at moderate electron exposures ('doses') of 2–10 $\mathrm{kC\,m^{-2}}$; there was no need for special low dose precautions, because of the relative stability of these specimens under the electron beam. Hexagonal ice samples were examined according to the technique developed by Talmon *et al.*[22] to use radiation damage patterns to reveal latex microstructure: a suitable area was selected at low magnification and minimal electron exposure, focus and image brightness adjustment was done on an area adjacent to it, and a series of images were recorded of the area of choice at increasing electron exposures, from several hundreds to several tens of thousands of coulombs per square metre.

Differential scanning calorimetry

The glass transition temperatures (T_gs) of the latexes were measured with a Mettler TA 3000 system consisting of a DSC-30 low temperature cell differential scanning calorimeter and a TC 10A thermal analysis processor. D.s.c. samples were prepared by drying the latex down at room temperature in air, followed by drying overnight under vacuum at room temperature. Thermograms were typically obtained over the range of −30 to 130°C with a heating rate of 10°C $\mathrm{min^{-1}}$. In general, two scans were made on each sample. For comparison, samples of PS with various levels of the non-ionic oligomeric surfactant were prepared from dichloromethane solutions of these materials.

RESULTS

Electron microscopy of vitreous specimens

In order to observe the effects of the surfactant on the microstructure of the latex system, we first examined a reference sample, namely, a PS latex containing 0.5 wt% $K_2S_2O_8$ initiator and 4.0 wt% oleyl sulphate stabilizer, a relatively short-chain surfactant. *Figure 1a* shows a thin vitrified layer of undiluted latex (9.7 wt%) spanning a hole (~3.5 μm in diameter) in the holey carbon film. Because the ice layer is thin, the polymer particles are arranged in most of the area in a single layer. The size distribution of the latex seems to be bimodal: particles with diameters of ~20 and ~70 nm are seen. Despite the close proximity of the particles, they do not adhere to each other. *Figure 1b* shows a vitreous specimen of the same latex diluted to 1.9 wt%. As will be shown later,

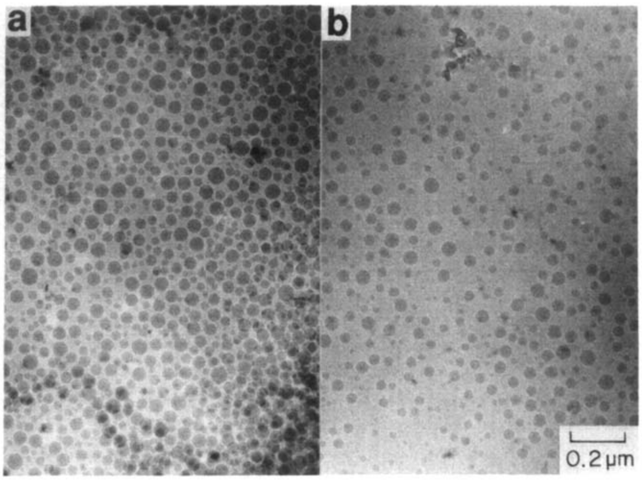

Figure 1 Vitrified aqueous dispersions of ordinary PS latex: (a) 9.7 wt% solids; (b) 1.9 wt% solids

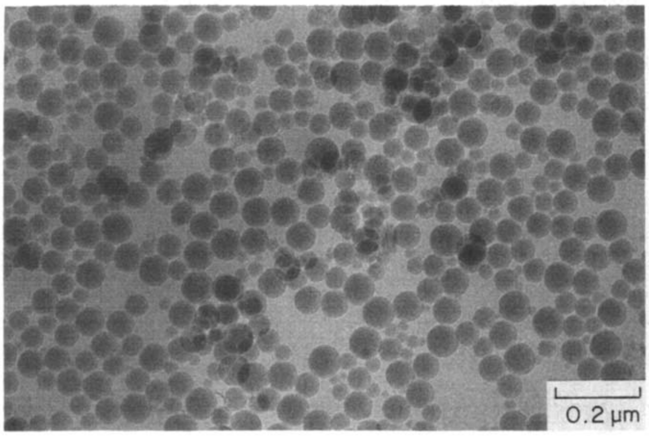

Figure 2 Vitrified specimen of 0.9% solids PS latex containing 4.0% cationic oligomeric surfactant

we need both these micrographs as reference for comparison with the latex made with the oligomeric surfactant.

A PS latex quite similar in size distribution to the reference of *Figure 1* was produced by using the cationic initiator V-50 and 4.0 wt% of the cationic oligomeric surfactant. A vitrified specimen of 0.9 wt% (diluted from the 9.7 wt% of the original preparation) of this oligomeric surfactant-containing PS latex is shown in *Figure 2*. The most striking feature in this micrograph is network formation by the latex particles, most of which have at least two points of contact with neighbouring particles. In some areas this takes place in the third dimension too (overlap of spheres). Although the concentration of the sample in *Figure 2* is 10 times lower than that in *Figure 1a*, the amount of suspended material in the vitrified matrix seems to be on the same order of magnitude, a result of network formation that reduces considerably the amount of suspended material which is swept away from the specimen during blotting and thinning in sample preparation[23].

Replacement of the cationic oligomeric surfactant with the non-ionic oligomeric surfactant in the polymerization, leads to the formation of much larger, uniform particles, as seen in the vitrified sample of *Figure 3*. Because of the uniformity of these particles, and because their size is close to the vitreous ice layer thickness, the latex particles form a fairly well-ordered, two-dimensional hexagonal lattice. The 'halos' seen around the particles are Fresnel fringes, a result of the objective lens underfocus, applied to enhance image contrast. These fringes may give the impression that the particles are separated by a small gap, whereas they are, in fact, touching. See also *Figure 4*. As in *Figure 2*, the particles occupy a substantial part of the field of view despite the rather low original concentration of 0.86 wt%, and most of them touch their neighbours at two points or more.

Results quite similar to those of *Figure 3* were obtained with a different preparation based on 0.5 wt% $K_2S_2O_8$ as the initiator and 4.0% non-ionic oligomeric surfactant as the emulsifer. A vitrified specimen of the resulting PS latex, 0.96 wt% (dilution by a factor of 10 from the original preparation) is shown in *Figure 4a*. As in the previous preparation, the latex particles are quite large and uniform, and tend to pack in well-ordered two-dimensional arrays. Additional information on the interaction between the particles was obtained by examining areas in these specimens that had been air-dried during specimen preparation, before vitrification. Such a dried area, in a specimen of the same latex system shown in *Figure 4a*, is depicted in *Figure 4b*. Although the water matrix has been removed from the area shown

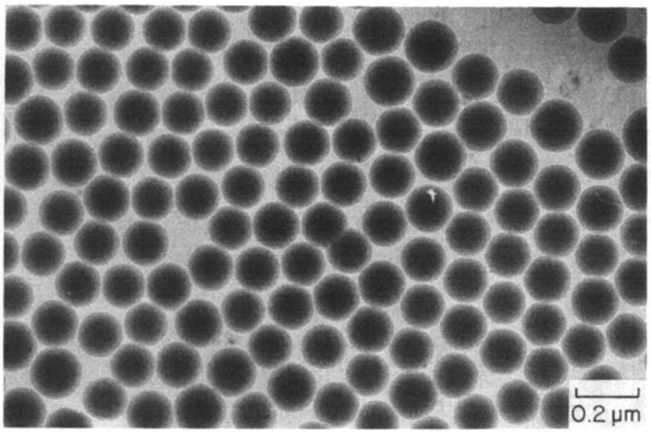

Figure 3 0.89% solids PS latex containing 4.0% non-ionic oligomeric surfactant – vitrified cryo-TEM specimen. Latex prepared with V-50 initiator

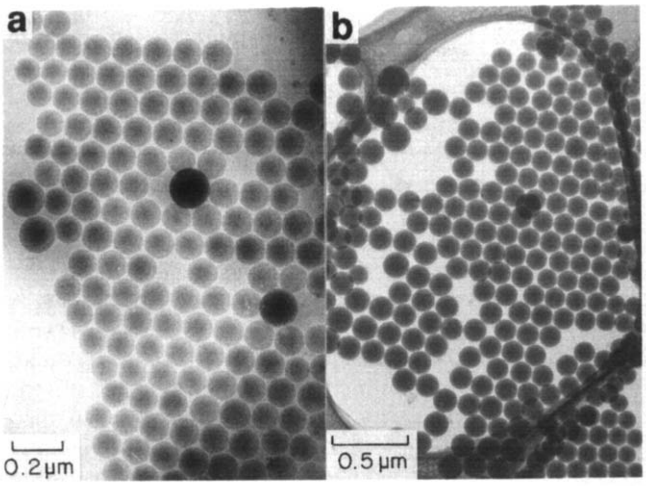

Figure 4 Cryo-specimen of 0.96% solids PS latex made with 4.0% non-ionic oligomeric surfactant and 0.5% $K_2S_2O_8$: (a) a vitrified area; (b) a dry area

in the micrograph, the latex particles have retained the packing order they had assumed in the liquid phase. The forces between them lead in fact to formation of a film that spans the holes of the carbon film. Many dried areas were examined in vitrified specimens of the reference latex, but none showed film formation as in *Figure 4b*, whereas such areas were easily seen in the oligomeric surfactant-stabilized latex specimens.

Electron microscopy of crystalline specimens: radiation damage effects

Organic materials embedded in ice undergo complicated radiolytic processes when exposed to the electron beam, processes that are quite different from radiolysis in the absence of the ice matrix. These phenomena, which are usually more severe in crystalline than in vitreous ice, have been documented in detail by Talmon and co-workers[22,24–26].

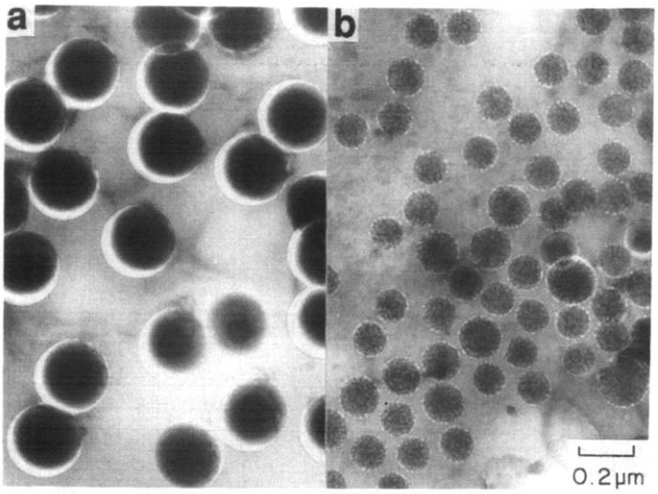

Figure 5 Cryo-TEM micrographs of frozen (matrix is hexagonal ice) PS latex samples after prolonged exposure to the electron beam: (a) 0% non-ionic oligomeric surfactant, 160 kC m^{-2}; (b) 6% surfactant, 140 kC m^{-2}

Polystyrene is a crosslinking-type, hydrophobic polymer. As such it is very stable to radiolytic attack by the electron beam even when embedded as latex particles in a crystalline ice matrix[24]. High exposures ('doses') to the electron beam cause formation of cavities in the ice around it, while the PS particles themselves are not visibly affected (*Figure 5a*). The progress of this damage pattern is shown in Figure 1 of reference 24. Polymers that are hydrophilic or of the 'scission type' (i.e. bond scission is the more probable radiolytic process in them) undergo radiolysis in the presence of ice quite differently[24–26]. They expand in the ice matrix, lose mass, and develop a sponge-like appearance. A detailed example in the case of poly(methyl methacrylate) is given in Figure 5 of reference 24. We have found (*Figure 5b*) that similar radiolytic behaviour is observed when oligomeric surfactant-stabilized PS latex is irradiated in the ice matrix by the electron beam. In this particular case the latex contained 6% non-ionic oligomeric surfactant. As can be seen in the micrograph, only very narrow cavities developed in the ice around the particles, while the particles developed into a sponge-like structure, indicating extensive mass loss. These phenomena indicate that the surface (and possibly the interior) of the particles have been modified by the oligomeric surfactant.

The finding described above called for a careful study of radiation damage to the oligomeric surfactant-stabilized latex before firm conclusions could be drawn. *Figure 6* shows the progression of electron beam radiation damage to the latex with increasing electron exposure. At moderate exposure of 57 kC m^{-2} (*Figure 6b*), damage is first noticed, and becomes very prominent at the higher exposures shown in *Figures 6c* and *d*. Cavity formation is limited, while expansion of the particles is manifested by an 11% increase, on average, of their diameters, which corresponds to a 37% increase in volume. These effects were almost absent in latexes that contained 2% and 4%

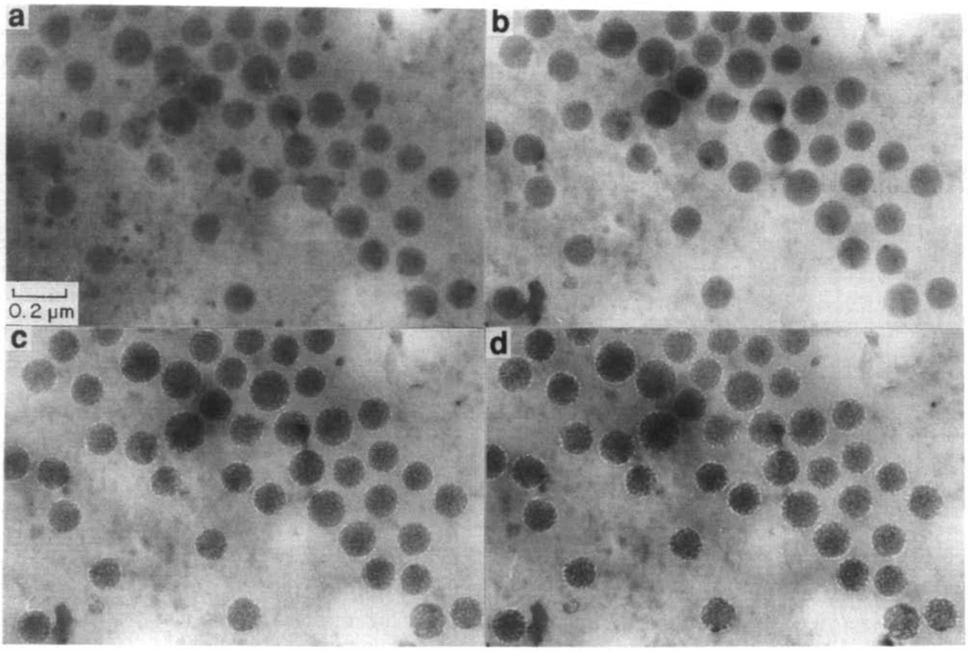

Figure 6 A frozen specimen of PS latex containing 6% non-ionic oligomeric surfactant at increasing electron exposures: (a) 0.45 kC m^{-2}; (b) 57 kC m^{-2}; (c) 110 kC m^{-2}; (d) 140 kC m^{-2}

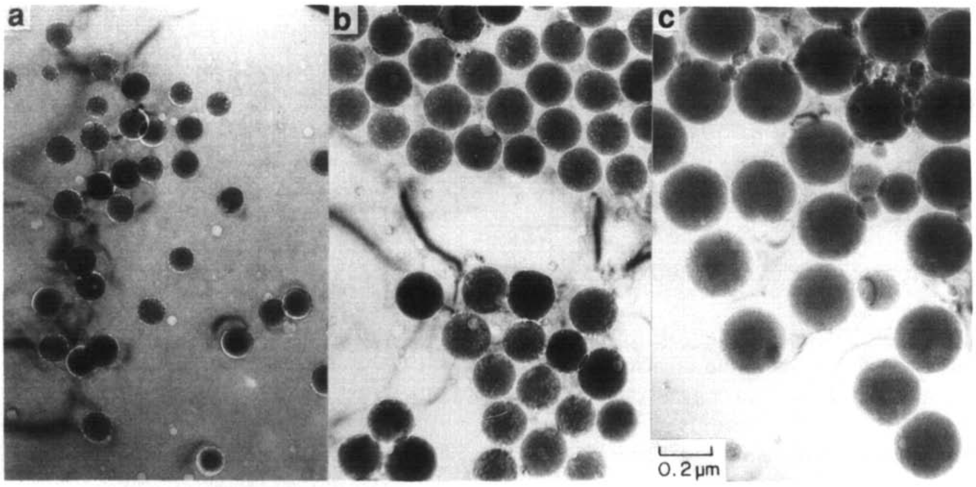

Figure 7 Electron beam radiation damage to frozen specimens of PS latex of different average diameters all prepared with 6% non-ionic oligomeric surfactant after approximately the same electron exposure: (a) average particle diameter of 0.14 µm, exposure of 79 kC m^{-2}; (b) 0.25 µm, 80 kC m^{-2}; (c) 0.32 µm, 81 kC m^{-2}

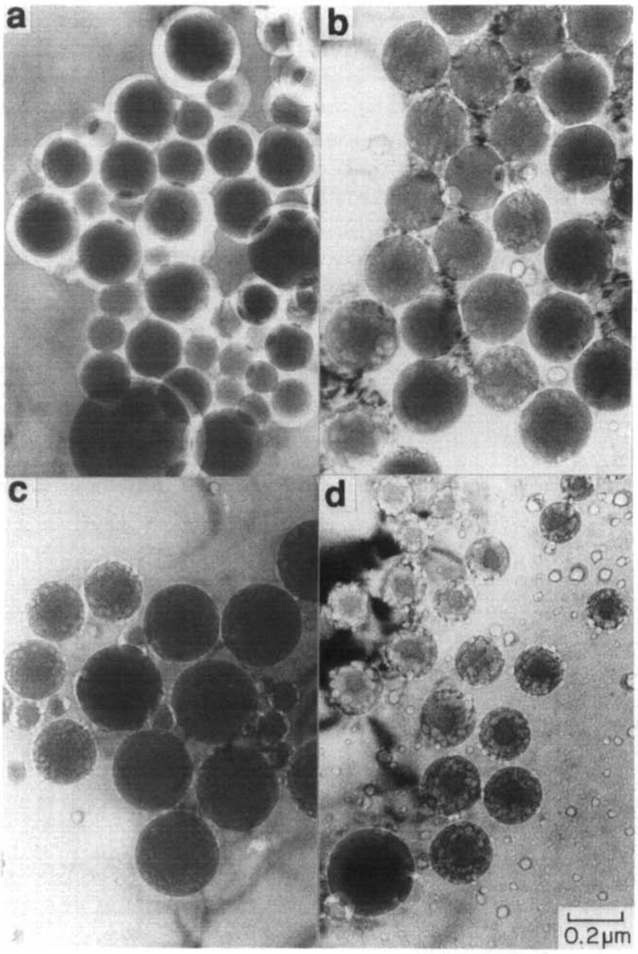

Figure 8 Electron beam radiation damage to frozen specimens of PS latex made with the non-ionic oligomeric surfactant at different levels, exposed to about the same electron doses: (a) 0% non-ionic oligomeric surfactant, exposure of 100 kC m^{-2}; (b) 6%, 120 kC m^{-2}; (c) 10%, 110 kC m^{-2}; (d) 20%, 120 kC m^{-2}

oligomeric surfactant. Because different surfactant concentrations normally (when all other parameters are kept constant) yield different latex particle sizes, and because particle size has a profound effect on the radiolytic behaviour of the particles^{24}, we ran two series of radiolysis experiments: one with different particle sizes at constant oligomeric surfactant concentration, and the second at the same average particle size but at different surfactant levels. *Figure 7* shows three frozen specimens of PS latexes prepared with 6% non-ionic oligomeric surfactant to give particles of different diameters: 0.14, 0.25 and 0.32 µm. The three specimens were irradiated by the same dose of ~80 kC m^{-2}. Latex with average size of 0.14 µm (*Figure 7a*) shows substantial damage to the particles, whereas the biggest particles of 0.32 µm average diameter show hardly any damage (*Figure 7c*). The start of damage can be seen in the intermediate case of 0.25 µm particles (*Figure 7b*). *Figure 8* shows radiolysis effects in latex particles of average size of 0.25 µm with increasing levels of oligomeric surfactant, all after electron exposures of 100–120 kC m^{-2}. The effect of increasing surfactant concentration on the extent of damage is clear from these images. Note that the damage to the latex with 10% surfactant is limited, and is concentrated close to the perimeter of the particles. This is seen most clearly in the four particles on the left-hand side of *Figure 8c*. In the 20% surfactant, however, the damage is much more extensive, and it extends all the way close to the centre of the particles. Only a small 'kernel' at the centre seems undamaged. This residual kernel is not always exactly at the centre of the particles, excluding the possibility of damage obscured by mass–thickness effects. This indicates that at very high surfactant concentration, surfactant is present in the bulk of the latex. This renders the bulk of the polymer hydrophilic, leading to extensive electron beam radiation damage.

Differential scanning calorimetry

D.s.c. analyses were made on latex samples that had been dried at room temperature. Each sample was scanned twice. The T_gs measured for each scan are given in *Table 2*. A typical d.s.c. thermogram is shown in *Figure 9*. Latex samples that were prepared with ⩾10% non-ionic oligomeric surfactant have an endotherm that corresponds to the melting of the poly(ethylene oxide) (PEO) portion of the oligomeric surfactant between 20°C and 40°C. This endotherm is not seen in the second scan if the sample is rapidly cooled after the first run. However,

Table 2 Effect of stabilizer level and particle size on T_g

Volpo-20 level (%)	Particle diameter (μm)	T_g (°C) First scan	T_g (°C) Second scan
0	0.25	100	100
6	0.17	102	86
6	0.25	100	88
6	0.32	98	87
10	0.25	93	80
12	0.24	89	75

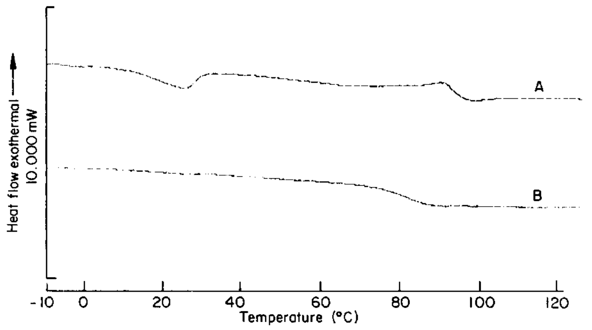

Figure 9 First scan (A) and second scan (B) d.s.c. thermograms of latex solid specimens made with 10% non-ionic oligomeric surfactant. The sample was rapidly cooled between scans

if the sample is slowly cooled (10°C min^{-1}), the endotherm is present at a slightly higher temperature and slightly reduced in intensity. On the first scan, the T_g transitions were complicated by sample relaxation effects. On the second scan clearly defined transitions were obtained.

DISCUSSION

It was quite obvious from the onset of the project that true direct visualization of a surfactant-rich layer on the particle surface is not possible because of contrast and resolution limitations. However, we hoped to get indications to its presence from the way it affects microstructure, and from the way it affects specimen–electron beam interactions. As it turned out, the presence of an oligomeric surfactant-rich layer was indicated by the way the latex particles arranged themselves in the vitreous ice matrix of vitrified specimens. At low surfactant concentrations, electron beam radiation damage in hexagonal ice specimens was observed mostly close to the surface of the latex particles, indicating the surfactant was close to the polymer–water interface as expected. But through the way the oligomeric surfactant affected electron beam radiation damage at very high surfactant concentrations, it was apparent that those latex particles had become hydrophilic, indicating some surfactant presence in their bulk.

Cryo-TEM of vitreous specimens has given us clear direct images of the latex in its preserved native state. The particles formed either networks or well-ordered two-dimensional arrays, features absent in samples of ordinary PS latex. This provides a very strong indication of particle surface modification by the introduction of an oligomeric surfactant into the polymerization formulation.

The presence of a few per cent of water even in a crosslinking-type polymer particle is sufficient to modify its behaviour in an electron beam radiation damage experiment[26]. This is a result of the generation of free radicals by water (ice) radiolysis, and their interaction with the otherwise stable polymer. Our experiments indicate that when oligomeric surfactant concentrations were 6% or higher, the latex particle, especially its outer regions, was very radiation-sensitive, exhibiting typical radiolotyic behaviour of hydrophilic polymers. The only explanation for this observation is induction of hydrophilicity in the bulk of the particles. These effects were more prominent at very high oligomeric surfactant concentrations, indicating more hydrophilic moieties in the polymer bulk. This conclusion is also supported by our d.s.c. work.

Initial T_g values are not significantly depressed until oligomeric surfactant levels are 10% or more. Thus, the surfactant in these samples is phase segregated, most likely located at the particle surface (polymer–water interface in latex). Samples with higher levels of surfactant have depressed first-scan T_g values. This observation indicates that some oligomeric surfactant is intermixed or trapped within the PS particle. However, the observation of the PEO melting transition supports the idea that the polymer and surfactant are still primarily in separate domains. That the second scan lowers T_g values for all samples containing the oligomeric surfactant, shows that under conditions where chain mobility is possible, some mixing can occur. Particle size appears to have no effect for a given surfactant level.

Mixing PS and the oligomeric surfactant by drying down a solution of these materials in methylene chloride gives a polymer sample which has a T_g of 60–65°C, even for 6% surfactant levels. Mixing PS with PEO, molecular weight 1000, in solution gave samples with T_g values above 90°C. Oleyl alcohol and PS mixtures, prepared from solution, had depressed T_g values similar to those obtained with PS–stabilizer mixtures prepared from solution. Thus, the oleyl portion of the stabilizer readily blends with PS while the ethoxylate chain portion does not readily mix with PS.

The difference in the T_gs of latex polymers prepared with and without non-ionic stabilizers has been studied by Ottewill and Satgurunathan[27]. They found that the latexes prepared with grafted non-ionic stabilizers have depressed T_g values. This suggests that some of the surfactant is mixed with the latex polymer within the particles. However, their samples were dried at 60°C for several days, so some mixing may have occurred during drying.

The T_g values of the first scans are higher than the values obtained from the second scan except for the surfactant-free latex. As mentioned above, this suggests that some mixing of the surfactant and PS occurs after the sample is heated above its T_g.

In conclusion, electron microscopy gives a clear indication that a surfactant-rich layer exists in all latex samples examined. At very high surfactant concentration (>6%, not typically used in commercial latexes), electron beam radiation damage reveals the presence of a surfactant gradient from the particle surface to its core. These results are in good agreement with our d.s.c. data.

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REFERENCES

1 Roe, C. P. in 'Polymer Colloids' (Ed. R. M. Fitch), Plenum Press, New York, 1971, p. 139
2 Roe, C. P. *J. Colloid Interface Sci.* 1971, **37**, 93
3 Woo, J. T. K., Marcinko, R. M. and Ting, V. *Proc. ACS Polym. Mater. Sci. Eng.* 1983, **49**, 20
4 Dannals, L. E. and Peaker, C. R. *Fr. Pat. 1 521 995*, 1968
5 Bahadur, D. *Surf. Sci. Technol.* 1985, **8**, 126
6 Barrette, K. E. J. *Br. Polym. J.* 1973, **5**, 259
7 Dawkins, J. V. and Grahams, T. *Polymer* 1979, **20**, 599
8 Hsieh, B. R., Litt, M. H., Demopolis, T. N. and Krieger, I. M. *Am. Chem. Soc. Div. Polym. Chem. Prepr.* 1986, **27**, 122
9 Tsuda, Y., Nochimori, S., Kimura, S. and Abe, M. *Jpn. Kokai Tokyo Koho JP 60 217 211*, 1985
10 Jain, M. and Piirma, L. *Proc. ACS Div. Polym. Mater. Sci. Eng.* 1986, **54**, 358
11 Noda, I. *Nature* 1991, **350**, 143
12 Noda, I. *US Pat. 4 735 843*, 1988
13 Noda, I. and Hager, D. F. *US Pat. 4 785 030*, 1988
14 Noda, I. and Hager, D. F. *US Pat. 4 835 211*, 1989
15 Sharma, A. K., Millich, F. and Hellmuth, E. W. *J. Appl. Polym. Sci.* 1981, **26**, 2205
16 Gagnon, D. R. and McCarthy, T. J. *J. Appl. Polym. Sci.* 1984, **29**, 4335
17 Talmon, Y., Narkis, M. and Silverstein, M. *J. Electron Microsc. Technique* 1985, **2**, 589
18 Narkis, M., Talmon, Y. and Silverstein, M. *Polymer* 1985, **26**, 1359
19 Smith, W. V. *J. Am. Chem. Soc.* 1948, **70**, 3696
20 Bellare, J. R., Davis, H. T., Scriven, L. E. and Talmon, Y. *J. Electron Microsc. Technique* 1988, **10**, 87
21 Talmon, Y. and Miller, W. G. *J. Colloid Interface Sci.* 1978, **67**, 284
22 Talmon, Y., Adrian, M. and Dubochet, J. *J. Microsc.* 1986, **141**, 375
23 Talmon, Y. *Colloids Surf.* 1986, **19**, 237
24 Talmon, Y. *Ultramicroscopy* 1984, **14**, 305
25 Talmon, Y. in 'Cryotechniques in Biological Electron Microscopy' (Eds R. A. Steinbrecht and K. Zierold), Springer-Verlag, Berlin, 1987, Ch. 3
26 Talmon, Y. in 'Advances in Interpenetrating Polymer Networks' (Eds D. Klempner and K. C. Frisch), Vol. 2, Technomic Publishing Co., Basle, 1990, pp. 141–156
27 Ottewill, R. F. and Satgurunathan, R. *Colloid Polym. Sci.* 1987, **285**, 845