Latex Preparation and Stabilization by Hydrophobically Modified Hydroxyethyl Celluloses

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Synopsis

Hydrophobically modified hydroxyethyl celluloses (HMHEC) are derivatives of water-soluble hydroxyethyl-ethers of cellulose. Because these amphiphilic molecules are known to adsorb strongly on water–oil interfaces, they were tested as nonionic surfactants and stabilizers in emulsion polymerization. Styrene and methyl acrylate were used as water-insoluble and slightly water-soluble monomers, respectively. In situ nucleation, seed latex polymerization, and postpolymerization addition of HMHEC were examined. The main difficulty with the HMHEC materials is their bridging effect, which enhances aggregation. However, these nonionic materials impart pronounced stability to latices against electrolytes. This property can be achieved also by postaddition of the HMHEC to a preformed emulsion.

INTRODUCTION

Hydrophobically modified hydroxyethyl celluloses (HMHEC) are amphiphilic macromolecules containing hydrophilic water-soluble back bones and hydrophobic water-insoluble side chains. They are produced from the water-soluble hydroxyethyl ethers of cellulose[1] by substituting some of the hydroxyl groups by long-chain alkyl groups.

The alkyl side-chain length and the degree of hydrophobic modification can vary. We have examined mainly HMHECs containing 1% (by weight) of C_{16} side chains.

Previous work with these materials in our laboratories has shown that the amphiphilic molecules of HMHEC adsorb strongly on water–air and water–oil interfaces.[2,4] It was suggested, therefore, that HMHECs be used in emulsion polymerization as nonionic surfactants, as well as postaddition latex stabilizers.

The main forces involved in polymer colloids stabilization or destabilization are:

1. Those arising from the surface electrical potential and counter-ion cloud, that is, electrostatic forces, which are strong repulsive forces, thus contributing to the stability of the dispersed system. These forces are sensitive to the ionic nature and type of electrolytes present in the system. As a

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result, latices stabilized by ionic surfactants are easily coagulated by the addition of electrolytes to the system.

2. Those involving electromagnetic fluctuations, i.e., the van der Waals attractive forces.

3. Those contributing to the "steric stabilization" by formation of a "protective barrier," usually by adsorbed molecules in the interfacial region of the colloidal particles. These "barriers" prevent the latex particles from approaching to a critical distance at which they coagulate.

4. Solvation forces which arise from the rearrangement of molecules in the interfacial region.

Detailed and comprehensive discussions of the basis of steric stabilization can be found elsewhere.[5,6]

It is hence assumed that amphiphilic macromolecules, like HMHEC, which are adsorbed on the surface of colloidal particles, could therefore confer stability to the colloidal dispersion at electrolyte concentrations high enough to cause coagulation in the absence of such polymers.

In addition to providing steric stabilization to latex systems, adsorbed macromolecules may cause an opposite effect of inducing instability in dispersed systems. This phenomenon, referred to as the "bridging effect," occurs under conditions where the particle surfaces are incompletely covered by the protective polymer if its molecular weight is sufficiently high. The macromolecule can, under such conditions, attach itself to the surfaces of two particles and span the distance across the stabilizing energy barrier.

Another hypothesis regarding the effect of the macromolecules on the instability of the colloidal systems, suggests that even the nonadsorbed, solvated, macromolecules may cause instability by restricting the volume available to the colloidal particles.[7]

It was the purpose of this work to test the effect of the amphiphilic HMHEC on the formation and stabilization of polymer latices.

EXPERIMENTAL

Materials

Hydrophobically modified hydroxyethyl cellulose (HMHEC) were made and supplied to us by Hercules Chemical Incorporated (Wilmington, DE). They all contained 1% of C_{16} hydrophobic substitution. The main difference among the three materials tested was the molecular weight:

Code	$\overline{M}$
X-300	~ 300,000
X-100	~ 100,000
X-50	~ 50,000

A simple calculation based on the above data, shows that the X-300 contains 15 hydrophobic side chains per HEC macromolecule, the X-100 has 5–6, and the X-50 has 2–3.

Aqueous solutions of the HMHEC materials were prepared by slow addition of the powdered material to water and stirring for a few hours or overnight. A solution containing 0.5% (w/w) of X-300 in water was gel-like and difficult to work with. The X-100 produced a 0.5% (w/w) low-viscosity solution, whereas X-50 produced a 1% (w/w) low-viscosity solution.

The styrene used was 99% pure (Aldrich). It was distilled under vacuum at 65–70°C and stored at −18°C. The methyl acrylate was 99% pure (Aldrich), and was distilled under vacuum at 40°C, and stored at 4°C.

Potassium persulfate ($K_2S_2O_8$) was the initiator, and sodium dodecyl sulfate, the ionic surfactant in some of the polymerizations. Distilled water was used in all the experiments.

Apparatus and Procedures

All the emulsion polymerizations were carried out in a 500 mL three-neck flask equipped with a mechanical stirrer, condenser, and nitrogen inlet. The temperature was controlled by a thermostatted bath.

For the in situ nucleation polymerizations the aqueous phase (water and surfactant solution) was first thoroughly degassed and purged with nitrogen. The monomer was then added and stirred for 30 min or until emulsified. The $K_2S_2O_8$ was added and the mixture was heated to the reaction temperature. Nitrogen was bubbled slowly through the reaction medium during the entire time of the reaction.

The methylacrylate polymerizations were carried out at 55–60°C over 2–3 h, whereas those involving styrene were at 65–70°C for 5–6 h.

When "seed" latex polymerizations were performed the monomer was first added to the "seed" latex and mixed overnight to ensure that swelling equilibrium of the polymer particles by the monomer was reached. The degassed aqueous phase and the initiator were then added and the reaction proceeded as described.

A detailed description of the emulsions' compositions is given in the Appendix.

The particle size was measured, wherever possible, by the HOTS technique[8] or by electron microscopy. Higher Order Tyndall Spectra (HOTS) are exhibited by monodisperse colloids when the particle size is on the order of the wavelength of visible light. Under these circumstances, the angular dependence of the scattering intensity is highly wavelength-dependent such that beautiful colors are observed. The angular positions of the red bands are used to obtain a measure of the particle size to an accuracy on the order of a few percent when the refractive index is known. The electron micrographs were taken of samples made by depositing a dilute latex drop on "Formvar" and carbon-coated grids and evaporating the water. A Hitachi HU-200F electron microscope was used at 200 kV.

RESULTS AND DISCUSSION

Latex Formation in Presence of HMHEC

Three main methods were used to test the various HMHEC materials as stabilizers in emulsion polymerization: (a) In situ nucleation and growth in the presence of HMHEC as a surfactant and stabilizer. (b) Seed latex polymerization. (c) In situ nucleation in presence of a combination of HMHEC and an ionic surfactant (SDS).

The latex preparation techniques, mentioned above, were applied to two types of monomers: a relatively water-soluble and water-insoluble one, methyl acrylate (MA) and styrene (St), respectively. The main differences between

the two monomers in these systems is in the nucleation step. The MA nucleates in the water phase, whereas the styrene is assumed to nucleate primarily inside the polymeric micelles.

Surface coverage determination. In order to understand the factors governing colloidal stability in these systems, it is important to estimate or establish the average area per molecule. We have estimated the area per X-100 molecule to be 5000 $\mathring{A}^2$ based on the stable portion of emulsion MA-3 (see Appendix for description of emulsions), as follows:

S - total surface of latex particles
V - total volume of latex particles
W - total weight of latex particles = 8 g
r - radius of particles
N - number of molecules of HMHEC
n - number of moles of HMHEC = 5.0×10^{-6}
N_A - Avogadro's number
A - surface area per molecule.

$$\frac{S}{V} = \frac{4\pi r^2}{4/3\pi r^3} = \frac{3}{r} \tag{1}$$

$$\frac{S}{W} \simeq \frac{S}{V} = \frac{3}{r} \qquad S = W \cdot \frac{3}{r} \tag{2}$$

$$A = \frac{S}{N} = \frac{3W}{rnN_A} = 5 \cdot 10^{-13} \frac{cm^2}{molec.} = 5000 \, \mathring{A}^2/molec. \tag{3}$$

This value seemed to be a reasonable one, based on previous work done in this laboratory,[4] and we have used it throughout our work.

In situ nucleation vs. "seed" latex polymerization. Comparing the results from two techniques suggests that the best latices were made by the "seed" polymerization technique. In these polymerizations the number of particles was known initially and was kept constant while the reaction proceeded. The final surface area of the particles was thus known. It was possible, therefore, to supply the exact amount of HMHEC molecules needed for a *complete coverage* of the newly formed surface.

Such emulsions are MA-7 and St-4 (see Appendix). In both cases the seed was a stable latex of known composition and size, and the particles were swollen by sufficient monomer to double the particle weight (or volume). It is important to note that both "seed" latices had minor amounts of ionic surfactant on their surfaces.

An important and interesting case is that of "seeded" latex MA-15 based on MA-12, which was surfactant free (free from HMHEC or ionic surfactants). When the MS-12 particles were swollen with an amount of MA monomer to

double their volume, immediate coagulation occurred. When, on the other hand, sufficient HMHEC was supplied to the system *prior* to the addition of the monomor, a stable colloid was formed, resulting in MA-15 upon polymerization. The HMHEC molecules have probably been adsorbed onto the PMA seed particles and provided the necessary stabilization against coagulation upon the swelling with MA monomer. By providing the HMHEC stabilizer prior to the addition of MA monomer, the protective barrier formed might slow down the rate of diffusion of the monomer into the particles.[4]

It is important to note that all the experiments involving the high molecular weight X-300 HMHEC failed, resulting in coagulated partly polymerized latices.

Based on our results, it is suggested that the main difficulty with the HMHEC materials lies in the bridging effect which induces aggregation of the particles. It seems that when the availability of the HMHEC molecules is less than that necessary for complete surface coverage, a macromolecule may be adsorbed on more than one particle simultaneously, behaving like a connecting "rubber band" and causing aggregation of the particles. When the availability of the HMHEC molecules exceeds that necessary for complete coverage of the particles, the protective macromolecules will each be only partially adsorbed, sticking out of the surface and enabling the formation of interparticle "bridging" via hydrophobic interactions, resulting again in aggregation of particles. Because no coalescence of the particles takes place, the aggregation is reversible, and the colloid may be redispersed by high-shear forces. Apparently, there exists only a narrow region of complete surface coverage at which aggregation does not occur and the latex is stable.

It is difficult to reach the stable region by in situ nucleation, since the number of particles, and hence the total surface area, is uncontrolled. "Seeded" latex polymerization produces stable emulsions because the number of particles is well defined and controlled. MA-9 and St-4 are two examples of aggregated colloids which were re-emulsifiable by ultrasonic vibrations, resulting in stable latices.

Latex formation via nucleation in situ in the presence of ionic surfactant and HMHEC. Several experiments were carried out in the presence of sodium dodecyl sulfate (SDS) as an ionic cosurfactant, combined with the nonionic HMHEC. Stable latices were produced by this method (i.e., St-11 and MA-18). When the amount of HMHEC was increased above that necessary to form a stable emulsion, aggregates and precipitates formed in the reaction mixtures. This suggests, again, the formation of flocculates due to the bridging caused by an excess of HMHEC in the system.

Stability of the Latices

Stability against electrolyte addition. Common polymeric emulsions prepared with ionic surfactant are usually sensitive to electrolytes and are more or less easily coagulated by them, depending upon the counterion valence according to the DLVO theory, at least approximately.[9] One of the potential advantages of the nonionic HMHEC molecules is that they hold the promise of acting as good steric stabilizers.

A 0.01 M La(NO$_3$)$_3$ solution was used as the electrolyte medium in which the stability was tested. La(NO$_3$)$_3$ produces electrolyte solutions of high ionic strength because the cation has a charge of $+3$. This is highly destabilizing for electronegative colloids, such as ours.

Three types of latices were tested:

1. A stable latex made by "seed" or in situ nucleation polymerization in which the HMHEC was present during the polymerization reaction. The HMHEC molecules in these systems are adsorbed physically, although some chemical bonds, resulting from chain-transfer grafting by the propagating free-radicals, may also exist. These emulsions were MA-7 and MA-9-DIS.

2. A stable latex made by "seed" polymerization, but *without any HMHEC*. As mentioned in a previous section, the latices obtain their stability from minor amounts of anionic surfactants present, as well as from the ionic surface groups produced by the K$_2$S$_2$O$_8$ initiator. This emulsion was MA-7-CF.

3. An *HMHEC-free* emulsion (MA-7-CF), to which HMHEC was *postadded* to supply a complete coverage of the particle surfaces. This emulsion was MA-7-CF + (X-100).

Two drops of a latex were added to 10 mL of 0.01 M La(NO$_3$)$_3$ solution while stirring.

The HMHEC-free latex formed an immediate thick precipitation, leaving a clear serum solution. The other three, including the one containing postadded HMHEC, remained completely dispersed and stable.

The same test was performed with St-10, which is an ionically stabilized latex, and St-11, which is stabilized with a combination of ionic surfactant and HMHEC. The first formed an immediate thick precipitate, leaving a clear serum solution, whereas the second remained stable and dispersed.

These results point out two major properties of the HMHEC. One is the excellent stability it imparts to latices against electrolytic coagulation. The second is the ability to adsorb the HMHEC macromolecules by postaddition, thereby producing latices which are stabilized against electrolyte addition. It should be stressed that 0.010 M La^{+3} constitutes an extremely rigorous test of electrocratic stability.

Stability of uncoated latices against HMHEC addition. It is possible to stabilize a latex by postaddition of the HMHEC. It was, therefore, of great importance to examine the effect of added HMHEC on the stable, uncoated latices. First, 1, 4, and 8 g of a 1% solution of X-100 were added to 10 g samples of MA-12. A fine precipitate was immediately formed in the first, whereas the other two remained stable. After stirring for several hours, the first completely coagulated, a slight coagulum developed in the second, but the third remained completely stable.

A similar test with St-4-CF gave somewhat similar results: 2, 6, 10, and 20 g of a (X-100, 1%) solution were added to 10 g of St-4-CF. Aggregates appeared in all the samples, being coarse in the HMHEC-poor sample and getting finer and finer as the level of HMHEC was increased.

Although these are kinetically determined phenomena and, as such, are probably affected by rates of mixing and agitation, nevertheless these results confirm our assumption that the HMHEC macromolecules have a strong bridging effect, causing coagulation and flocculation to occur.
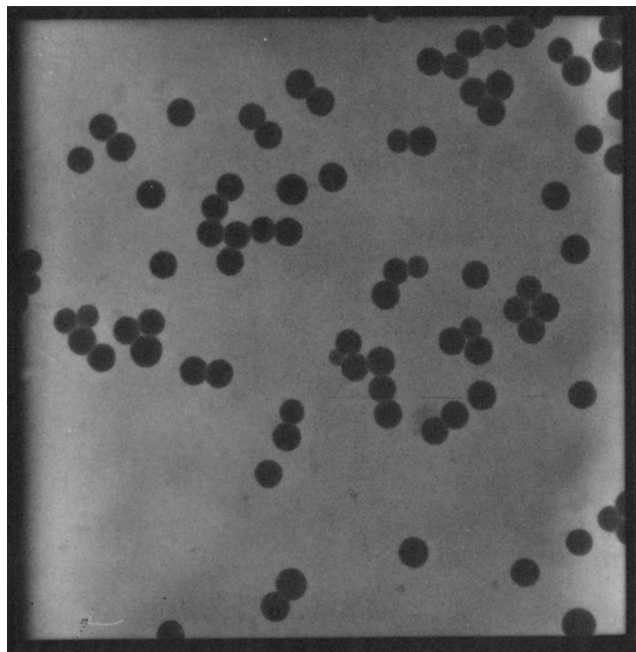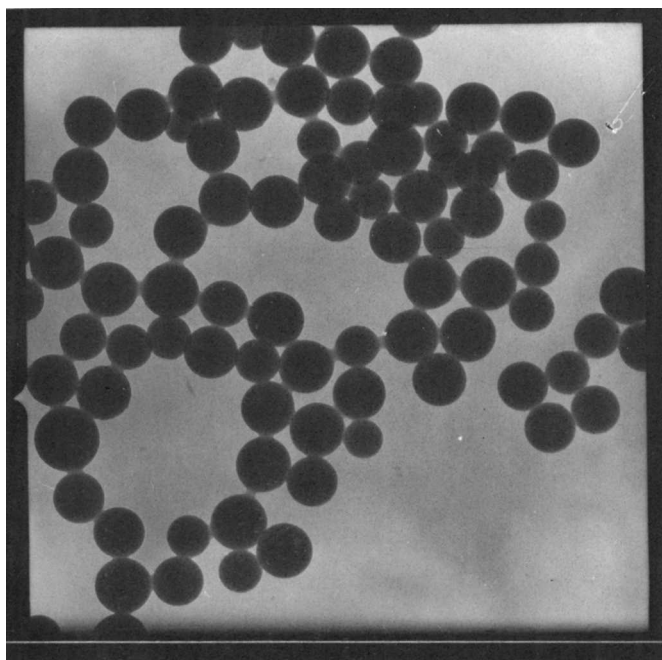
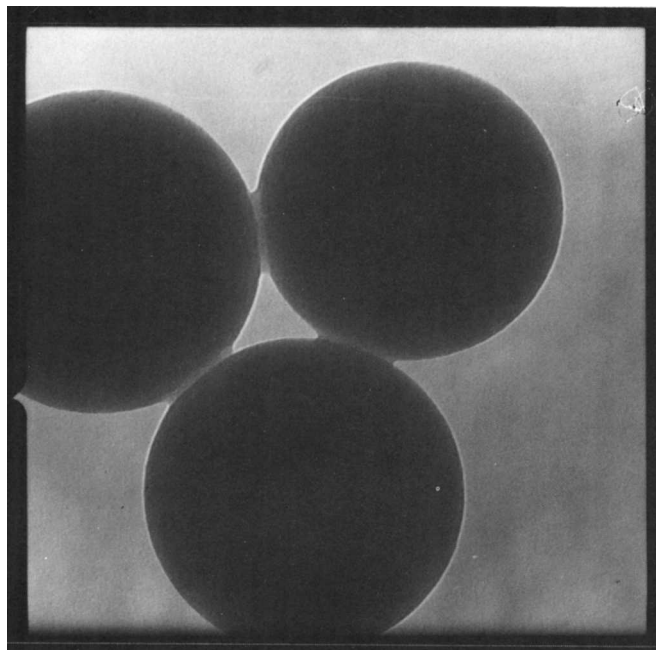Fig. 1. Seed latex PS-B1, ×20,000.

Fig. 2. Seeded latex St-4-CF, ×20,000.

Fig. 3.   Seeded latex St-4-CF, ×130,000.
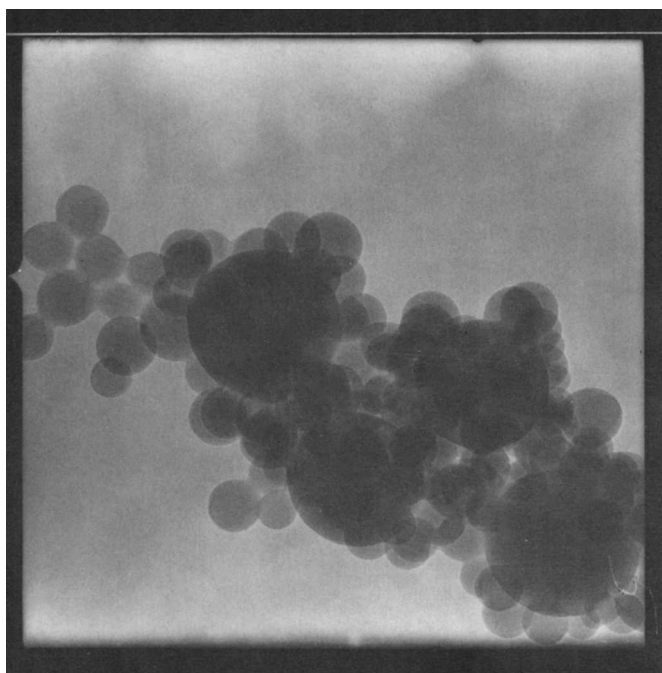

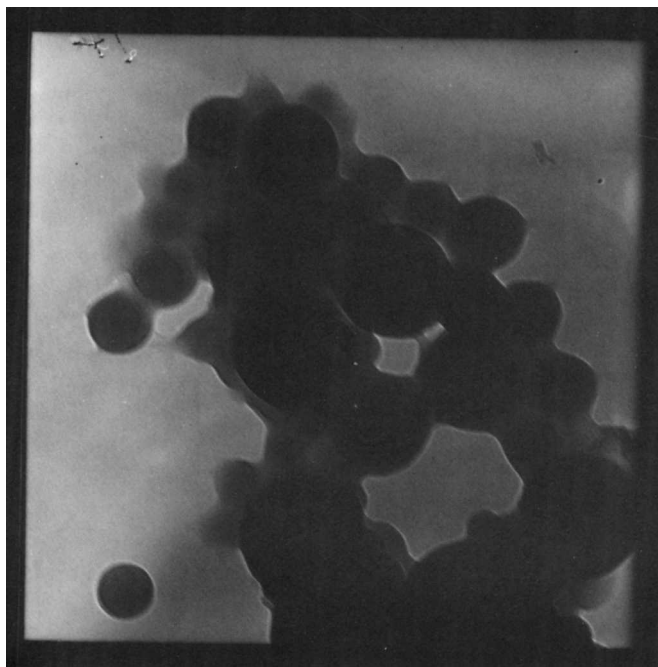Fig. 4.   Seeded latex St-4, showing aggregation of particles, ×70,000.

Fig. 5. Seeded latex St-4, showing aggregation of particles, ×55,000.
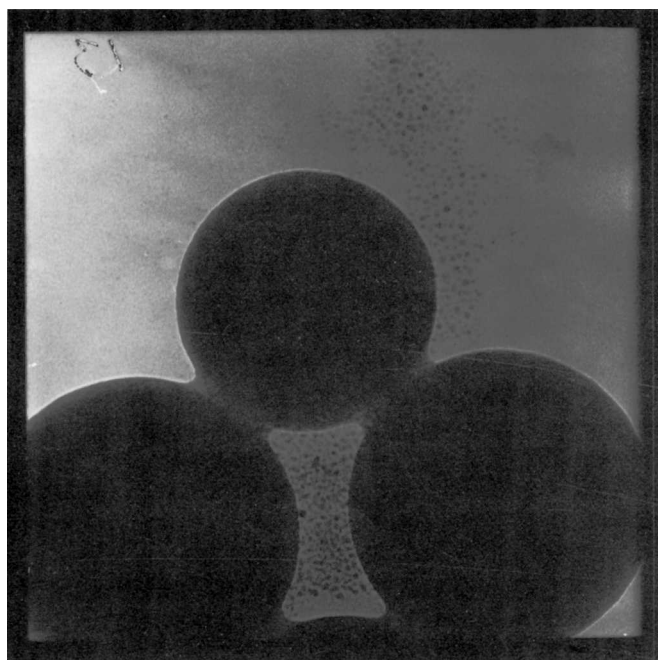

Fig. 6. Seeded latex St-4-CF with postadded HMHEC. Micellar formations are visible, ×130,000.

Electron Microscopy

Several of the polystyrene latices were examined by electron microscopy: (a) PS-B1: the "seed" latex for the St-4 and St-4-CF emulsions. (b) St-4-CF: HMHEC free. (c) St-4: HMHEC stabilizer. (d) St-4-CF + (X-100): HMHEC-free colloid to which HMHEC was postadded.

Figure 1 shows the PS-B1 "seeds" having a narrow-size dispersity and a particle diameter of 1900 Å. Figures 2 and 3 show the "seeded" particles of St-4-CF having a relatively uniform size distribution and a particle size of 3500 ±150 Å. The uniform size and the particle dimensions point to the occurrence of a truly "seeded" polymerization, without the formation of new second-generation particles.

Figures 4 and 5 are micrographs of the HMHEC-containing St-4 emulsion. The aggregates of particles are clearly visible; this morphology was found over the entire grid. In Figure 5 the particles seem to be embedded in some material, and fibrouslike "bridges" can be recognized.

In contrast to the aggregations noted in the St-4 latex samples, no agglomerated material is detected in the St-4-CF to which HMHEC was postadded. The postadded HMHEC seems, actually, to form a protective coat which stabilizes the latex particles and produces a system which is better dispersed than the HMHEC-free St-4-CF latex. An interesting phenomenon is seen in Figure 6: whenever postcoated particles are forced together during sample preparation, a filmy region containing very fine particles is observed. This fact, as well as the shape and size—about 50 Å—of these particles, suggest that they are micelles of HMHEC macromolecules, which have become desorbed from the surface.

CONCLUSIONS

1. The most pronounced property of the HMHEC-stabilized colloids is their stability against electrolytes. This effect is observed in systems where the HMHEC is incorporated during the polymerization reaction or is postadded after the reaction. It seems that the postaddition is favorable, as the required surface coverage can be controlled and bridging effects can thus be avoided.

2. The most suitable system, where the HMHEC materials are used, is the "seed" latex polymerization in which the number of particles, and hence the total surface area, is known and controlled. By combining ionic surfactant and HMHEC, further stabilization is achieved, resulting in good colloids which are stabilized against the bridging effect, as well as against the addition of electrolyte.

3. The disadvantage of the bridging effect causing aggregation can be turned to advantage and a useful property as a means to form controlled aggregates. Commercially, there is wide interest in methods of formation of aggregates of definite and controlled size. As shown in this work, the HMHEC causes formation of aggregates generally as a function of the surface coverage. Hence, by adjusting the proper amount of HMHEC in the system, desirable aggregate morphologies could be obtained.

APPENDIX

Description of Various Emulsions[a]

Code	"Seed" Type	Amount	Water	Momomer MA	St	HMHEC X-100	X-50	SDS	K$_2$S$_2$O$_8$	Emulsion solids %	Remarks
MA-3			180	20		0.50			0.04	3–4	Latex plus coagulum ($r = 0.24$ μm)
MA-7	Em-P[b]	60	130	10		0.90			0.02	10.2	Good latex.
MA-7-CF	Em-P	60	130	10		—	—		0.02	10.2	HMHEC-free. Good latex.
MA-9			180	20		1.80			0.04	7	Fine precipitate of all the solids. Re-emulsification by ultrasonication results in a good latex.
MA-12			180	20		—	—		0.04	7.5	Good HMHEC-free latex, includes some precipitate. Seed latex.
MA-15	MA-12	66	80	5		0.80			0.01	5.5	Good latex, little precipitate.
MA-18			180	20			0.40	0.10	0.06	9.7	Good latex.
St-4	PS-B1[c]	46.2	90		12	0.90			0.024	10.1	Fine dispersion of PS particles. Ultrasonication resulted in a good latex (i.e., St-4-DIS).
St-4-CF	PS-B1	46.2	90		12	—	—		0.12	7.1	Good latex. Some precipitate around the stirrer.
St-10			180	20		—	—	0.10	0.06	9.5	Good latex.
St-11			180	20			0.40	0.10	0.06	9.7	Good latex. Slight precipitate.

[a] All values are in grams.

[b] Em-P is a crosslinked MA emulsion containing 17% solids, having a particle radius of 0.18 μm.

[c] PS-B1 is a PS emulsion containing 6.5% solids and having a particle radius of 0.095 μm.

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