

Surfactants in Heterophase Polymerization: A Study of Film Formation Using Atomic Force Microscopy

S. LAM,¹ A. C. HELLGREN,¹ M. SJÖBERG,¹ K. HOLMBERG,¹ H. A. S. SCHOONBROOD,² M. J. UNZUÉ,² J. M. ASUA,² K. TAUER,³ D. C. SHERRINGTON,⁴ A. MONTOYA GONI⁴

¹ Institute for Surface Chemistry, P.O. Box 5607, SE-114 86 Stockholm, Sweden

² Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastian, Spain

³ Max Planck Institut für Kolloid- und Grenzflächenforschung, Kantstrasse 55, D-121 69 Berlin, Germany

⁴ Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

Received 31 January 1997; accepted 3 April 1997

ABSTRACT: Film formation of three different latices was studied using atomic force microscopy. The latices were made from a mixture of butyl acrylate, styrene, and acrylic acid using either a polymerizable or an unreactive anionic surfactant as an emulsifier. Sodium 11-crotonoyloxyundecan-1-ylsulfate and sodium 3-(sulfopropyl)tetradecylmaleate were used as a reactive surfactant and the unreactive surfactant was sodium dodecylsulfate (SDS). The conventional surfactant was found to migrate to the surface of the latex film to a much greater extent than did the reactive surfactants; however, also, the latter were incompletely anchored to the particle. The maleate surfactant was bound to a higher degree than was the crotonate, a finding which is in line with the relative reactivities of the two surfactants. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 187–198, 1997

Key words: reactive surfactant; polymerizable surfactant; atomic force microscopy; latex; film formation

INTRODUCTION

Polymerizable surfactants are of interest as emulsifiers in emulsion and suspension polymerization.^{1,2} By using surfactants that become covalently attached to the latex particle, many of the problems encountered with conventional emulsifiers can be avoided or at least minimized. Positive

effects may be obtained both on the latex as such and on properties of the dried film.^{3,4}

The surfactant-related problems in latices, as well as in many other dispersions, arise from the fact that physically adsorbed surfactants may desorb into the bulk aqueous phase and that the equilibrium between the surface and bulk is governed by factors such as particle concentration, temperature, electrolyte concentration, and pH, all of which may be changed during storage and use of the product. Since a certain surface concentration of the surfactant is needed to give proper emulsion stabilization, a change in the adsorption–desorption equilibrium may severely affect the rheology and stability of the dispersed system.

Correspondence to: K. Holmberg.

Contract grant sponsor: European Union; contract grant number: CHRX CT 930159.

Contract grant sponsor: Swedish Natural Science Research Council; contract grant number: ERB4001GT953910.

Journal of Applied Polymer Science, Vol. 66, 187–198 (1997)

© 1997 John Wiley & Sons, Inc.

CCC 0021-8995/97/010187-12

Formulations containing a latex in combination with another dispersion, such as a pigment slurry, constitute a particular problem from a stability point of view. The physically adsorbed latex surfactant may have a higher affinity for the pigment than for the latex, a situation which often leads to latex instability. In addition, most pigments are dispersed with a dispersant which is different from the surfactant used as a latex emulsifier. The two surfactants will then compete for both surfaces, the latex and the pigment, and the surface composition and coverage obtained in the equilibrium situation may be very different from that of the two components before mixing.^{5,6} This type of competitive adsorption may drastically affect the rheology and stability of a formulation.

The presence of a surfactant in the dried latex film may also impair film properties. During drying, the surfactant is adsorbed on the latex particles. As the particles coalesce during the annealing process, the surfactant migrates out of the bulk phase and concentrates at the substrate–film and film–air interfaces. It has been shown that surfactant molecules preferably go to the film–air interface, where they align with their hydrophobic tails pointing toward the air. Calculations from ESCA spectra show that a lacquer film containing 1% surfactant may have an average surface surfactant concentration of around 50%.⁷ Such a high concentration of a nonchemically incorporated, water-soluble component at the film surface will affect the adhesion properties and the water resistance of the film adversely.

In the present investigation, atomic force microscopy (AFM) was used to study the film formation of latices prepared with two different types of polymerizable surfactants. The results obtained are compared with those obtained with the commonly used surfactant, sodium dodecylsulfate (SDS). The degree of the surfactant migration to the surface was estimated for the three surfactants. The investigation is part of a broad project titled “Reactive Surfactants for Heterophase Polymerization of High Performance Polymers,” sponsored by the European Union within its Human Capital and Mobility program. Other publications deal with kindred aspects of the project.^{8–13}

EXPERIMENTAL

Surfactants

Two reactive surfactants were used in the study: sodium 11-crotonyloxyundecan-1-ylsulfate, ab-

breivated “crotonate,” and sodium 3-(sulfopropyl)-tetradecylmaleate, abbreviated “maleate.” Detailed synthesis of the crotonate and maleate were described elsewhere.^{8,9} Sodium dodecylsulfate (SDS) was from BDH, Germany (Biochemical Product No. 44244, specially pure).

Surfactant Characterization

The critical micelle concentration (CMC) was determined by the Du Nouy ring method using a KSV Sigma 70 tensiometer and by applying the Zimeda Waters correction. A concentrated surfactant solution was titrated into a vessel containing deionized water and the surface tension was measured at various dilutions. The CMC was obtained from the surface tension vs. the log(concentration) curve.

Adsorption of the surfactant on the latex was measured using a surfactant-free latex based on butyl acrylate (49.5%), styrene (49.5%), and acrylic acid (1.0%) having a mean diameter of 116 nm. The method, developed by Paxton,¹⁴ takes advantage of the fact that the latex particles are not surface-active. The surfactant solution was titrated into a 9.8 wt % latex suspension while monitoring the reduction in surface tension. Using the surface tension vs. log(concentration) curve from the determination of CMC for the specific surfactant as the calibration curve, the equilibrium bulk surfactant concentration, and, hence, the adsorption isotherm, could be calculated.

Latices

Latices were made by emulsion terpolymerization of butyl acrylate (49.5%), styrene (49.5%), and acrylic acid (1.0%) using the crotonate, the maleate, or SDS as the surfactant. The amount of the surfactant used was 2% (w/w) based on total amount of the monomer. Butyl acrylate and styrene were distilled before use and then stored at -18°C . Acrylic acid was stabilized with 10 ppm *p*-methoxyphenol. Polymerizations were initiated by potassium persulfate and the emulsions were neutralized with sodium hydrogen carbonate. Samples were taken during the polymerization process and conversion of the main monomers was determined by gravimetry. Gas chromatography was used for analysis of the ratio between the residual monomers. The copolymer composition was calculated from the values of monomer conversion and the ratio of the residual monomers. The solids content of the latices was 50–55%.

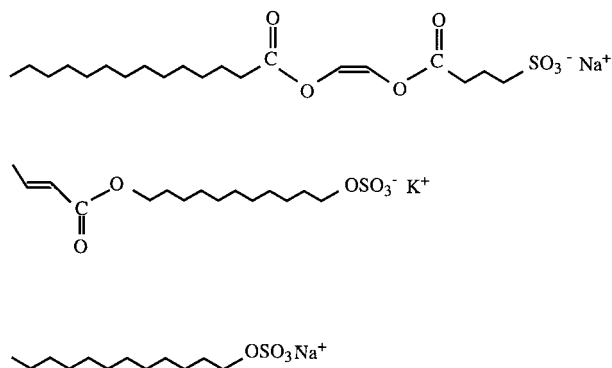


Figure 1 Surfactants used as latex stabilizers: (top) maleate; (middle) crotonate; and (bottom) SDS.

More details of the latex preparation can be found elsewhere.^{8,10,15} The final degree of incorporation of the maleate and the crotonate was 64 and 15–20%, respectively, as determined by two-phase titration of the unreacted surfactant recovered by serum displacement. The latex particle size was determined by light scattering, using a Malvern System 4700c.

Dialysis of Latices

To remove excess salt from the latices while maintaining the surfactant adsorbed at the particle surface, dialysis was performed using a Spectrapor 6.4 mm diameter membrane with 12–14 k cutoff. Approximately 8 mL of the latex was dialyzed at a time. The dialysate was changed 10 times.

The latices stabilized with the crotonate or the maleate surfactant, which adsorb strongly, were dialyzed against deionized water containing $1 \cdot 10^{-3} M$ NH_3 . The latex stabilized with SDS, which readily desorbs from the latex surface, was dialyzed against the same quantity of deionized water containing $1 \cdot 10^{-3} M$ NH_3 and $8 \cdot 10^{-2} M$ SDS. The SDS concentration is the same as that used in the latex synthesis; thus, the dialysis procedure should not affect the degree of SDS adsorption at the latex surface.

To obtain latices free of the adsorbed surfactant, the following procedures were used: The latex stabilized by SDS was dialyzed 10 times against deionized water containing $1 \cdot 10^{-3} M$ NH_3 . The latices containing the crotonate or maleate surfactants were dialyzed three times against methanol–water 50 : 50, once against methanol–water 30 : 70, once against methanol–water 10 : 90, and, finally,

five times against deionized water containing $1 \cdot 10^{-3} M$ NH_3 .

Atomic Force Microscopy (AFM)

Images were taken on a Digital Instruments Dimension 3000 atomic force microscope working in a tapping mode. Latex films were prepared by applying 2 drops of the latex dispersion on a glass microscope slide which had been carefully cleaned by chromic acid. The latex films were then cast at 75°C for 48 h. After allowing the dispersion to dry at ambient temperature, the samples were stored at 5°C until they were imaged. All AFM measurements were performed at ambient temperature.

RESULTS AND DISCUSSION

Surfactant Characterization

The structures of the three surfactants used are shown in Figure 1. As can be seen, they all contain a strongly anionic, pH-insensitive head group. The maleate surfactant, which has a straight tetradecyl chain as the hydrophobic tail, is expected to be considerably more hydrophobic than are the other two surfactants which have smaller hydrophobic parts. A quantitative estimation and comparison of the hydrophilic–lipophilic balance of the surfactants is not straightforward, however, since the contributions from a *cis* double bond (maleate), a *trans* double bond (crotonate), and ester bonds (both maleate and crotonate) are uncertain. The CMC values may be helpful in this respect (Table I). The crotonate and the maleate surfactants were found to have CMC values of $1.3 \cdot 10^{-2} M$ and $1.4 \cdot 10^{-4} M$, respectively. Under the same conditions, SDS has a CMC of $8.0 \cdot 10^{-3} M$. Thus, using the CMC values as a

Table I Critical Micelle Concentration (CMC), Maximum Amount of Adsorbed Surfactant (Γ_{\max}), and Cross-sectional Area of the Surfactant (A_o), for Sodium Dodecylsulfate (SDS), and the Reactive Maleate and Crotonate Surfactants

Surfactant	CMC (M)	Γ_{\max} (mg/m ²)	A_o (Å ²)
SDS	$8 \cdot 10^{-3}$	3.0	16
Maleate	$1.4 \cdot 10^{-4}$	2.1	36
Crotonate	$1.3 \cdot 10^{-2}$	6.1	10

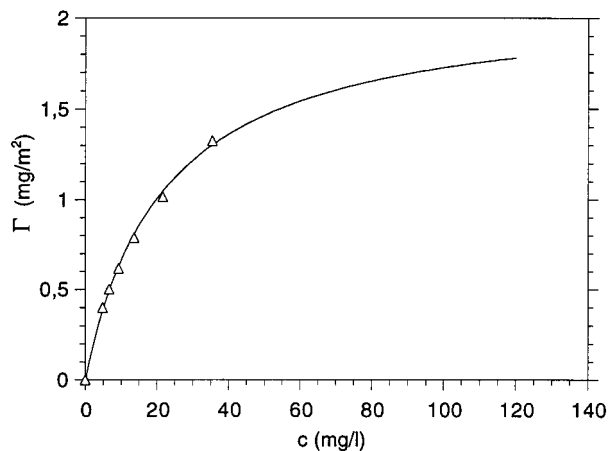


Figure 2 Adsorption isotherm for the maleate surfactant. Γ is the amount of adsorbed surfactant and C is the equilibrium surfactant concentration.

rough measure of surfactant hydrophobicity, the crotonate is slightly more hydrophilic than is SDS, which is considerably more hydrophilic than is the maleate.

Transformation of CMC values into a measure of surfactant hydrophobicity is, of course, a rough approximation. It does not account for differences in geometry of the surfactants, a factor which may influence the CMC considerably. For instance, the maleate surfactant has a kink in the hydrophobic tail caused by the *cis* double bond. This increases the effective hydrophobe volume, which, in turn, may disfavor surfactant self-assembly, thus increasing the CMC.

Figures 2–4 show adsorption of the maleate, crotonate, and SDS, respectively, at a surfactant-

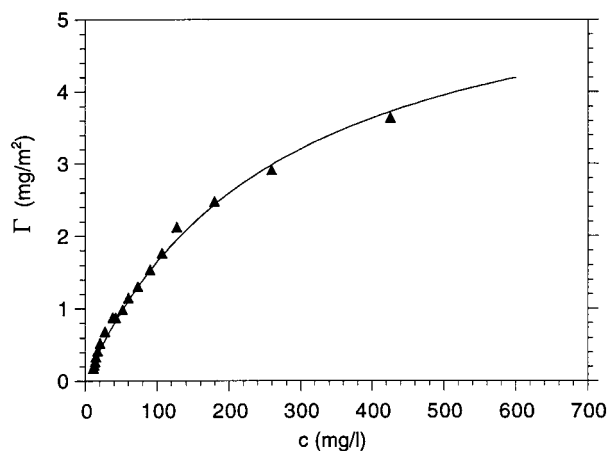


Figure 3 Adsorption isotherm for the crotonate surfactant. Γ is the amount of adsorbed surfactant and C is the equilibrium surfactant concentration.

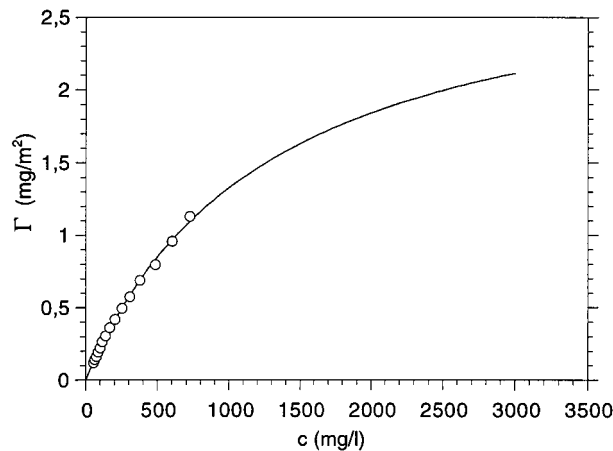


Figure 4 Adsorption isotherm for SDS. Γ is the amount of adsorbed surfactant and C is the equilibrium surfactant concentration.

free model latex, consisting of butyl acrylate (49.5%), styrene (49.5%), and acrylic acid (1.0%). The amount of adsorbed surfactant, Γ , is plotted as a function of equilibrium surfactant concentration, C , up to a value corresponding to the CMC value of each individual surfactant. Assuming Langmuir-type adsorption, the fraction of the surface that is covered by the surfactant can be written as¹⁶

$$\frac{\Gamma}{\Gamma_{\max}} = \frac{KC}{1 + KC}$$

where K is the equilibrium constant of adsorption and Γ_{\max} corresponds to a densely packed surfactant monolayer. The above expression can be rewritten as

$$\Gamma = \frac{\Gamma_{\max} \cdot KC}{1 + KC}$$

and

$$\frac{1}{\Gamma} = \frac{1}{KC \cdot \Gamma_{\max}} + \frac{1}{\Gamma_{\max}}$$

Figure 5 shows a plot of $1/\Gamma$ vs. $1/C$ for the maleate surfactant. The intercept gives the value of $1/\Gamma_{\max}$ of 4670 g/mol, from which a Γ_{\max} value of 2.1 mg/m² was obtained. Calculating the cross-sectional area per surfactant, A_0 , from the expression

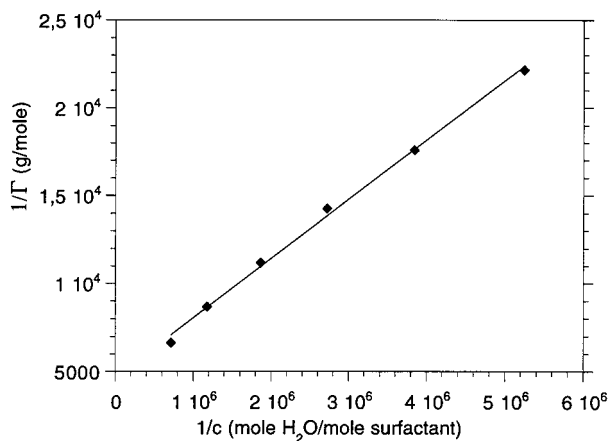


Figure 5 A plot of $1/\Gamma$ vs. $1/C$ for the maleate surfactant. Values are taken from Figure 2. Γ is the amount of adsorbed surfactant and C is the equilibrium surfactant concentration.

$$A_0 = \frac{M}{\Gamma_{\max} \cdot 6.023 \cdot 10^{23}}$$

where M is the molecular weight of the surfactant, gives the value 36 \AA^2 for the maleate. Similar calculations were made for the crotonate surfactant and for SDS. The results are collected in Table I.

The value of Γ_{\max} for SDS, 3.0 mg/m^2 , is in line with expectations. SDS adsorption at various types of latices is typically in the range of $2\text{--}4 \text{ mg/m}^2$, with a higher value for the more hydrophobic latices. Going from poly(vinyl chloride) (very hydrophobic) via poly(butyl methacrylate), polystyrene, and poly(methyl methacrylate) to poly(vinyl acetate) (hydrophilic) gives a gradual reduction of the adsorbed amount¹⁷ from 4 to 2 mg/m^2 . Hence, the butyl acrylate/styrene/acrylic acid latex used in this study behaved as a latex of medium hydrophobicity in the adsorption experiments.

The Γ_{\max} value of 6.1 mg/m^2 obtained for the crotonate surfactant is much higher than expected. As a result, the calculated cross-sectional area, 10 \AA^2 , is unrealistically low. The reason for the deviation from expected values for this surfactant is not clear.

The slope of the initial part of the adsorption isotherms is indicative of the driving force of adsorption. As can be seen from Figures 2–4, the maleate shows the strongest adsorption followed by the crotonate. SDS exhibits a much weaker driving force for adsorption. (Note that the scale of the x -axis differs among the three figures.) It is

noteworthy that the crotonate surfactant adsorbs stronger than does SDS, even though the latter has a somewhat lower CMC. Judging from the adsorption measurements, and also from the dialysis experiments (see below), it seems that there are specific interactions between the crotonate and the latex surface that are absent in the case of SDS. Such attractive interactions can be dipole–dipole interactions or hydrogen bonding involving the α,β -unsaturated ester bond of the surfactant and ester or carboxyl groups at the latex surface. Such attractive surfactant–latex interactions may also be present with the maleate. However, this surfactant has a much longer hydrophobic tail and can be expected to adsorb strongly also without involvement of specific interactions.

Both the crotonate and the maleate are capable of copolymerization at least to some extent with common monomers such as styrene or butyl acrylate. Reactivity ratios, as well as a discussion about the copolymerization process, are given elsewhere.^{8,10}

Latex Characterization

The particle size of the latices stabilized by the crotonate, the maleate, and SDS were found to be 178, 171, and 163 nm, respectively. All three latices had a T_g of 20°C .

Film Formation

During setting and drying of a latex film, the physically adsorbed surfactant may either remain adsorbed at the particle surface or phase separate with the polymer. If the surfactant undergoes phase separation, the water flux may carry it to the film surface. Alternatively, it may accumulate in the interstices between the particles. From there it will migrate to the film–air or film–substrate interface through a long-term exudation process.

The mobility of surfactants during film formation has been the subject of many studies. Techniques used in such investigations include FTIR–ATR,^{18–23} TEM,^{24–26} XPS–SIMS,²⁷ and, more recently, AFM.^{28–31} AFM is an attractive technique for this type of study. Since it is nondestructive, it can be used under ambient conditions and it does not influence the process under study. AFM is today seen as an indispensable tool for monitoring latex film formation in general.^{32–36} In this investigation, AFM was used to observe the surface morphology of the films directly and to moni-

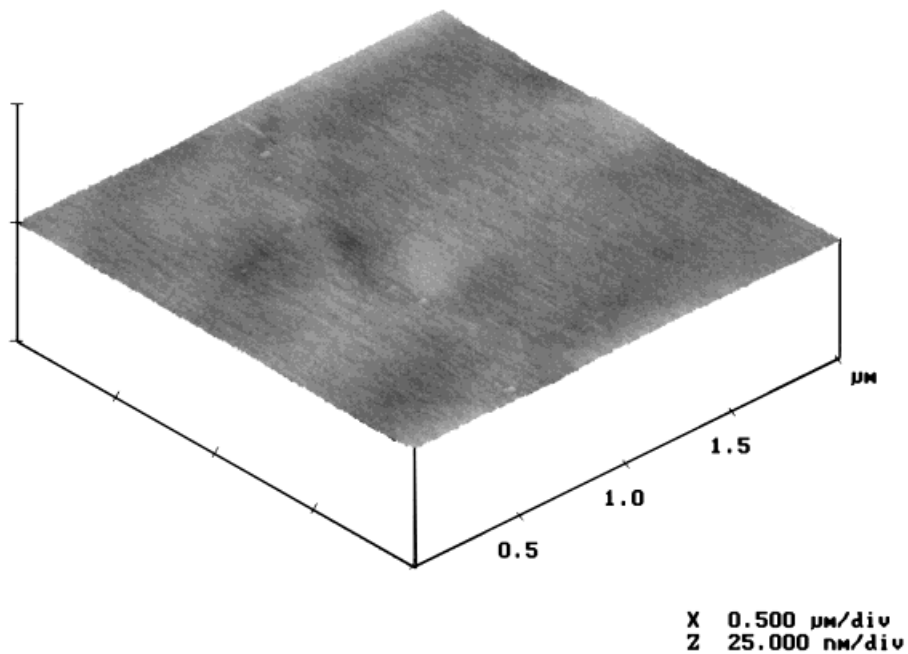


Figure 6 AFM image of a film cast from SDS-stabilized latex.

tor possible migration of unanchored reactive surfactant. Films made from SDS-stabilized latex were used as reference samples.

The topology of films made from latex stabilized by SDS, the maleate, and the crotonate are given in Figures 6–16. The same scale is used in all

figures but one should note that in each picture the z -dimension is plotted at 20 times larger magnification than the x - and y -dimensions.

Figure 6 shows a film formed from SDS-stabilized latex. The film has a smooth, wavy surface as would be expected after annealing for 48 h at

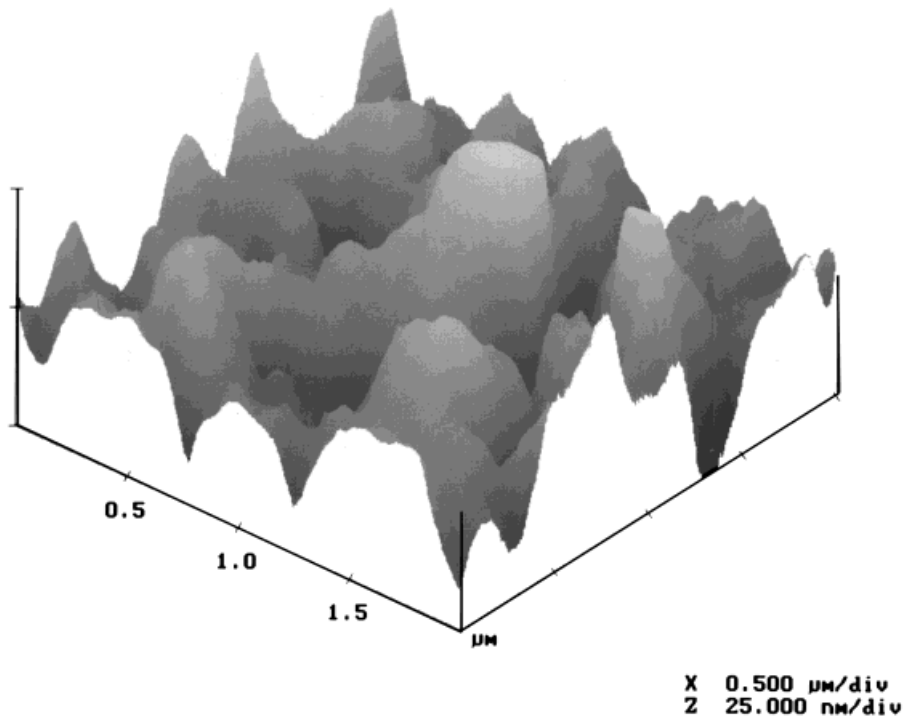


Figure 7 AFM image of a rinsed film cast from SDS-stabilized latex.

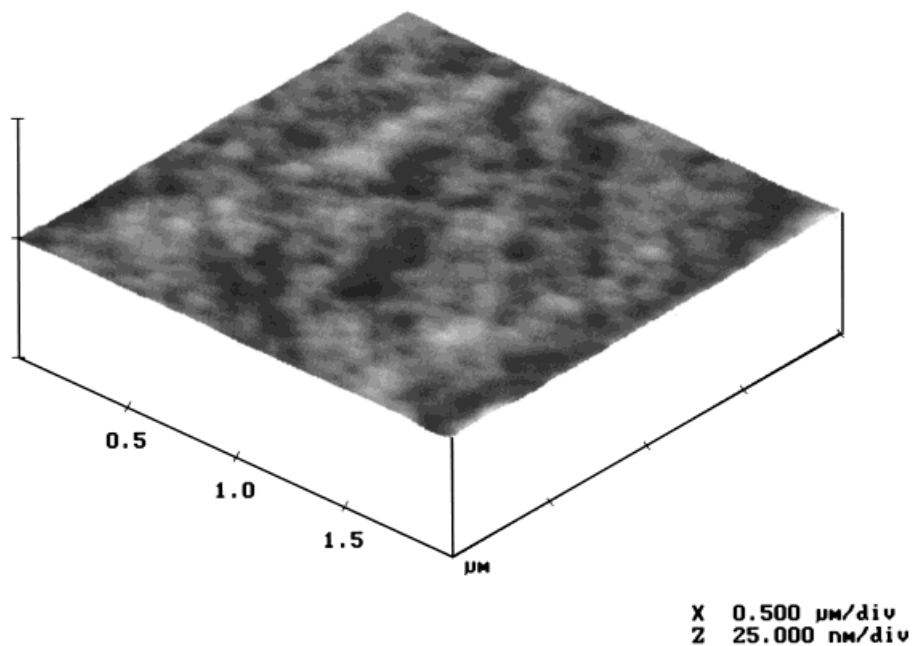


Figure 8 AFM image of a film cast from SDS-stabilized latex dialyzed against deionized water.

55°C above the film T_g . After rinsing with water, large pits were created (Fig. 7). This change in the film morphology is an effect of the migrating surfactant. During the drying stage, SDS moves

with the evaporating water toward the film surface where it crystallizes to form a continuous separate phase, covering the total surface area. Upon rinsing with water, the highly water-solu-

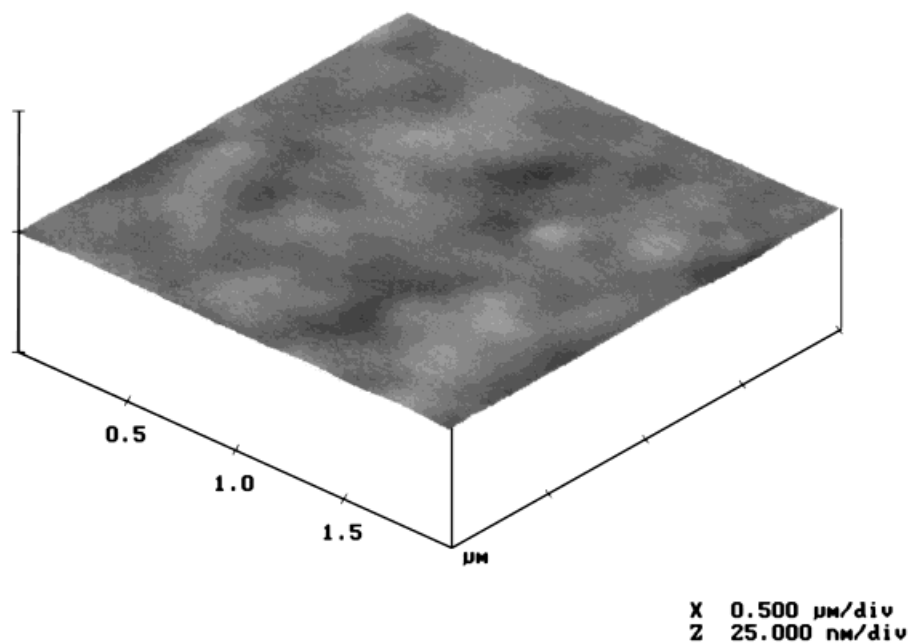


Figure 9 AFM image of a rinsed film cast from SDS-stabilized latex dialyzed against deionized water.

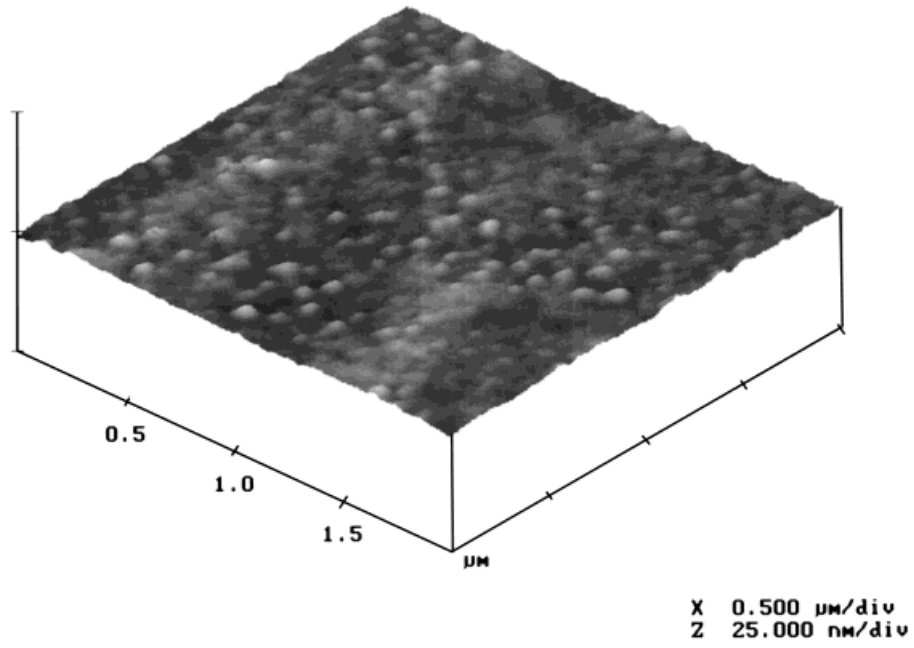


Figure 10 AFM image of a film cast from maleate-stabilized latex.

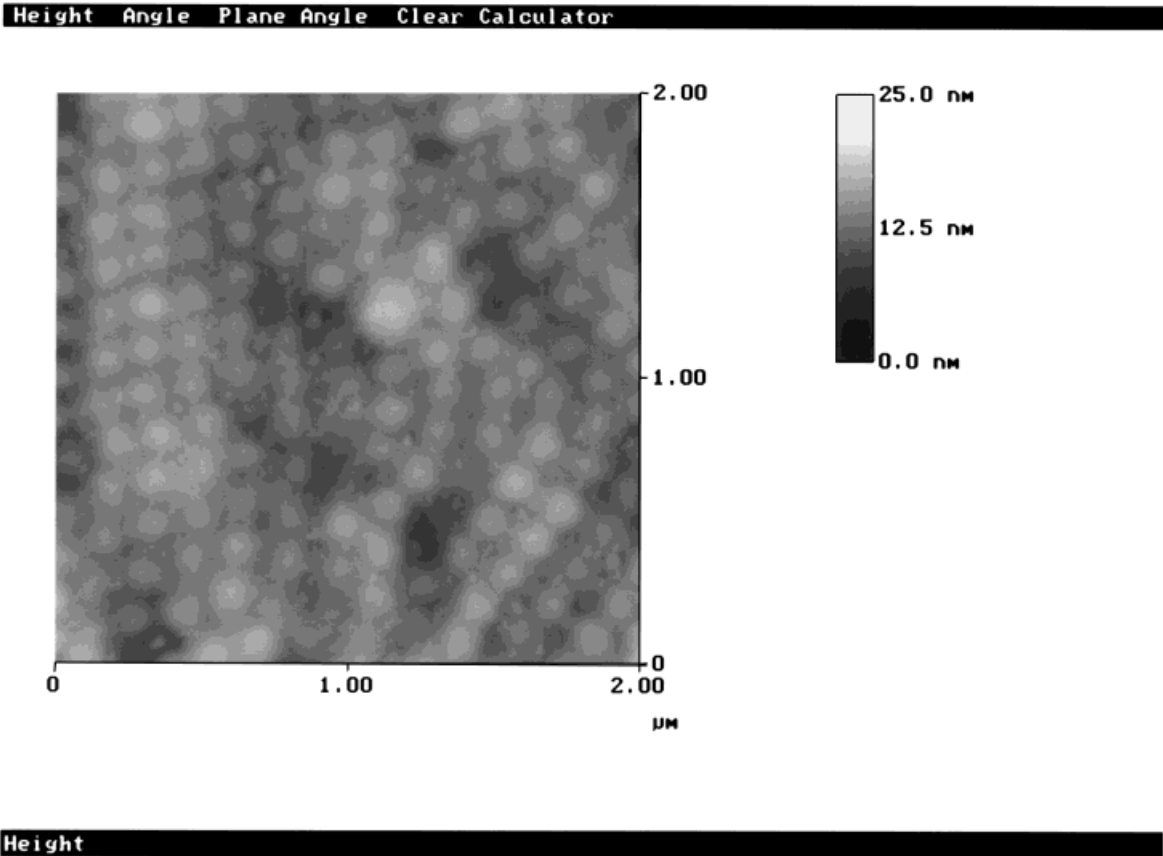


Figure 11 AFM image of a film cast from maleate-stabilized latex after annealing.

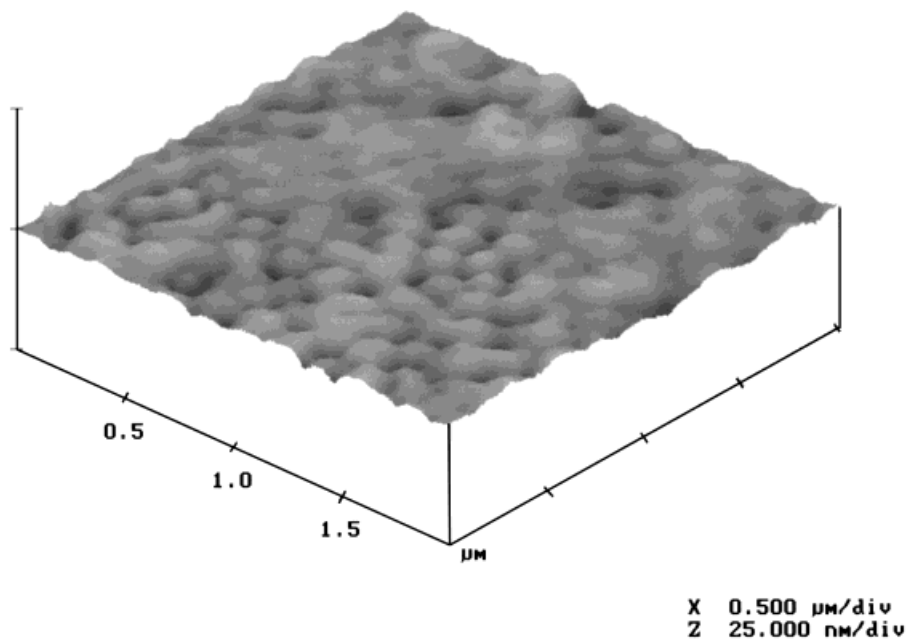


Figure 12 AFM image of a rinsed film cast from maleate-stabilized latex.

ble SDS is washed away. The roughness of the remaining film surface is caused by a disruption of particle packing by the migrating surfactant phase. This phenomenon was previously described by Juhué et al.²⁸

The morphology of a film formed with the same

latex from which the surfactant, SDS, has been removed by dialysis is shown in Figure 8. As can be seen, the morphology of the film is similar to that of the unrinsed SDS-containing film of Figure 6. Contrary to the film of Figure 6, the SDS-free film did not change its appearance after rinsing

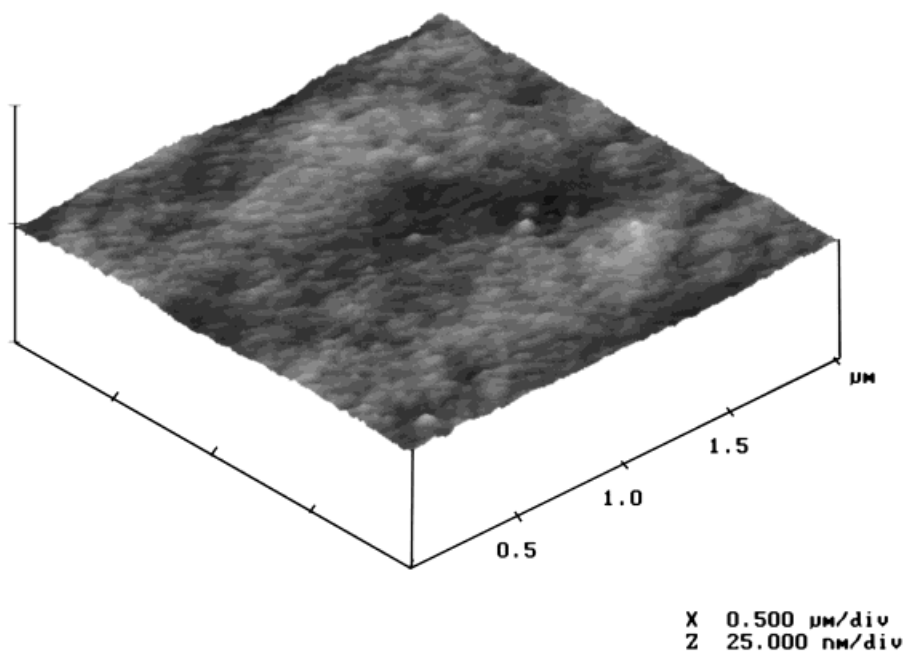


Figure 13 AFM image of a film cast from maleate-stabilized latex dialyzed against methanol.

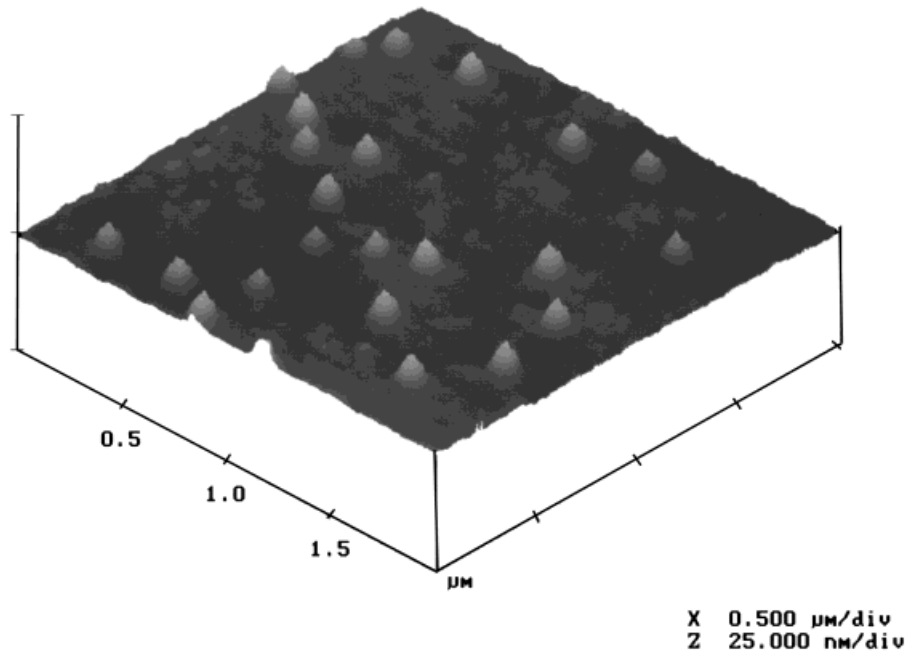


Figure 14 AFM image of a film cast from crotonate-stabilized latex after annealing.

with water (Fig. 9). This is consistent with the surface roughness of the film of Figure 7 being due to the removal of the water-soluble surfactant from the film surface.

Figures 10–12 show the topologies of films cast from maleate-stabilized latex that was cleaned by dialysis against $1 \cdot 10^{-3} M \text{NH}_3$. Figure 10 shows

the surface of the dried film before annealing. The surface is filled with “hills” and “valleys.” This morphology suggests incomplete particle coalescence but may also be due to the surfactant that has migrated to the surface. The appearance after several hours annealing (Fig. 11) indicates that the hills consisted of the surfactant that has

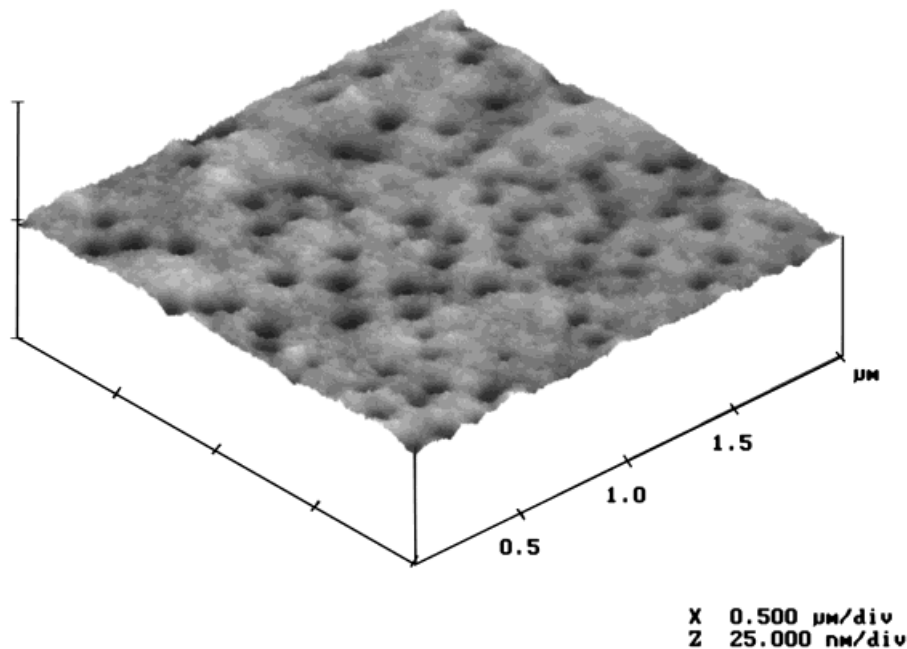


Figure 15 AFM image of a rinsed film cast from crotonate-stabilized latex.

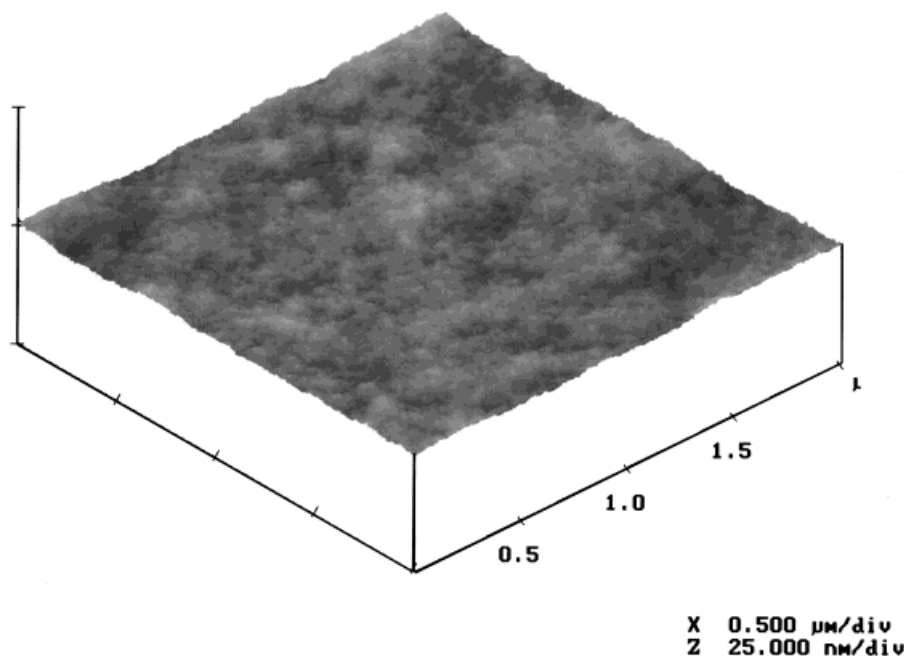


Figure 16 AFM image of a film cast from a crotonate-stabilized latex dialyzed against methanol.

phase-separated and accumulated in the voids between the particles during the annealing process. This clearly indicates that even with the reactive maleate surfactant a substantial portion is not anchored to the latex particle. This observation is in agreement with the level of incorporation of 64%, as determined by two-phase titration. After the film was rinsed with water, holes appeared in a regular pattern, as shown in Figure 12. This is indicative of removal of the surfactant from the surface.

The maleate-stabilized latex was cleaned by dialysis against methanol before the film was cast. The annealed film was smooth, confirming the absence of free surfactant on the surface, as seen in Figure 13.

A corresponding series of AFM pictures for the latex stabilized by the crotonate surfactant gave similar results. The film after annealing (Fig. 14) shows a very pronounced hill-and-valley type of surface. Figure 15 shows the same film after rinsing with water. Deep holes appeared, again indicative of removal of the surfactant. A comparison between Figures 11 and 14 and between Figures 12 and 15 indicates that the latex stabilized with the crotonate contains a larger portion of unanchored surfactant than does the maleate-based latex.

Figure 16 shows a film cast from the crotonate-

stabilized latex dialyzed against methanol to remove the free surfactant. This film gave a smooth appearance, much like that of the maleate-stabilized latex (Fig. 13).

CONCLUSIONS

The AFM pictures clearly indicate that the latices stabilized by the reactive maleate and crotonate surfactants contain a substantial amount of surfactant not attached to the particle surface. During the drying stage, the unbound surfactant migrates to the film surface where it can be removed by rinsing with water. However, compared with the film formed from the SDS latex, the films formed from the latices based on reactive surfactants exhibited smaller defects. The AFM investigation indicates the following order of the amount of the migrated surfactant: SDS \gg crotonate $>$ maleate. The results obtained do not give a quantitative measure of the ratio of the reacted-to-unreacted surfactant.

The fact that a smaller portion of the maleate than the crotonate surfactant seems to migrate to the surface may be due to a difference in reactivity against the latex monomers, i.e., a higher degree of grafting of the maleate onto the latex surface. This is consistent with earlier work showing the

maleate surfactant to be much more reactive than is crotonate.¹⁰ The effect may also be due to the stronger interaction between maleate and latex than between crotonate and latex, as was found in the adsorption experiments. AFM measurements cannot distinguish between these two phenomena.

This work is part of the project CHRX CT 930159 within the Human Capital and Mobility program sponsored by the European Union. S.L. and H.A.S.S. acknowledge grants from the program (Swedish Natural Science Research Council and ERB4001GT953910). We are indebted to Professor Alain Guyot for coordination of the network.

REFERENCES

1. A. Guyot and K. Tauer, *Adv. Polym. Sci.*, **111**, 45 (1994).
2. A. Guyot, *Curr. Opin. Colloid Interf. Sci.*, **1**, 580 (1996).
3. K. Holmberg, *Prog. Org. Coat.*, **20**, 325 (1992).
4. K. Holmberg, *Surf. Coat. Int.*, **76**, 481 (1993).
5. B. Kronberg, J. Kuortti, and P. Stenius, *Colloids Surf.*, **18**, 411 (1986).
6. M. Huldén and E. Sjöblom, *Prog. Colloid Polym. Sci.*, **82**, 28 (1990).
7. M. Torstensson, B. Rånby, and A. Hult, *Macromolecules*, **23**, 126 (1990).
8. M. J. Unzué, H. A. S. Schoonbrood, J. M. Asua, A. Montoya Goni, D. C. Sherrington, K. Stähler, K.-H. Goebel, K. Tauer, M. Sjöberg, and K. Holmberg, to appear.
9. K. Tauer, K.-H. Goebel, S. Kosmella, K. Stähler, and J. Neelsen, *Makromol. Chem. Makromol. Symp.*, **31**, 107 (1990).
10. H. A. S. Schoonbrood, M. J. Unzué, O. J. Beck, A. Montoya Goni, D. C. Sherrington, and J. M. Asua, to appear.
11. A. Montoya Goni, D. C. Sherrington, H. A. S. Schoonbrood, and J. M. Asua, to appear.
12. H. A. S. Schoonbrood, M. J. Unzué, J. I. Amalvy, and J. M. Asua, *J. Polym. Sci. Part A Polym. Chem.*, to appear.
13. H. A. S. Schoonbrood and J. M. Asua, to appear.
14. T. R. Paxton, *J. Colloid Interf. Sci.*, **31**, 19 (1969).
15. M. J. Unzué, PhD Thesis, Universidad del Pais Vasco, Spain, 1996.
16. M. J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd ed., Wiley, New York, 1989, p. 67.
17. I. Piirma, in *Polymer Colloids II*, R. M. Fitch, Ed., Plenum Press, New York, 1980, p. 220.
18. L. K. Tebelius and M. W. Urban, *J. Appl. Polym. Sci.*, **56**, 387 (1995).
19. B.-J. Niu and M. W. Urban, *ACS Div. PMSE*, **69**, 196 (1993).
20. T. A. Thorstenson and M. W. Urban, *ACS Div. PMSE*, **69**, 192 (1993).
21. C. L. Zhao, Y. Holl, T. Pith, and M. Lambla, *Colloid Polym. Sci.*, **265**, 823 (1987).
22. E. Kientz, F. Dobler, and Y. Holl, *Polym. Int.*, **34**, 125 (1994).
23. E. Kientz and Y. Holl, *Colloids Surf. A*, **78**, 255 (1993).
24. B. R. Vijayendran and T. Bone, *J. Disp. Sci. Technol.*, **3**, 81 (1982).
25. Y. Wang, A. Kats, D. Juhué, and D. M. A. Winnik, *Langmuir*, **8**, 1435 (1992).
26. J. W. Vanderhoff, *Br. Polym. J.*, **2**, 161 (1970).
27. C. L. Zhao, F. Dobler, T. Pith, Y. Holl, and M. Lambla, *J. Colloid Interf. Sci.*, **128**, 437 (1989).
28. D. Juhué, Y. Wang, J. Lang, O. Leung, M. C. Goh, and M. Winnik, *J. Polym. Sci. Polym. Phys.*, **33**, 1123 (1995).
29. D. Juhué and J. Lang, *Doub. Liais. Phys. Chim. Peint. Adhes.*, **41**, 464 (1994).
30. D. Juhué and J. Lang, *Colloids Surf. A*, **87**, 177 (1994).
31. R. M. Rynders, C. R. Hegedus, and A. G. Gilicinski, *J. Coat. Technol.*, **67**(845), 59 (1995).
32. D. Juhué and J. Lang, *Langmuir*, **9**, 792 (1993).
33. A. Goudy, M. L. Gee, S. Biggs, and S. Underwood, *Langmuir*, **11**, 4454 (1995).
34. F. Lin and D. J. Meier, *Langmuir*, **11**, 2726 (1995).
35. H.-J. Butt and B. Gerharz, *Langmuir*, **11**, 4735 (1995).
36. J. M. Geurts, M. Lammers, and A. L. German, *Colloids Surf. A*, **108**, 295 (1996).