

Surface and Interfacial Fourier Transform Infrared Spectroscopic Studies of Latexes. XV. Orientation of the Sodium Dioctyl Sulfosuccinate Surfactant Molecules in Core/Shell-Type Styrene/Butyl Acrylate Latex Films at the Film–Air and Film–Substrate Interfaces

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SYNOPSIS

This study addresses the effect of particle structure and composition on the mobility and orientation of sodium dioctyl sulfosuccinate (SDOSS) surfactant molecules in polybutyl acrylate/polystyrene core/shell-type latex films near the film-air (F-A) and film-substrate (F-S) interfaces. In an effort to determine how the surface tension of the substrate influences the migration and orientation of the SDOSS surfactant molecules, polytetrafluoroethylene (PTFE) and liquid Hg substrates were used. It appears that, as the concentration of styrene monomer in the latex increases, SDOSS migrates toward the F-A and F-S interfaces. As the surface tension of the substrate changes from 18 mN/m in PTFE to 400 mN/m for liquid Hg, the surfactant also migrates toward the two interfaces. For the latex particles composed of 50%/50% styrene/*n*-butyl acrylate (Sty/*n*-BA) latex copolymer, the hydrophilic SO_3Na^+ groups of SDOSS surfactant are present primarily near the F-A interface, and they appear to be mostly parallel to the surface for the films cast on the PTFE surface. For the latex films cast on the liquid Hg surface, the SDOSS hydrophilic surfactant groups are found to be preferentially parallel near the F-A interface and perpendicular near the F-S interface. These studies indicate that the surfactant concentration and its orientation throughout the latex film change as a function of the initial monomer composition and the surface tension of the substrate. Furthermore, the SDOSS concentration appears to vary with depth into the latex interfaces. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Our previous studies^{1–13} have shown that the diffusion and mobility of low-molecular-weight species may play a significant role in the numerous macroscopic properties of organic coatings. This issue is particularly pronounced for latex films, which require the presence of surfactants during their synthesis. Although the entire concept of surfactants and low-molecular-weight additives is a “Pandora’s box” with perhaps more questions than answers, this study will focus not only on the mobility and dif-

fusion of sodium dioctyl sulfosuccinate (SDOSS) surfactant molecules in latexes, but also the elucidation of how the surfactant concentration may change near the film-air (F-A) and film-substrate (F-S) interfaces for the core/shell-like structures of styrene/*n*-butyl acrylate (Sty/*n*-BA) latex particles. Orientation changes of SDOSS are also of significant importance because they may alter numerous properties near the F-A and F-S interfaces.

Substrate surface tension and mechanical deformations,³ surfactant and copolymer structures,^{4,5} and hydrophobic surfactant copolymer interactions^{4,5} have been previously identified as being some of the factors affecting surfactant mobility and the dynamics of migration.^{1–7} The interactions between SDOSS and sodium dodecylbenzene sulfonate

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(SDBS) surfactants and the acid groups of the copolymer latex have been addressed.^{6,7} These surfactants have highly polar sulfonate groups and, therefore, form hydrogen bonding with the acid groups present in the latex copolymer and the residual water molecules in the coalesced films. Thus, the equilibrium between water and/or acid with $\text{SO}_3^- \text{Na}^+$ hydrophilic groups is affected not only by the partial water vapor pressure over the latex film during coalescence, but also after the stabilization of the liquid latex suspension prior to coalescence to a solid film.⁷ In an attempt to understand the nature of these interactions, several latex systems including Sty/*n*-BA,¹¹⁻¹³ butyl acrylate/methyl methacrylate/methacrylic acid (BA/MMA/MAA),^{7,10} and ethyl acrylate/methacrylic acid (EA/MAA)^{3,4,10} were studied. This particular study, being part of a larger research program, focuses on the phenomena near the F-A and F-S interfaces of the hard core/soft shell Sty/*n*-BA latex films cast on polytetrafluoroethylene (PTFE) and liquid Hg surfaces.

EXPERIMENTAL

The following latex copolymers were synthesized by the use of procedures described in the previous studies:^{5,6} 50% Sty/50% *n*-BA, 30% Sty/70% *n*-BA, and 10% Sty/90% *n*-BA. In a typical experiment, the following formulation for the 50% Sty/50% *n*-BA latex copolymer was used: styrene (Sty), *n*-butyl acrylate (*n*-BA), and methacrylic acid (MAA) monomers (Aldrich Chem. Co.) were copolymerized by a semicontinuous emulsion copolymerization process. In a typical formulation, 45 wt % monomer (48.5 wt % Sty, 48.5 wt % BA, 3 wt % MAA), and 55 wt % of solvent and other additives (51.74 wt % double deionized (DDI) water, 0.26 wt % $\text{K}_2\text{S}_2\text{O}_8$ initiator, and 3 wt % SDOSS surfactant) were used. SDOSS surfactant (Aerol OT-100; American Cyanamid) was dissolved in 90 w/w % DDI water (Millipore Filtration System), and it was stirred and heated to 70°C, while the reaction vessel was purged with nitrogen. After the SDOSS surfactant was dissolved, the remaining 10 w/w % DDI water containing dissolved potassium persulfate initiator (Aldrich Chem. Co.) was added to the system. After 20 min, one-fourth of the *n*-BA/MAA mixture was added to the vessel. The remaining mixture was fed over a 90 min period. When this step was completed, a mixture of Sty/MAA was added dropwise to the reaction vessel over a 90 min period. The temperature was maintained at 70°C, and the latex emulsion was continuously stirred for

30 min after the reaction was completed. A 50%/50% Sty/*n*-BA copolymer was synthesized with 1.65% SDOSS surfactant. The remaining compositions were obtained in a similar manner. The samples were prepared by drying a latex film on PTFE or liquid Hg surfaces, and the films were allowed to dry for 72 h under ambient conditions (relative humidity (RH) = 70–80%). The latex films were then removed from the substrate, and the F-A and F-S interfaces were examined by the use of attenuated total reflectance Fourier transform infrared (ATR) FTIR spectroscopy.

The procedures, using polarized ATR FT-IR spectroscopy, have been described in the previous studies.¹⁰ ATR FTIR spectra were collected at the F-A and F-S interfaces on a Mattson Sirius 100 spectrometer, equipped with a Spectra-TechTM variable-angle multiple-reflection ATR accessory, equipped with a KRS-5 crystal. Q-ATRTM software was utilized to eliminate spectral distortions resulting from ATR measurements in a Spectra CalcTM software environment.

RESULTS AND DISCUSSION

In the previous studies, we have shown that the presence of the 1,046 and 1,056 cm^{-1} bands at the F-A and F-S interfaces is attributed to the surfactant $-\text{SO}_3^- \text{Na}^+$ hydrophilic entities.³⁻⁶ The S—O stretching band, originally detected for the SDOSS surfactant at 1,050 cm^{-1} , splits into two bands at 1,046 and 1,056 cm^{-1} . The band at 1,046 cm^{-1} is due to the $-\text{SO}_3^- \text{Na}^+$ ends of the SDOSS surfactant associations with water molecules, and the band at 1,056 cm^{-1} is due to the hydrogen bonding between the $-\text{SO}_3^- \text{Na}^+$ ends of the SDOSS and acid groups.

In this study, we shall use a similar approach to examine the mobility and orientation changes of SDOSS surfactant molecules at the F-A and F-S interfaces in the core/shell-type Sty/*n*-BA copolymer latex films cast on PTFE or Hg substrates. A particular emphasis will be given to the concentration and orientation changes of SDOSS near the interfaces. While the concentration changes throughout the latex film can be monitored by changing the angle of incidence in an ATR experiment,¹⁰ the orientation changes will be facilitated by using an IR light polarized in parallel (TE) and perpendicular (TM) directions. Since changing the angle of incidence in an ATR cell allows us to conduct surface depth profiling, we will utilize this feature and vary the angle of incidence from 60 to 40°. These values will allow us to vary the depth of

penetration of IR light from approximately 1.35 to 2.30 μm .

In an effort to determine how the monomer composition of the latex films influences the surfactant concentration and its orientation throughout the film, the following latex copolymers were synthesized: 50% Sty/50% *n*-BA, 30% Sty/70% *n*-BA, and 10% Sty/90% *n*-BA. Traces A, B, C, D, and E of Figure 1(a) illustrate the ATR FT-IR spectra of the 50% Sty/50% *n*-BA latex copolymer. The spectra were recorded by the use of parallel (TE) polarization. For reference purposes, the spectrum of neat SDOSS surfactant is shown in trace F. The presence of the 1,046 and 1,056 cm^{-1} bands indicates that there is a significant amount of water and hydrogen-bonded acid groups associated with the $\text{SO}_3^- \text{Na}^+$ surfactant groups near this interface.⁵ On the basis of the analysis of the spectra shown in Figure 1(a), it appears that there is a decrease in the surfactant concentration of the $\text{SO}_3^- \text{Na}^+$ groups associated with water and acid entities when going from approximately 1.35 to 2.30 μm . This is demonstrated by the decrease of the 1,046 and 1,056 cm^{-1} band intensities. However, when the perpendicular (TM) polarization spectra are examined, the situation changes. Instead of the 1,046 and 1,056 cm^{-1} bands, the 1,050 cm^{-1} S—O stretching band is detected for the penetration depths ranging from 1.35 to 1.48 μm . This is illustrated by traces E and D in Figure 1(b). As the penetration depth increases, the 1,046 and 1,056 cm^{-1} bands become more pronounced [traces C, B, and A, Fig. 1(b)].

The data presented in Figure 1 indicate that the $\text{SO}_3^- \text{Na}^+$ hydrophilic groups of SDOSS are present in three forms: nonassociated (1,050 cm^{-1}), associated with H_2O (1,046 cm^{-1}), and associated with COOH groups (1,056 cm^{-1}). Furthermore, while nonassociated $\text{SO}_3^- \text{Na}^+$ groups are perpendicular at shallow depths from the surface, the $\text{SO}_3^- \text{Na}^+$ associations with H_2O and COOH groups are preferentially parallel. Going deeper into the F-A interface, the $\text{SO}_3^- \text{Na}^+$ are preferentially parallel, and no free $\text{SO}_3^- \text{Na}^+$ groups are detected. Although at this point it is too early to assess the origin of the free SDOSS near the surface, the presence of the hydrophobic styrene groups near the F-A interface may repel water, acid groups, or other hydrophilic entities, therefore leaving surfactant groups in a nonassociated form.

With these data in mind, let us examine the same latex films at the F-S interface. For the 50% Sty/50% *n*-BA latex films cast on PTFE, SDOSS is present at significantly lower concentration levels than that detected at the F-A interface. As shown

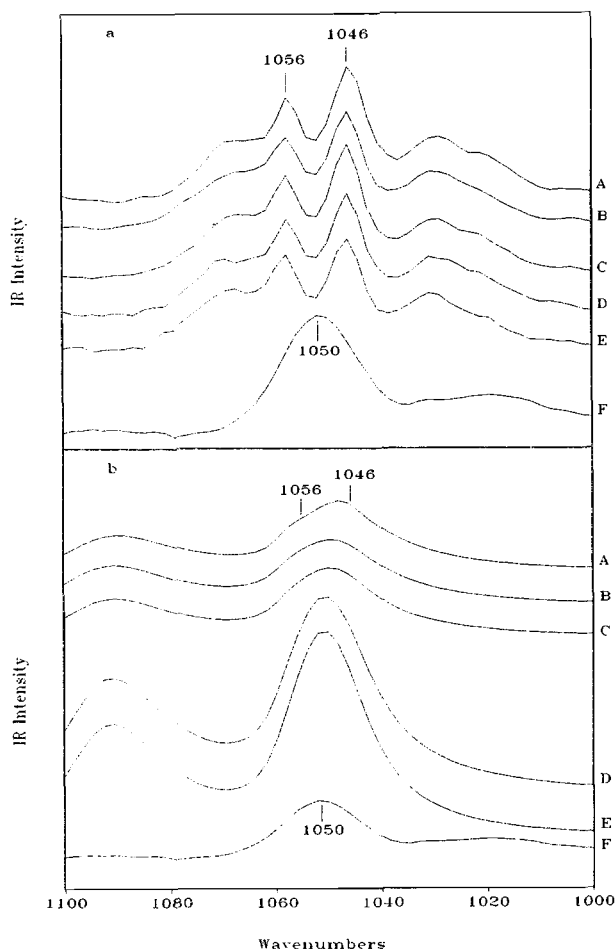


Figure 1 (a) Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/*n*-BA latex cast on PTFE: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant. (b) Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/*n*-BA latex cast on PTFE: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

in Figures 2(a) and (b) for both parallel (TE) and perpendicular (TM) polarizations, respectively, the 1,050 cm^{-1} band is detected at the penetration depths ranging from 1.35 to 1.48 μm . Furthermore, the band shifts to 1,046 cm^{-1} when the penetration depth approaches 1.65 μm . Thus, on the basis of this analysis, it is apparent that not only the concentration of SDOSS is much smaller near the F-S interface, but its environment also changes. This behavior is attributed to the fact that the PTFE surface is hydrophobic and repels water molecules present

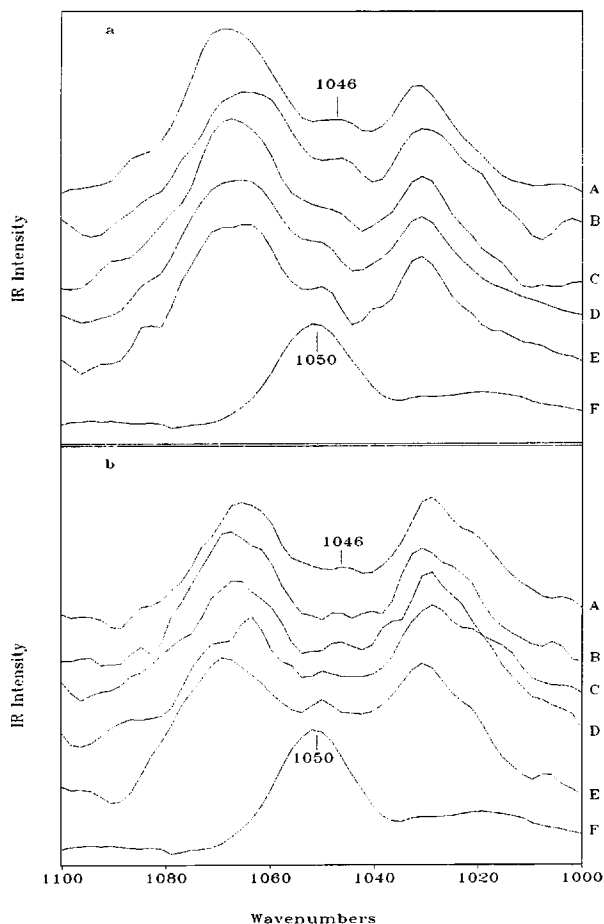


Figure 2 (a) Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty/*n*-BA latex cast on PTFE: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant. (b) Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty/*n*-BA latex cast on PTFE: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

near the F-S interface. Therefore, only small fractions of SDOSS are detected as not associated with water molecules. However, when the distance from the PTFE substrate increases, the hydrophobic effect of the PTFE substrate diminishes, making it easier for the surfactant molecules to become associated with water.

Let us now consider the effect of substrate surface tension on the distribution and/or orientation of SDOSS across the 50%/50% copolymer Sty/*n*-BA latex films. In our effort to determine this effect, latex films were deposited on liquid Hg, which ex-

hibits a surface tension significantly higher than that of PTFE (approximately 420 mN/m). Figure 3(a) illustrates ATR FTIR spectra recorded from the F-A interface by the use of parallel (TE) polarization. It appears that the 1,046 and 1,056 cm^{-1} bands are strong, indicating that a high concentration of SDOSS hydrophilic surfactant groups is present at this interface. Furthermore, $\text{SO}_3^- \text{Na}^+$ surfactant groups associated with water and acid groups are preferentially parallel to the surface and, as observed in Figure 3(a), decrease, while penetrating deeper

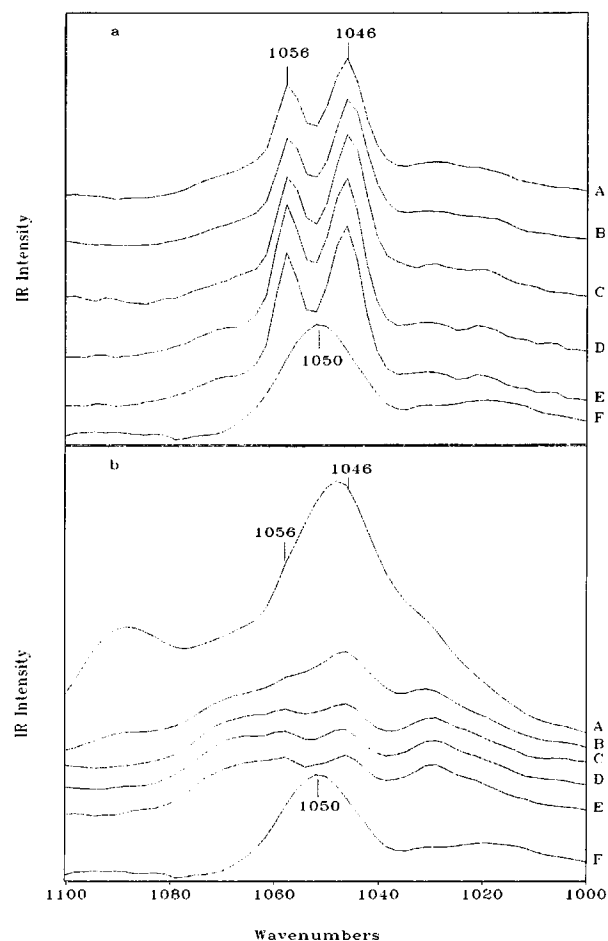


Figure 3 (a) Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant. (b) Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

into the film (traces E through A). When, however, TM polarization is used, the situation changes again. Figure 3(b) depicts a series of the ATR FT-IR spectra recorded from the F-A interface by the use of perpendicular (TM) polarization. As shown in Figure 3(b) (traces E through A), an increase of the 1,046 and 1,056 cm^{-1} bands is observed up to 1.65 μm into the surface. However, 1.89 μm below the surface, the 1,046 cm^{-1} band dominates this spectral region. These data indicate that these are not only orientation changes of the $\text{SO}_3^- \text{Na}^+$ groups, but also there are significantly different environments at various depths. Furthermore, a comparison of traces A and E in Figures 1(b) and 3(b) also indicates that there is a significant effect of the substrate on the distribution and environment of the $\text{SO}_3^- \text{Na}^+$ groups. For example, at approximately 1.35 μm depth [trace E in Figure 1(b)] near the F-A interface, the SDOSS in a nonassociated form is present when PTFE is used as a substrate. However, on liquid Hg, the SDOSS is detected, but its concentration levels are significantly smaller, and moreover, the $\text{SO}_3^- \text{Na}^+$ environment contains water and acid groups [Figure 3(b)].

When liquid latex is cast on a solid PTFE substrate, the surface tension differential between the liquid latex and the solid substrate influences the migration and orientation of $\text{SO}_3^- \text{Na}^+$ hydrophilic surfactant groups at both F-A and F-S interfaces. This surface tension differential is present during coalescence, but it diminishes as the latex becomes a solid film on a solid PTFE surface. The situation is different for the latex cast on a liquid Hg surface: the liquid latex film is deposited on a liquid substrate, therefore creating a surface tension differential as coalescence occurs, and after the solid latex film is formed. For the latex cast on the Hg surface, the surface tension differential is present during coalescence, and it increases as the latex becomes a solid film cast on a liquid Hg surface. The surface tension differential effect is illustrated in Figures 1(b) and 3(b) for the F-A interface and Figures 2(b) and 4(b) for the F-S interface of the 50/50 Sty/*n*-BA latex films. As seen, the 1,046 and 1,056 cm^{-1} bands increase substantially while going deeper into the interfaces for the latex films cast on liquid Hg. This observation indicates that the $\text{SO}_3^- \text{Na}^+$ surfactant groups are greatly influenced by the surface tension differential between the solid latex film and the liquid Hg substrate.

Figure 4(a), traces E through A, illustrate ATR FT-IR data recorded from the F-S interface of the 50% Sty/50% *n*-BA latex films cast on Hg. The spectra were recorded by the use of parallel (TE)

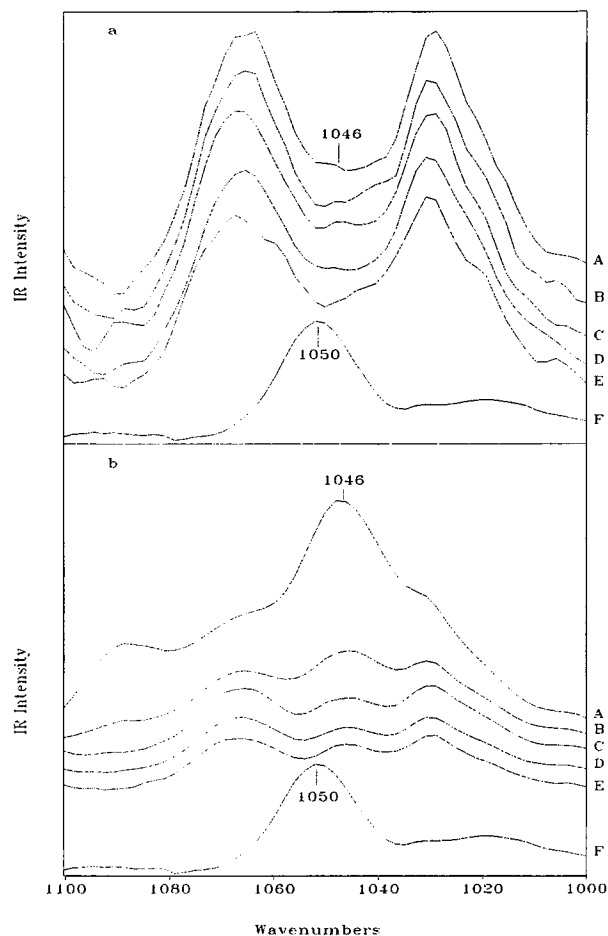


Figure 4 (a) Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant. (b) Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty-*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

polarization. Although traces of surfactant are present at the F-S interface, in essence, the surfactant present is mostly associated with water. The situation changes, however, when the F-S interface is examined by the use of perpendicular (TM) polarization. Figure 4(b) illustrates that the intensity of the 1,046 cm^{-1} band increases dramatically when penetrating deeper into the latex film (trace A). Again, the 1,056 cm^{-1} band is not detected at this interface, indicating that, at this depth, the acid groups are not present. The presence of the 1,046 cm^{-1} band results from the presence of residual wa-

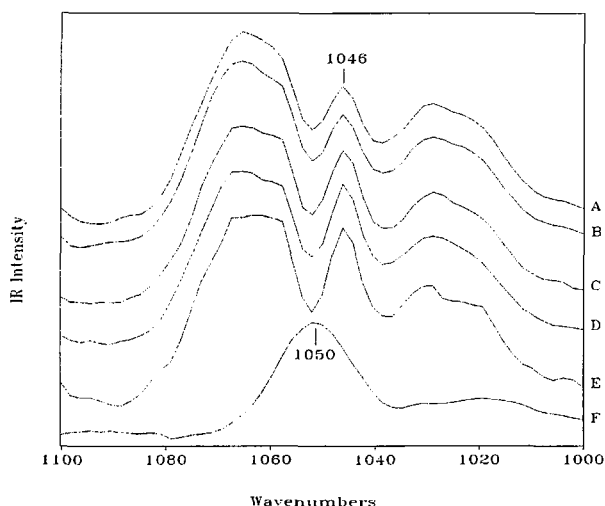


Figure 5 Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 30/70 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

ter molecules trapped between the latex film and the substrate.

A comparison of the data for 50% Sty/50% *n*-BA latex films cast on PTFE [Figs. 1(b) and 2(b)] and on liquid Hg [Figs. 3(b) and 4(b)] indicates that the surface tension of the substrate greatly influences the migration and orientation of the SDOSS

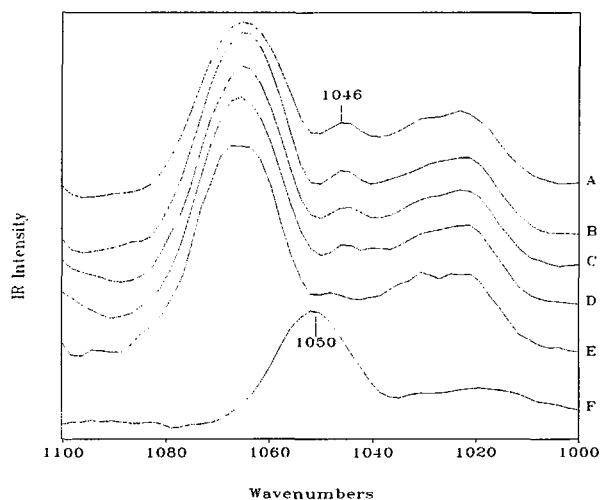


Figure 6 Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 30/70 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

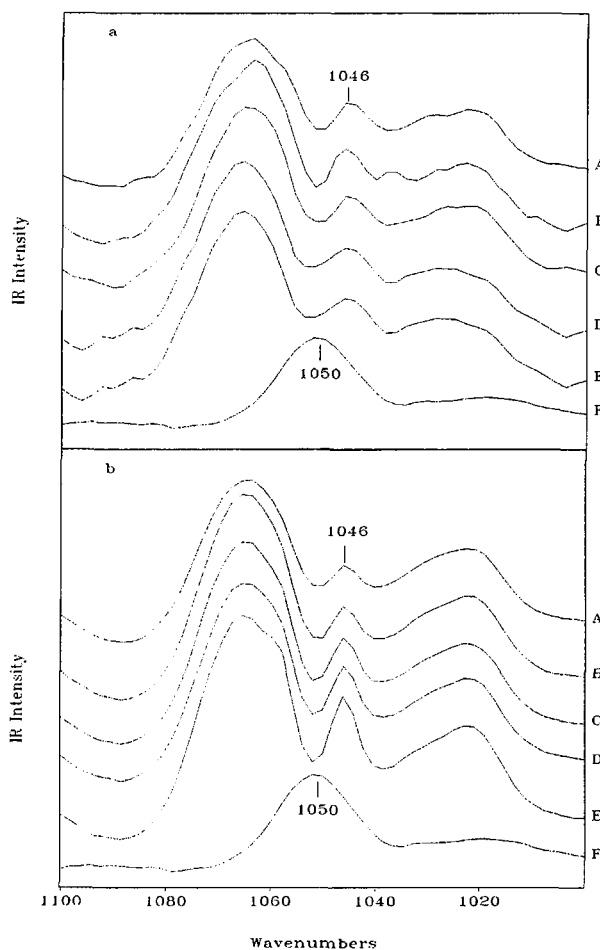


Figure 7 (a) Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 10/90 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant. (b) Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 10/90 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

surfactant in a latex film. Although this observation may not be very surprising, the effect is so pronounced that it requires further considerations. When the latex film is deposited on liquid Hg, the concentration of the $\text{SO}_3^- \text{Na}^+$ groups associated with water near the F-S interface increases. In addition, the spectra recorded from the F-S interface by the use of perpendicular (TM) polarization show a significant intensity increase of the $1,046 \text{ cm}^{-1}$ band while penetrating deeper into the film for the film cast on Hg. These observations suggest that the

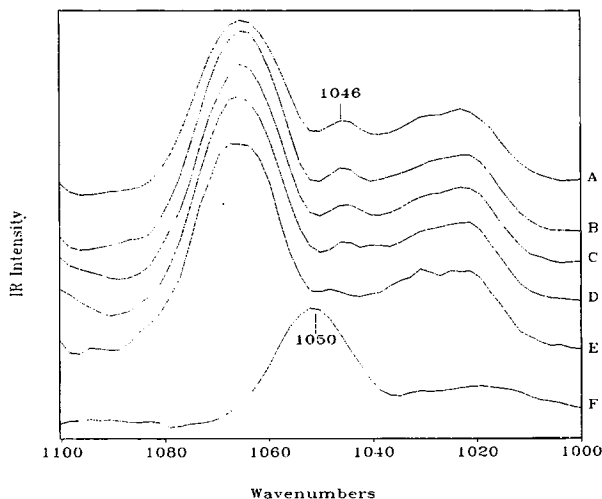


Figure 8 Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 10/90 Sty/*n*-BA latex cast on Hg: (trace A) 2.30 μm , (trace B) 1.89 μm , (trace C) 1.65 μm , (trace D) 1.48 μm , (trace E) 1.35 μm , and (trace F) transmission spectrum of SDOSS surfactant.

higher surface tension of Hg causes the surfactant migration toward the F-S interface, and the hydrophilic $\text{SO}_3^- \text{Na}^+$ surfactant groups are preferentially perpendicular to the surface. This behavior results from the fact that SDOSS lowers the surface tension of the latex, and the latex film, after being deposited on Hg with a high surface tension, attracts the surfactant to the F-S interface, in an attempt to lower the surface tension difference between Hg and the latex copolymer. Liquid Hg has also an effect on the F-A interface, as shown by a comparison of the

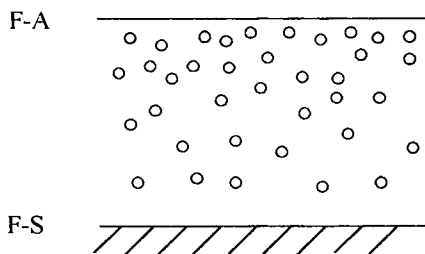


Figure 9a

Low surface tension substrate
○ surfactant

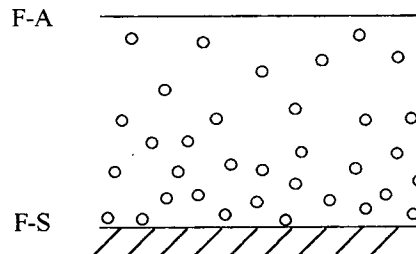


Figure 9b

High surface tension substrate
○ surfactant

Figure 9 A schematic representation of the distribution of surfactant molecules as a function of substrate surface tension: (a) low surface tension substrate, (b) high surface tension substrate.

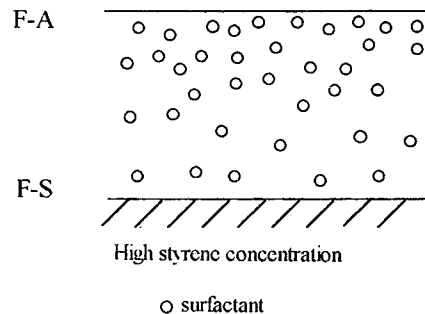


Figure 10 A schematic representation of the distribution of surfactant molecules for a high-styrene-concentration latex copolymer.

spectra shown in Figures 1(b) and 3(b). The $1,050 \text{ cm}^{-1}$ band due to nonassociated $\text{SO}_3^- \text{Na}^+$ surfactant groups is not detected when the latex films are cast on liquid Hg. Furthermore, the concentration of the $\text{SO}_3^- \text{Na}^+$ surfactant groups increases while going deeper into the F-A interface for the latex film deposited on the Hg substrate.

One of the factors that also affects the distribution and orientation of surfactant molecules near the interfaces is the latex copolymer composition. In essence, compatibility between the copolymer chemistry and surfactants will determine to what extent surface tension at the substrate will influence surfactant mobility. For that reason, we modified the Sty/*n*-BA particle composition. When the concentration of styrene in the latex copolymer is diminished, the SDOSS surfactant concentration near the F-A and F-S interfaces is smaller. For the 30% Sty/70% *n*-BA and 10% Sty/90% *n*-BA latex copolymers cast on the PTFE surface, no surfactant is detected at the F-A or F-S interfaces, for either

parallel (TE) or perpendicular (TM) polarizations. However, when the same latex copolymers were cast on the liquid Hg substrate, the surfactant concentration and its distribution throughout the latex films changes, especially near the F-S interface. As shown in Figure 5, for the 30% Sty/70% *n*-BA latex films cast on liquid Hg substrate, the F-A interface spectra show no surfactant bands present at this interface for either parallel (TE) or perpendicular (TM) polarizations, but at the F-S interface, 1,046 cm^{-1} surfactant bands are detected for both polarizations. Furthermore, the concentration of the SDOSS surfactant groups parallel to the surface decreases slightly when going deeper into the film for the parallel (TE) polarization. However, for the perpendicular (TM) polarization spectra recorded at the F-S interface shown in Figure 6, traces E through A, an increase of the 1,046 cm^{-1} band while penetrating deeper into the film is detected. These observations indicate that for this monomer composition, the F-S interface of the latex films contains most surfactant groups that are parallel to the surface near this interface, and the $\text{SO}_3^- \text{Na}^+$ groups become perpendicular to the surface while going deeper into the F-S.

Figure 7(a), traces E through A, show the data for 10% Sty/90% *n*-BA latex films cast on liquid Hg substrate. It appears that the SDOSS intensities remain constant throughout the examined depths near the F-A interface with the parallel (TE) polarization. However, they slightly decrease while penetrating deeper into the F-A interface with a perpendicular (TM) polarization. This is shown in Figure 7(b). These observations indicate that the amount of SDOSS surfactant groups parallel to the surface throughout the examined portion of the latex film remains constant, and the amount of the surfactant groups perpendicular to the surface decreases, while going deeper into the latex film.

No surfactant bands were detected over the examined depth near the F-S interface for the 10% Sty/90% *n*-BA composition with the perpendicular (TM) polarization. However, as illustrated in Figure 8, the 1,046 cm^{-1} surfactant band is detected for the parallel (TE) polarization, indicating that most of the surfactant present at this interface is parallel to the surface.

When 30% Sty/70% *n*-BA and 10% Sty/90% *n*-BA latex films cast on liquid Hg were examined, the 1,056 cm^{-1} band was not detected at either F-A or F-S interfaces, indicating that, for this composition, the mobility of surfactant is limited. However, as we recall the data shown in Figures 1(a) and 3(a), the 1,056 cm^{-1} band, due to the association of the $\text{SO}_3^- \text{Na}^+$ surfactant groups with the acid groups, was

detected only for the 50% Sty/50% *n*-BA copolymer mixture. Therefore, the latex composition clearly affects the mobility of SDOSS. For a higher concentration of styrene, the acid groups were driven toward the F-A interface, but when the styrene concentration is lowered to 30% Sty and 10% Sty, the surfactant groups are found to be only associated with water.

In summary, the data presented here allow us to depict a scenario concerning the orientation of SDOSS and the effect of the substrate surface tension for core/shell latex films. A schematic representation of the effect of surface tension on the surfactant mobility through the latex copolymer film is depicted in Figure 9(a). As shown in Figure 9(a), the low surface tension of the PTFE substrate drives the hydrophilic $\text{SO}_3^- \text{Na}^+$ surfactant groups toward the F-A interface of the latex film. However, when the surface tension of the substrate is increased (by the use of liquid Hg), the surfactant migrates toward the F-S interface of the latex film [Fig. 9(b)]. There is also the effect of latex composition, which influences the surfactant mobility through the latex film. A schematic representation of the effect of monomer composition on the surfactant mobility through the latex copolymer film is depicted in Figure 10(a). As the styrene concentration in a latex composition increases, the surfactant tends to migrate toward the F-A interface.

CONCLUSIONS

Polarized ATR FTIR spectroscopy was used to monitor how the surface tension of the substrate and the latex composition influence the mobility and orientation of SDOSS surfactant groups. This study shows that the latex particle composition may significantly influence the direction of the surfactant mobility to the F-A or F-S interfaces. It appears that the higher percentage of styrene in the latex copolymer greatly influences the surfactant mobility toward the film interfaces. While the effect of latex composition is one factor, higher surface tension of the substrate causes the surfactant groups to migrate toward that interface, in order to compensate for higher interfacial surface tension.

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