

Surface and Interfacial FTIR Spectroscopic Studies of Latexes. XI. The Effect of Sty/*n*-BA Copolymer Composition on the Orientation of SDOSS Surfactant Molecules

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SYNOPSIS

These studies examine how various latex copolymer compositions, ranging from 100% *n*-BA to 50%/50% Sty/*n*-BA, may influence sodium dioctylsulfosuccinate (SDOSS) mobility, diffusion, and orientation near the film-air (F-A) and film-substrate (F-S) interfaces. Polarized attenuated total reflection Fourier transform infrared spectroscopy is utilized to examine the surfactant behavior in Sty/*n*-BA latexes at the F-A and F-S interfaces. Based on the analysis developed for the purpose of these studies, the highest concentration of SDOSS is detected near the F-A interface for 50%/50% Sty/*n*-BA compositions. However, when the content of styrene in Sty/*n*-BA copolymer is diminished, the highest content of SDOSS is detected near the F-S interface. This behavior is particularly evident for 100% poly(*n*-BA) latexes. When SDOSS molecules are near the F-A and F-S interfaces, the SO₃⁻Na⁺ hydrophilic ends are preferentially parallel to the surface, whereas hydrophobic tails are perpendicular. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

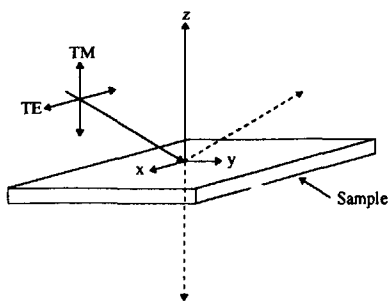
Inherent mobility of surfactant molecules resulting from numerous interfacial effects make possible the migration of these low-molecular-weight species to the film-air (F-A) or film-substrate (F-S) latex interfaces.¹⁻⁷ In spite of the fact that the films are coalesced, migration may occur, and it is often influenced by the amount of remaining water in the film, by free volume, by interfacial surface tensions, and by other interfacial effects. While these factors may or may not have desirable influences on the film properties, the same surfactant molecules can play quite unique roles prior to coalescence. Although it would be desirable to have surfactant molecules attached to the latex surface particles, surfactant molecules are also randomly distributed in a latex aqueous suspension. When dispersed in an aqueous medium, latex particles are deposited on a substrate and undergo a transition from liquid to solid phase. This process inherently introduces ri-

gidity to the system. While the diminished mobility of particles as a result of solvent evaporation is one issue, orientation and geometry changes in the solid state (which may also be influenced by other factors) is another issue. Such factors as H-bonding, hydrophilic and hydrophobic interactions of the latex matrix, water flux, free volume, and interfacial forces,⁸ may in one way or another affect a molecular architecture of the system.

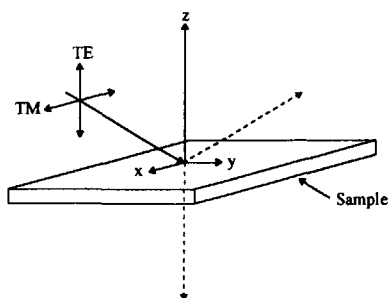
In this context, orientation of molecules with hydrophobic and hydrophilic segments, such as sodium dioctylsulfosuccinate (SDOSS), is important not only from the perspective of understanding structures that develop as a result of coalescence, but also because their behavior may impose numerous practical implications. One can envision that if a hydrophobic end of a surfactant molecule is oriented perpendicular to the F-A and F-S interfaces, surface and interfacial properties will be altered, especially such properties as wettability and adhesion. The same scenario, although with an opposite effect, is anticipated when hydrophilic entities form ordered arrays at the F-A and F-S interfaces.

This study addresses the issues of the orientation and geometry of SDOSS surfactant molecules in

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A: TE polarization (electric vector parallel to the crystal plane)



B: TM polarization (electric vector perpendicular to the crystal plane)

Figure 1 Schematic diagrams of polarization in ATR FTIR: (A) 90° (TE) polarization; (B) 0° (TM) polarization.

polybutyl acrylate (*n*-BA) homopolymer and styrene/butyl acrylate (Sty/*n*-BA) copolymers deposited on polytetrafluoroethylene (PTFE) substrate. Particularly, we are interested in the local arrangements near the F-A and F-S interfaces of SDOSS after latex coalescence. Polarized attenuated total reflection Fourier transform infrared (ATR FTIR) spectroscopy, with the recently developed quantitative algorithm,^{9,10} will be used as a proven tool in identification of local geometries of surfactant molecules.

EXPERIMENTAL

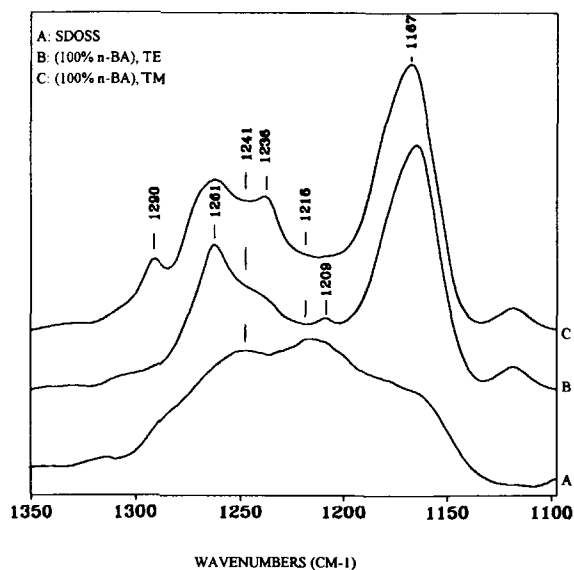
The latex compositions 100% poly(*n*-BA) and 10%/90%, 20%/80%, 30%/70%, 40%/60%, 50%/50% copolymers of Sty/*n*-BA were synthesized by a semicontinuous emulsion polymerization, as described in the previous publication.¹ Liquid latex films were cast on PTFE substrate and allowed to dry in air at 80% relative humidity for 72 h at 22°C. As in the previous studies,¹⁻⁵ films approximately 200 μm thick were prepared for the purpose of this study.

ATR FTIR spectroscopy was used to spectroscopically analyze F-A and F-S interfaces of latex

films. ATR FTIR spectra were recorded on a Digilab FTS-20 instrument equipped with a rectangular ATR attachment (Spectra Tech). In a typical experiment, 200 scans were collected at a resolution of 4 cm⁻¹, recorded at transverse magnetic (TM, 0°) and transverse electric (TE, 90°) polarizations. The rectangular ATR attachment (Spectra Tech) was equipped with a KRS-5 crystal aligned to give an incident beam angle of 45 degrees. All spectra were transferred to an PC-compatible computer for further spectra analysis utilizing Spectra Calc software (Galactic, Inc.). The spectra were corrected for optic effects using the recently published algorithm.^{9,10}

RESULTS AND DISCUSSION

In an effort to spectroscopically establish orientation of the surface species, it is necessary to use polarized light.¹¹ For that reason, polarized ATR FTIR spectra of several Sty/*n*-BA latex compositions were recorded from the F-S and F-A interfaces. A schematic diagram of the experimental setup and definitions of the TM and TE wave vectors are illustrated in Figure 1.¹² The TE polarization is defined as having the electric vector of electromagnetic radiation parallel to the crystal plane [or perpendicular to the plane of incidence; Fig. 1(A)], whereas the TM polarization has the electric vector perpendicular to the ATR crystal plane [Fig. 1(B)].

**Figure 2** ATR FTIR spectra of (A) pure SDOSS; (B) 100% *n*-BA with TE polarization, F-S interface; (C) 100% *n*-BA with TM polarization, F-S interface.

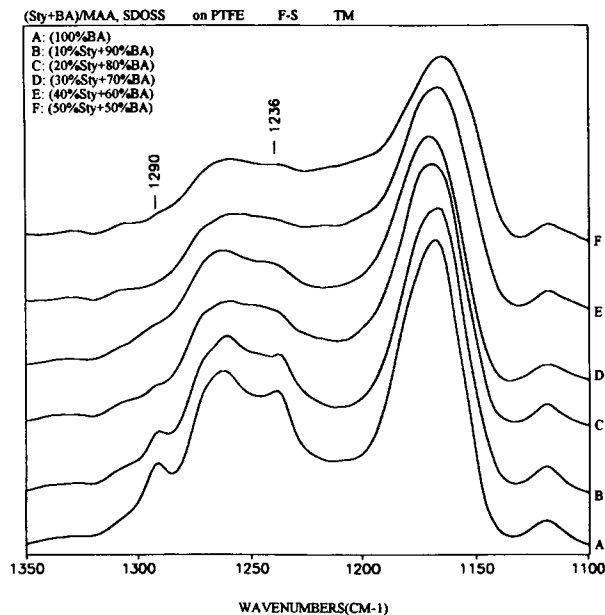


Figure 3 ATR FTIR spectra of S—O asymmetric stretching vibrations with TM polarization of (Sty/*n*-BA) latex copolymers at F-S: (A) 100% *n*-BA; (B) 10%/90% Sty/*n*-BA; (C) 20%/80% Sty/*n*-BA; (D) 30%/70% Sty/*n*-BA; (E) 40%/60% Sty/*n*-BA; (F) 50%/50% Sty/*n*-BA.

With these definitions in mind, let us analyze ATR FTIR spectra in the 1350–1100 cm^{-1} region of 100% *n*-BA latex recorded from the F-S interface, shown in Figure 2. According to trace (A), which illustrates the spectrum of pure SDOSS surfactant, the two bands at 1241 and 1216 cm^{-1} are due to the C—O and S—O asymmetric stretching modes,¹³ respectively. The situation changes, however, when SDOSS is surrounded by the copolymer latex environment. Surprisingly, for the TE polarization [trace (B)], there are two bands enhanced at 1261 and 1209 cm^{-1} . In contrast, the bands at 1290 and 1236 cm^{-1} are enhanced in TM polarization [trace (C)]. Because the $\text{SO}_3^- \text{Na}^+$ hydrophilic groups of SDOSS form H-bonding with COOH of latex copolymer and H_2O , a local geometry of the $\text{SO}_3^- \text{Na}^+$ environment changes, as compared to the undisturbed $\text{SO}_3^- \text{Na}^+$ environment. Due to the H-bonding associations, the undisturbed S—O asymmetric stretching vibrations at the 1216 cm^{-1} band in pure SDOSS [Fig. 2, trace (A)] splits to two S—O asymmetric stretching vibrations at 1261 and 1209 cm^{-1} when SDOSS is in the latex environment. This observation is consistent with the previous findings for the S—O symmetric stretching vibrations at 1050 cm^{-1} . This band splits into two bands at 1056 and 1046 cm^{-1} due to the H-bonding asso-

ciations with the acid groups and H_2O , respectively.¹ The same situation accounts for the splitting of the band at 1241 cm^{-1} due to the C—O asymmetric stretching modes of the undisturbed surfactant, which splits into two bands at 1290 and 1236 cm^{-1} as a result of H-bonding associations.¹⁴ The band at 1167 cm^{-1} in Figure 2, trace (A), is due to the C—O—C ester vibrational modes of the ester groups in SDOSS, and overlaps with the band at 1167 cm^{-1} due to ester groups in the butyl acrylate segments in latex copolymer.

As illustrated in Figure 2, the spectra recorded with TM and TE polarizations result in the intensity changes, indicating that the hydrophilic SDOSS ends have preferential surface orientations. Before we establish the origin of the orientation changes of the hydrophilic $\text{SO}_3^- \text{Na}^+$ groups, it seems appropriate to identify how hydrophobic or hydrophilic components of the latex may affect the $\text{SO}_3^- \text{Na}^+$ orientation. For that reason we modified the latex composition and examined the effect of Sty/*n*-BA ratio on the S—O asymmetric band intensities. Figure 3 illustrates a series of the TM polarization spectra recorded from the F-S interfaces for various Sty/*n*-BA compositions. It appears that an increase of the Sty content results in significantly weaker intensities of the S—O stretching bands. Due to a hydrophobic nature of the copolymer latex induced

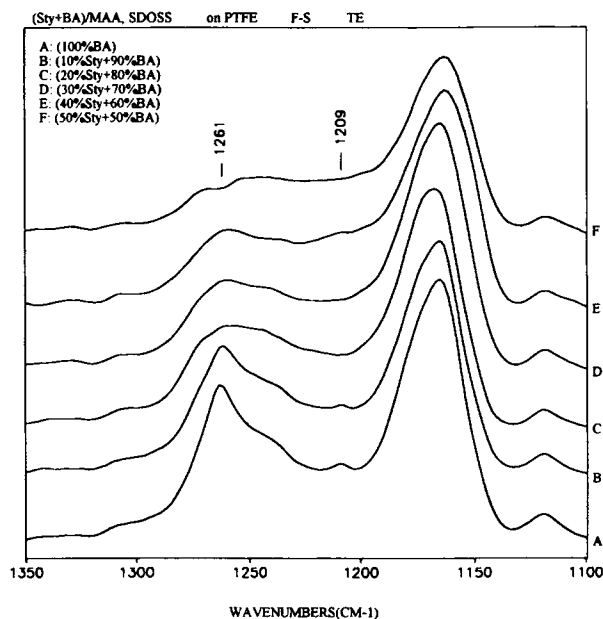


Figure 4 ATR FTIR spectra of S—O asymmetric stretching vibrations with TE polarization of Sty/*n*-BA latex copolymers at F-S: (A) 100% *n*-BA; (B) 10%/90% Sty/*n*-BA; (C) 20%/80% Sty/*n*-BA; (D) 30%/70% Sty/*n*-BA; (E) 40%/60% Sty/*n*-BA; (F) 50%/50% Sty/*n*-BA.

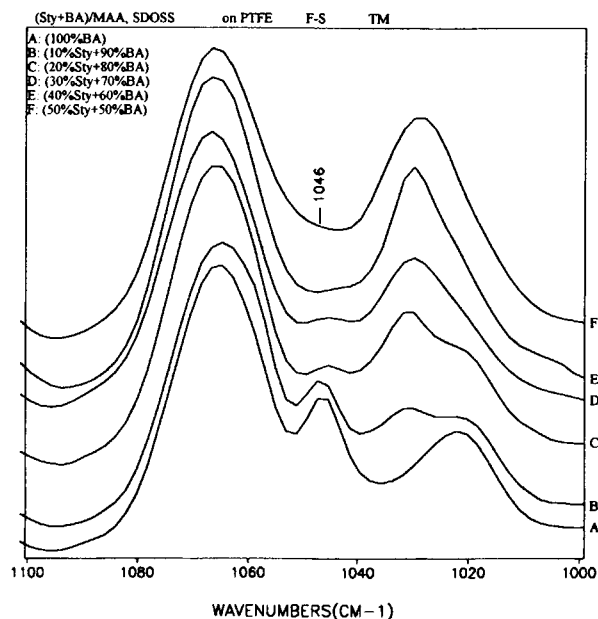


Figure 5 ATR FTIR spectra of S—O symmetric stretching vibrations with TM polarization of Sty/*n*-BA latex copolymers at F-S: (A) 100% *n*-BA; (B) 10%/90% Sty/*n*-BA; (C) 20%/80% Sty/*n*-BA; (D) 30%/70% Sty/*n*-BA; (E) 40%/60% Sty/*n*-BA; (F) 50%/50% Sty/*n*-BA.

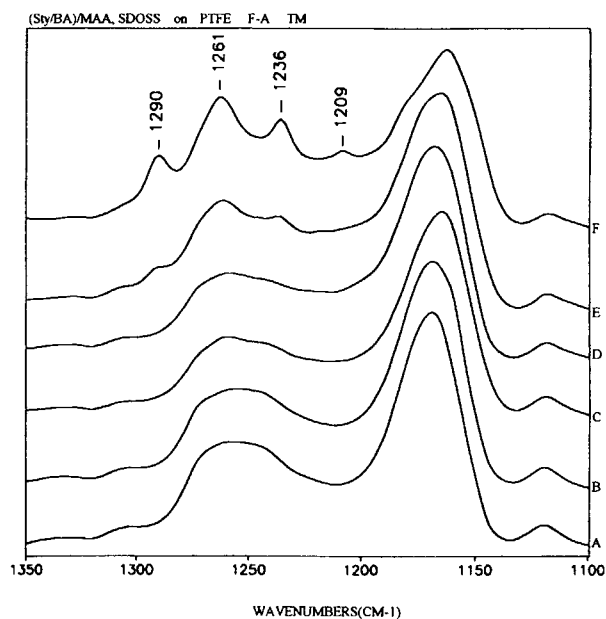


Figure 7 ATR FTIR spectra of S—O asymmetric stretching vibrations with TM polarization of Sty/*n*-BA latex copolymers at F-A: (A) 100% *n*-BA; (B) 10%/90% Sty/*n*-BA; (C) 20%/80% Sty/*n*-BA; (D) 30%/70% Sty/*n*-BA; (E) 40%/60% Sty/*n*-BA; (F) 50%/50% Sty/*n*-BA.

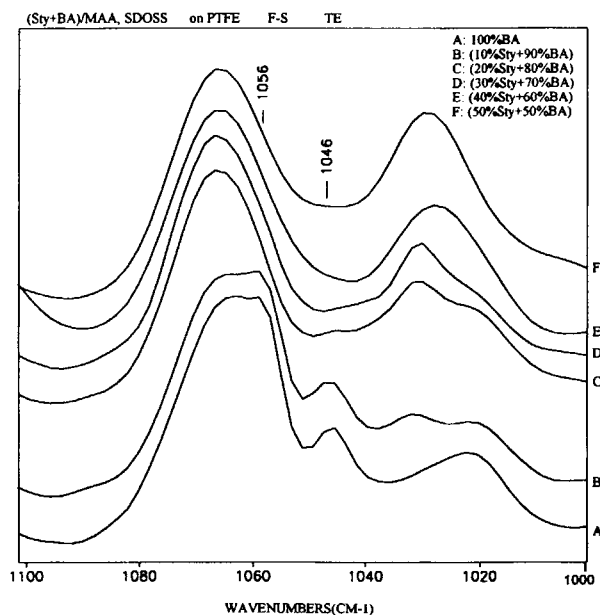


Figure 6 ATR FTIR spectra of S—O symmetric stretching vibrations with TE polarization of Sty/*n*-BA latex copolymers at F-S: (A) 100% *n*-BA; (B) 10%/90% Sty/*n*-BA; (C) 20%/80% Sty/*n*-BA; (D) 30%/70% Sty/*n*-BA; (E) 40%/60% Sty/*n*-BA; (F) 50%/50% Sty/*n*-BA.

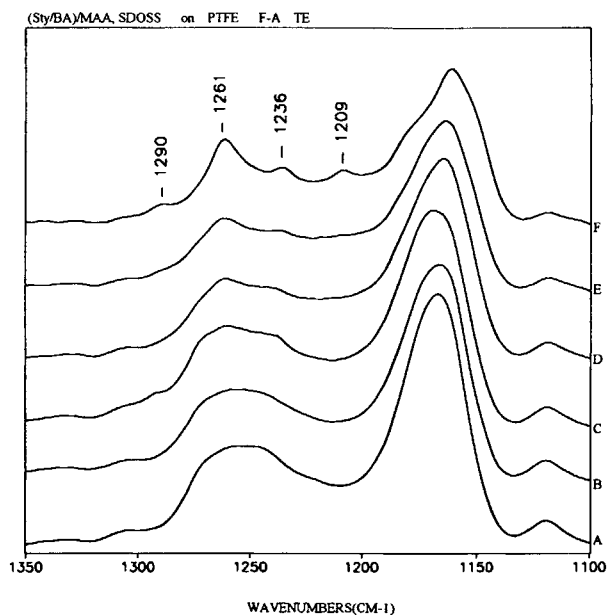


Figure 8 ATR FTIR spectra of S—O asymmetric stretching vibrations with TE polarization of Sty/*n*-BA latex copolymers at F-A interface: (A) 100% *n*-BA; (B) 10%/90% Sty/*n*-BA; (C) 20%/80% Sty/*n*-BA; (D) 30%/70% Sty/*n*-BA; (E) 40%/60% Sty/*n*-BA; (F) 50%/50% Sty/*n*-BA.

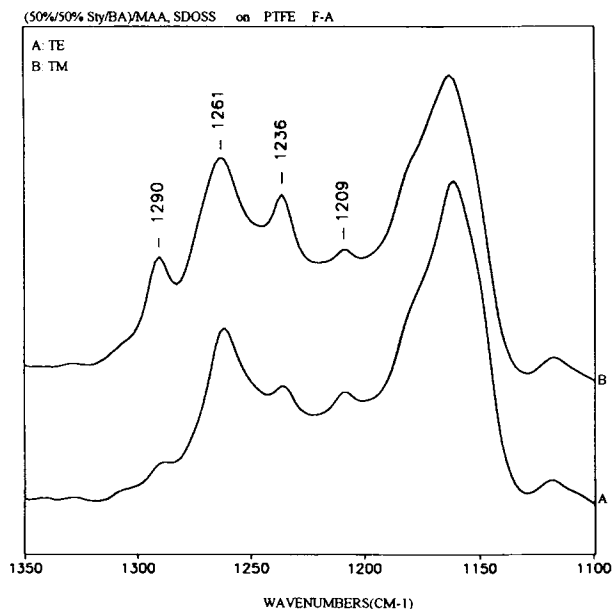


Figure 9 ATR FTIR spectra of 50%/50% Sty/*n*-BA latex copolymer with two polarizations at F-A interface: (A) TE; (B) TM.

by the Sty component and the presence of hydrophilic $\text{SO}_3^- \text{Na}^+$ groups, this behavior is not surprising. Based on the analysis of the TE-polarized ATR FTIR spectra recorded from the F-S interface, the intensities of the 1261 and 1209 cm^{-1} bands decrease with the increasing styrene content. This is shown in Figure 4, traces (A) through (F). All spectra were normalized against the 841 cm^{-1} band (not shown).¹⁴ As shown later, as the styrene content increases, more surfactant molecules are exuded toward the F-A interface. Since the 1290 and 1236 cm^{-1} bands are enhanced in the spectrum recorded with TM polarization [Fig. 2, trace (C)], hydrophobic segments of the surfactant molecules are preferentially perpendicular to the F-S interface. However, the bands at 1261 and 1209 cm^{-1} are enhanced in the TE polarization, indicating that the hydrophilic $\text{SO}_3^- \text{Na}^+$ ends on the surfactant molecules are preferentially parallel.

Let us examine the spectral changes, detected in the S—O symmetric stretching region, which are illustrated in Figure 5, traces (A) through (F). The spectra were recorded using a TM polarization. Similar to the data for the S—O asymmetric region, the 1046 cm^{-1} band, due to $\text{SO}_3^- \text{Na}^+$ groups associated with water, decreases as the styrene content increases. As we recall our previous studies,²⁻⁷ the band at 1056 cm^{-1} results from the $\text{SO}_3^- \text{Na}^+ \cdots \text{HOOC}$ associations, and was not detected at the F-S interface when TM polariza-

tion was employed. However, when polarization changes from TM to TE, the two bands at 1046 and 1056 cm^{-1} are detected for the latex films containing less than 20% Sty. This is illustrated in Figure 6, which depicts a series of the spectra recorded from the F-S interface using TE polarization for the same latex compositions as the ones reported in Figure 5. Traces (A) and (B) indeed show two pronounced bands due to S—O stretching modes, resulting from $\text{SO}_3^- \text{Na}^+ \cdots \text{H}_2\text{O}$ (1046 cm^{-1}) and $\text{SO}_3^- \text{Na}^+ \cdots \text{HOOC}$ (1056 cm^{-1}) associations.

The results obtained from the F-A interface appear to follow similar trends as far as the orientation of hydrophilic $\text{SO}_3^- \text{Na}^+$ entities is concerned. The major difference is the effect of latex composition. The surfactant exudation is pronounced at slightly higher styrene content, approximately 40%/60% Sty/*n*-BA, as opposed to the 10%/90% Sty/*n*-BA compositions for the F-S interface. One factor that influences the surfactant exudation during latex coalescence is the glass transition temperature (T_g) of latex copolymers. T_g of poly(*n*-BA) is approximately -50°C and increases with the increasing Sty content in the latex particle composition. When T_g of the latex copolymers increases, the rate of latex coalescence is increased in comparison with lower-

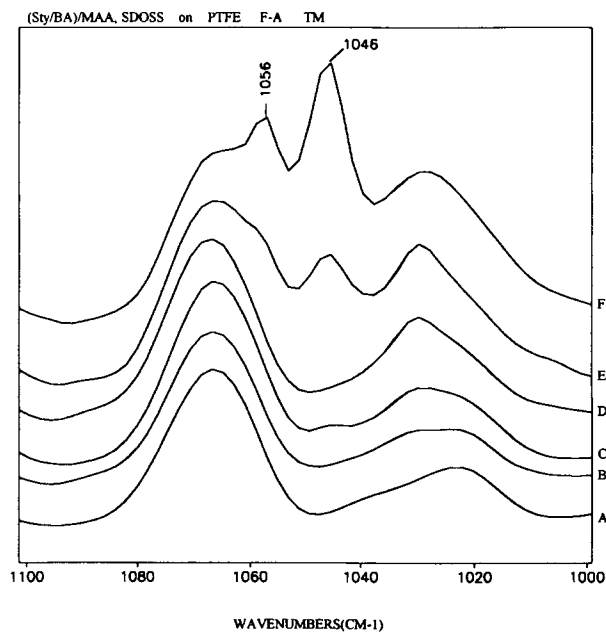


Figure 10 ATR FTIR spectra of S—O symmetric stretching vibrations with TM polarization of Sty/*n*-BA latex copolymers at F-A interface: (A) 100% *n*-BA; (B) 10%/90% Sty/*n*-BA; (C) 20%/80% Sty/*n*-BA; (D) 30%/70% Sty/*n*-BA; (E) 40%/60% Sty/*n*-BA; (F) 50%/50% Sty/*n*-BA.

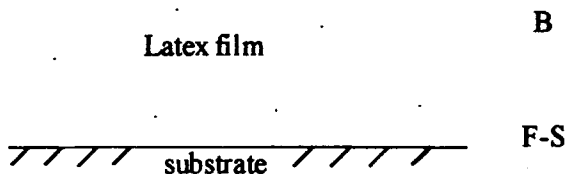
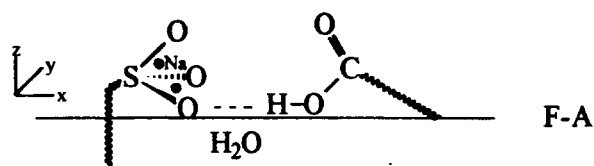
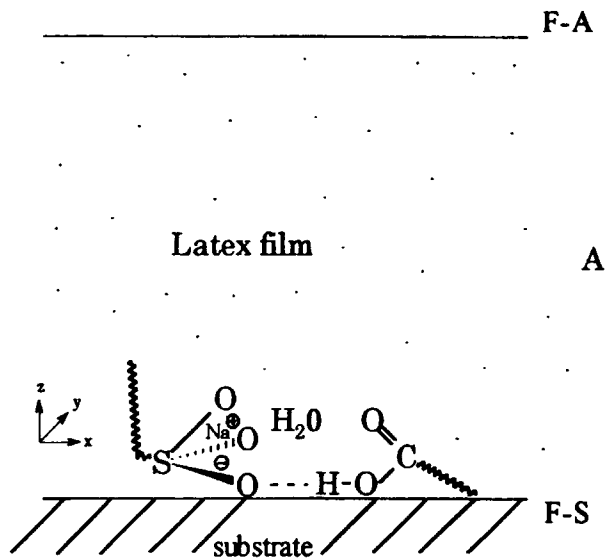


Figure 11 Geometric diagrams of SDOSS end group associated with acid group and H₂O: (A) S—O bonds lying out-of-plane, F-S; (B) S—O bonds lying out-of-plane, F-A; (C) S—O bonds lying in-plane and upward to film, F-A.

T_g latex copolymers, allowing migration of surfactant molecules which are carried out to the F-A interface by water evaporating out of the film. Because higher-*T_g* copolymers have less free volume available as a host side for SDOSS, and higher hydrophobicity due to Sty content is introduced, expulsion of H₂O from the latex interstices will be enhanced.

Another force influencing surfactant migration is the surface tension of a substrate.¹⁻⁷ It appears,

however, that the effect of surface tension of a substrate is diminished because surfactant molecules are unable to diffuse toward the F-S interface. The highest SDOSS content is detected for 40%/60% and 50%/50% Sty/*n*-BA compositions near the F-A interface. The copolymers with lower *T_g*, however, exhibit an excess of free volume that allows H₂O molecules to stay longer in the latex, resulting in a slower rate of latex coalescence. Therefore, SDOSS molecules, which are carried out towards the F-A interface, are able to diffuse towards the F-S interface during latex coalescence. Thus, a higher SDOSS content is detected for the 100% *n*-BA and 90%/10% Sty/*n*-BA latex compositions near the F-S interface.

Analysis of Figure 7, which illustrates a series of ATR FTIR spectra recorded from the F-A interface, shows that the bands at 1290 and 1236 cm⁻¹ are detected at the F-A interface with TM. However, the enhancement of the 1261 and 1209 cm⁻¹ bands is observed when the spectra are recorded with TE polarizations, as shown in Figure 8. Examination of the band intensity changes resulting from the polarization experiments indicates that, for TM polarization, the 1290 and 1236 cm⁻¹ bands are significantly stronger. The 1261 and 1209 cm⁻¹ bands, however, are stronger in TE polarization. These observations indicate that there is a preferential parallel orientation of the SO₃⁻Na⁺ groups near the F-A interface. Figure 9 shows the intensity enhancements of the 1290, 1261, 1236, and 1209 cm⁻¹ bands

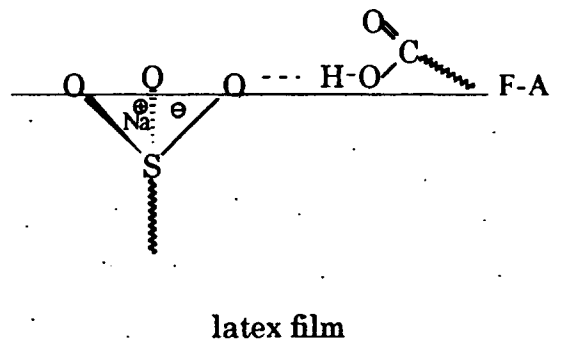


Figure 11 (Continued)

at F–A interface for TE (trace A) and TM (trace B) polarizations.

Temporarily postponing the analysis of these results, let us examine how the S—O symmetric stretching bands change with latex compositional changes. Figure 10 illustrates that for the 50%/50% Sty/*n*-BA composition, the intensity of the 1046 cm^{-1} band increases. However, in addition to the presence of this band, the 1056 cm^{-1} band is detected, which is strongly pronounced for the 50%/50% Sty/*n*-BA ratio. As we recall the results from Figure 5, it appears that the behavior of the 1046 cm^{-1} band is just opposite: the band increases at the F–A interface as the concentration of the latex reaches 100% *n*-BA. Although the magnitude of the two processes is significantly different, our future studies will address these issues again.¹⁵ In addition, the 1056 cm^{-1} band is also detected at the F–A interface when the spectra are recorded with TM polarization. This is illustrated in Figure 10.

Based on the presented data, it is apparent that the $\text{SO}_3^- \text{Na}^+$ groups are not randomly oriented at the interfaces, and the following scenario for the surfactant surface orientation as a function of latex composition can be proposed. When surfactant molecules exude to the F–S and F–A interfaces, they may take certain orientations which depend upon the copolymer environment. As illustrated in Figure 11(A), surfactant molecules can be out-of-plane near the F–S interface, forming associations with the acid groups along the *x*-direction. If we now return to the results presented in Figures 7–9, and realize that the 1261, 1209, and 1056 cm^{-1} bands are enhanced in the spectra recorded from the F–S interface with TE polarization for the latex compositions with a low styrene content, it is apparent that hydrophilic $\text{SO}_3^- \text{Na}^+$ ends of H-bonding surfactant molecules are preferentially out-of-plane. In contrast, the 1290 and 1236 cm^{-1} bands are more pronounced with the TM polarization, suggesting that the hydrophobic ends of surfactant molecules are preferentially in-plane with respect to the surface. A schematic representation of the orientation changes is illustrated in Figure 11(A) and agrees with our previous findings.⁶ When SDOSS surfactant molecules exude to the F–A interface, the $\text{SO}_3^- \text{Na}^+$ groups that are associated with the COOH acid groups may form the surface arrays with hydrophilic ends parallel to the surface, while hydrophobic ends of SDOSS maintain their perpendicular position. The former, however, is a function of the latex composition, and for a higher Sty content, the $\text{SO}_3^- \text{Na}^+$ groups may be perpendicular. This is

schematically illustrated in Figures 11(B) and 11(C), respectively.

CONCLUSIONS

It appears that the hydrophilic $\text{SO}_3^- \text{Na}^+$ ends on SDOSS molecules are preferentially parallel to the latex surface, whereas hydrophobic ends are preferentially perpendicular near the F–S interface. In contrast, the hydrophilic $\text{SO}_3^- \text{Na}^+$ ends have no preferential parallel and perpendicular orientation to the film, and the hydrophobic ends are preferentially perpendicular to the latex film at F–A interface. These effects may have a significant influence on the macroscopic properties of latex films, such as adhesion, wettability, and photolytic stability.

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