

Surface and Interfacial Fourier Transform Infrared Spectroscopic Studies of Latexes. XIV. Surface Phase Separation in Polystyrene/Poly-*n*-Butyl Acrylate Latex Films

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SYNOPSIS

This study focuses on the behavior of sodium dioctylsulfosuccinate (SDOSS) in 50/50 w/w % polystyrene/poly(butyl acrylate) (p-Sty/p-BA) latex films. Specifically, mobility and orientation are examined in the context of the film formation by the use of dynamic mechanical thermal analysis and attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy. While for the homopolymer blends of p-Sty and p-BA, two T_g values resulting from a phase separation of p-Sty and p-BA phases are observed, only a single T_g is detected for a copolymer of the same mixture, indicating a single phase within the film. ATR FTIR spectroscopic data indicate that the phase separation of p-Sty and p-BA blends does not occur uniformly across the film. After coalescence, p-Sty particles produce a significant degree of stratification at approximately $1.6 \mu\text{m}$ from the film surface. At this depth, the polystyrene rings assume preferentially parallel orientation to the film surface. At the same time, the hydrophilic groups of SDOSS surfactant ($\text{SO}_3^- \text{Na}^+$) are oriented preferentially parallel to the surface. Under high relative humidity conditions, water is able to diffuse into the film and swells the surface layers, thus causing them to expand. As a result, the top, predominately poly-*n*-BA surface becomes "thicker," and p-Sty phase appears to be near $2.3 \mu\text{m}$ from the surface. The polystyrene rings maintain their preferential parallel orientation to the surface, but the hydrophilic groups of SDOSS are able to diffuse into the film with the water uptake and are thus not present at the film-air interface. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Recently, we¹⁻¹³ have examined the behavior of sodium dioctylsulfocussinate (SDOSS) surfactant molecules in latex matrices. Although the primary focus of these studies was to examine surface and interfacial structures formed on ethyl acrylate/methacrylic (EA/MAA) and styrene/*n*-butyl acrylate (Sty/*n*-BA) latex copolymers, it became apparent that the surfactant mobility and structural changes of SDOSS after coalescence near the film-air (F-A) and film-substrate (F-S) interfaces may alter numerous properties. Because latex particles before coalescence exhibit random distribution of copolymerized individual monomers, a logical extension

of these studies is the determination of the interfacial properties of homopolymer mixtures. For this reason, we have chosen to examine the behavior of a mixture of separately homopolymerized polystyrene (p-Sty) and poly(butyl acrylate) (p-BA) latex dispersions mixed in equal volumes and allowed to coalesce. The choice of polymerizing separate batches of homopolymers of p-Sty and p-BA dispersions mixed in a 1 : 1 ratio was dictated by the fact that it allowed us to create an environment facilitating the determination of factors affecting the film formation.

Because of hydrophobicity differences of the latex components and transient effects affecting dispersion stability, several issues are of special interest in this study. For example, if a colloidal suspension tends to form aggregates before coalescence, the size and degree of aggregation may influence the distribution and mobility of individual homopolymer

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components. In the case of the p-Sty/p-BA homopolymer mixture, we will use attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy¹⁴ by monitoring the intensity changes of the 700 cm^{-1} band resulting from the aromatic out-of-plane C—H normal deformation modes.¹⁵ This may allow us to follow the behavior of the p-Sty component in p-Sty/p-BA latex film. Furthermore, the bands at 1,046 and 1,056 cm^{-1} , resulting from the splitting of the S—O stretching band at 1,050 cm^{-1} due to the $\text{SO}_3^- \text{Na}^+$ hydrophilic groups of SDOSS, will serve for tracing SDOSS near the F-A and F-S interfaces, allowing us to identify the interfacial composition and structural changes at various surface depths.

EXPERIMENTAL

n-Butyl acrylate (*n*-BA) and styrene (Sty) monomers were individually polymerized following previously outlined procedures.¹³ After the synthesis of separate batches, p-BA and p-Sty homopolymer suspensions were mixed in a 50/50 w/w % ratio, stirred, and stored for 3 days before coalescence. Such latex mixtures were deposited in a polytetrafluoroethylene (PTFE) mold to achieve a film thickness ranging from 100 to 150 μm and allowed to coalesce for 72 h under 40 or 100% relative humidities (RH).

ATR FTIR spectra were recorded on a Mattson Sirius 100 spectrometer equipped with a variable angle rectangular ATR attachment (Spectra Tech) with a KRS-5 crystal. Typically, 200 coadded sample scans were acquired at a resolution of 4 cm^{-1} and ratioed against the same number of scans of a single-beam spectrum of an empty ATR cell. Polarization of the IR radiation was accomplished with a Specac 12000 IR polarizer that was placed directly in the beam path and adjusted to the desired polarization. All spectra were corrected for optical distortions by the use of recently developed algorithms, allowing for simultaneous corrections for optical effects of strong and weak bands.¹⁵

Dynamic mechanical thermal analysis (DMTA) measurements were performed on a DMTA Mk-2 instrument (Polymer Laboratories Inc.) set at 5 Hz oscillating frequency. Each latex film, approximately 23 mm in length, was placed between a stationary clamp and a movable clamp. Initial parameters used were as follows: force = 0.1 N, strain \times 4, and a heating rate of 3°C/min.

RESULTS AND DISCUSSION

In our previous studies,¹⁻¹³ we focused on the 1,046 and 1,056 cm^{-1} bands which result from the splitting of the S—O stretching band at 1,050 cm^{-1} in $\text{SO}_3^- \text{Na}^+$ surfactant hydrophilic groups. Although in the case of a 50/50 p-Sty/p-BA mixture, we are particularly interested in the surfactant distribution across the film, stratification processes which may occur during and after coalescence are also of interest. In particular, the simultaneous presence of hard p-Sty and soft p-BA particles in latex aqueous suspensions appears to be an important factor. With this in mind, let us examine a series of ATR FTIR spectra obtained from the F-A interface of a 50/50 mixture of p-Sty/p-BA latex films. Figure 1, Traces A through E, illustrates the spectra recorded from the same specimen with transverse magnetic (TM) polarized light, obtained at angles of incidence between 60 and 40°. Such choice of the incidence angles was dictated by the fact that such a range allows us to vary the depth of penetration of light into the film from 1.3 to 2.3 μm . Therefore, molecular level information from different depths can be obtained. By using appropriate values of the optical constants for a KRS-5 crystal and knowing the refractive

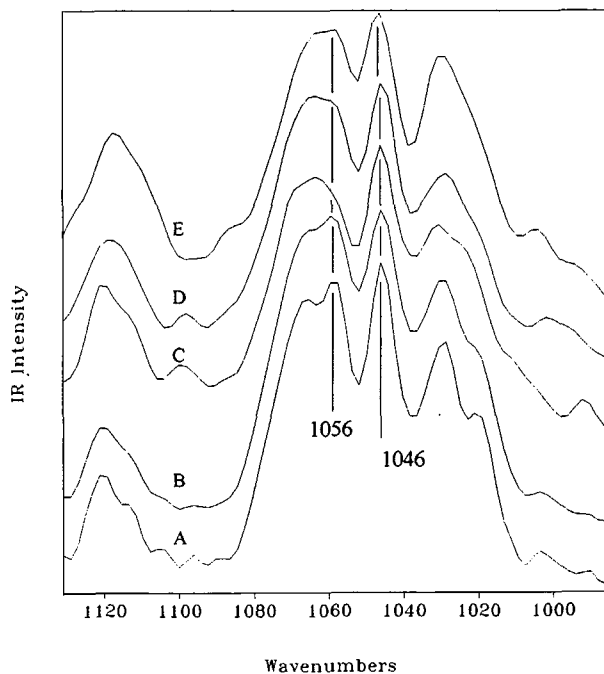


Figure 1 ATR FTIR spectra in the 950–1,150 cm^{-1} region, recorded at the F-A interface (TM polarization) of a 50/50 p-Sty/p-BA latex film coalesced under ambient conditions, at various angles of incidence. (A) 1.3 μm , (B) 1.4 μm , (C) 1.6 μm , (D) 1.9 μm , (E) 2.3 μm .

properties of a specimen in a nonabsorbing region, the penetration depths ranging from 1.3 to 2.3 μm into the surface can be examined.

Analysis of the spectra shown in Figure 1 shows that, while going from 1.3 to 2.3 μm depths into the F-A interface, the intensity of the S—O stretching bands, resulting from the presence of the $\text{SO}_3^- \text{Na}^+$ entities associated with H_2O and acid groups at 1,046 and 1,056 cm^{-1} , decreases with the increasing depth. At 1.6 μm (Trace C), the 1,056 cm^{-1} band is not detected, and the 1,046 cm^{-1} band continues to decrease at greater depths (Traces D and E). At the same time, the intensity of the 700 cm^{-1} band changes in such a way that the band reaches its maximum around 1.6 μm from the top surface layer (Fig. 2, Trace C). What is even more interesting is that, for the spectra recorded by the use of transverse electric (TE) polarization (Fig. 3, Traces A–E), the strongest intensity of the 700 cm^{-1} band is also detected around 1.6 μm , and the band is more pronounced in the TE polarization. Considering the fact that the 700 cm^{-1} band is due to the aromatic out-of-plane C—H normal deformation modes in Sty, these experiments indicate that styrene rings as well as the $\text{SO}_3^- \text{Na}^+$ hydrophilic groups exhibit prefer-

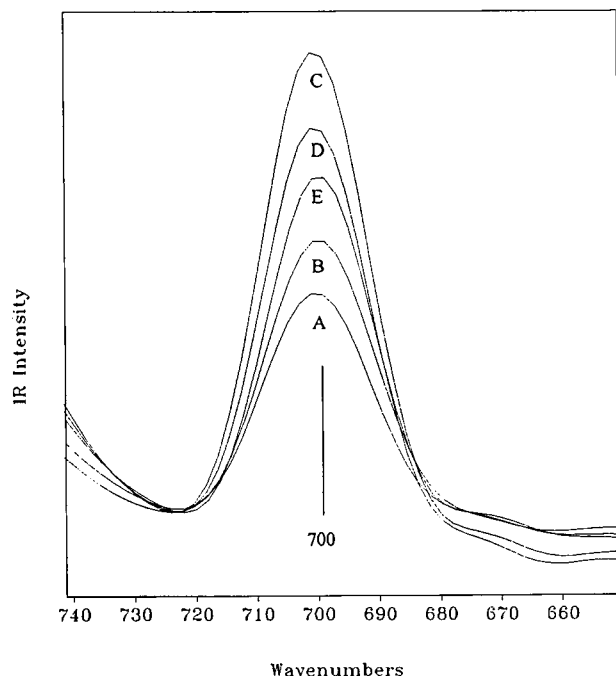


Figure 2 ATR FTIR spectra in the 650–750 cm^{-1} region, recorded at the F-A interface (TM polarization) of a 50/50 p-Sty/p-BA latex film coalesced under ambient conditions, at various angles of incidence. (A) 1.3 μm , (B) 1.4 μm , (C) 1.6 μm , (D) 1.9 μm , (E) 2.3 μm .

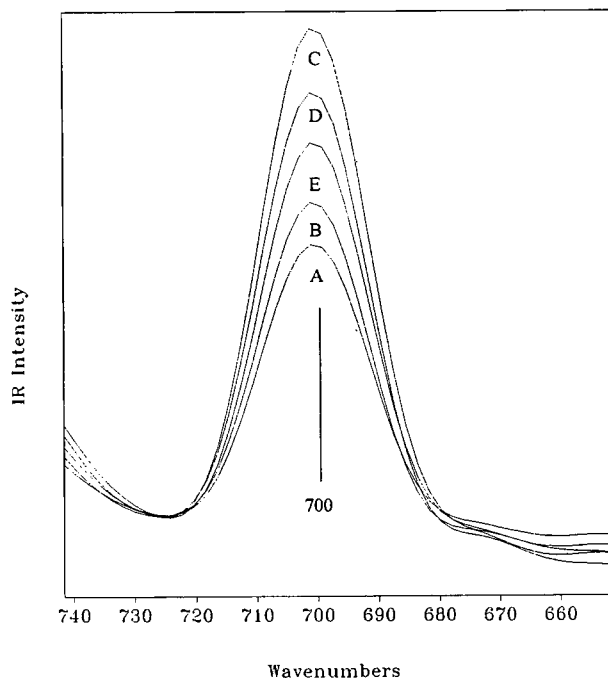


Figure 3 ATR FTIR spectra in the 650–750 cm^{-1} region, recorded at the F-A interface (TE polarization) of a 50/50 p-Sty/p-BA latex film coalesced under ambient conditions, at various angles of incidence. (A) 1.3 μm , (B) 1.4 μm , (C) 1.6 μm , (D) 1.9 μm , (E) 2.3 μm .

ential orientation near the surface. Whereas the $\text{SO}_3^- \text{Na}^+$ groups are parallel near the surface, the styrene rings of the p-Sty phase also appear to be parallel, at depths around 1.6 μm from the surface. This is schematically shown in Figure 4 (A).

In view of the above observations and considering our previous data pertaining to the behavior of the $\text{SO}_3^- \text{Na}^+$ groups of SDOSS, one of the puzzling issues is the intensity changes of the 700 cm^{-1} band. Because this band can serve as a probe for p-Sty behavior, let us examine if there are changes in the p-Sty content as a function of the coalescence time at various surface depths. For that reason, we followed the intensity changes of the 700 cm^{-1} band over a period of time at various angles of incidence. Figure 5 illustrates Sty intensity changes as a function of depth from the surface from 24 to 72 h. After 24 h, the Sty intensity increases at greater depths. After 40 h, at the shallower depths, ranging from 1.3 to 1.6 μm , the 700 cm^{-1} band further increases. The 700 cm^{-1} band reaches its maximum at 1.6 μm from the F-A interface after 56 h and, at depths beyond 1.6 μm , continues to decrease with the increasing penetration depths. The same trend is found in the F-A interface spectra recorded 72 h after coalescence. However, when the penetration

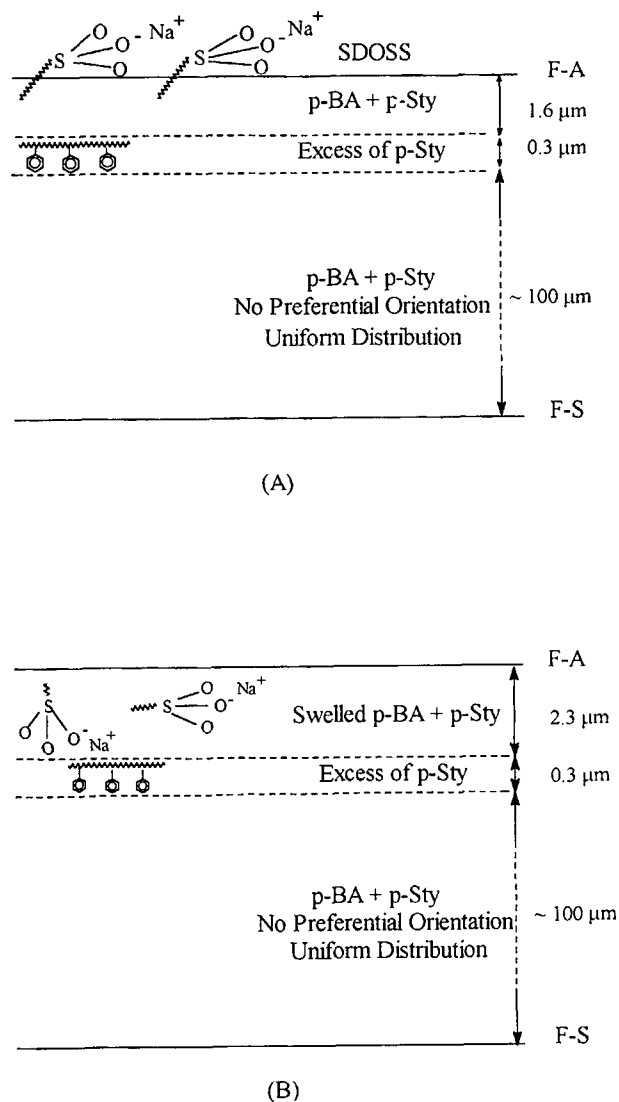


Figure 4 Schematic representation of the processes in a 50/50 w/w % p-Sty/p-BA latex film. (A) 40% RH, (B) 100% RH.

depth reaches approximately $2 \mu\text{m}$ (corresponding to a 43° angle of incidence), the band intensities converge for both polarizations. Although from the latex film formation point of view, it is apparent that there are changes in the latex composition across the film, at this point, one should realize that the effect of critical angle needs to be addressed. The question arises if the results presented here are not affected by the optical distortions resulting from a proximity of the critical angle.^{14,15} For that reason, we measured the refractive index of the latex films in the nonabsorbing region. It appears that the refractive index is 1.53 ± 0.01 . This value of refractive index gives a critical angle of 40° and, solving over the spectral range of interest, gives a critical angles

between 39.6 and 40.5° . Thus, the data convergence at 43° is not affected by the proximity of the critical angle and results from coalescence. In contrast, the 700 cm^{-1} band showed no intensity changes at the F-S interface for either the TM or TE polarizations, indicating that stratification of Sty occurs only near the F-A interface.

Although on the basis of the data presented here, it is quite apparent that there is a preferential phase separation near the F-A interface, let us utilize DMTA and examine the $\tan \delta$ values as a function of temperature. Their maximum values represent a glass transition temperature (T_g) of a polymer.¹⁶ Analysis of the DMTA $\tan \delta$ curves (not shown) for the 50/50 p-Sty/p-BA latex mixture indicates the presence of two T_g values at -52°C and at 98°C , indicating the presence of two separate phases within the latex film. While the T_g of -52°C is due to the p-BA latex component in a mixture, the 98°C T_g is that of p-Sty. These observations indicate that, at this stage of coalescence, the two latex homopolymers in the mixture do not coalesce into a uniform network, and although DMTA data indicate that the separation occurs, these, and for that matter any other measurements, are unable to distinguish which portion of the film is phase separated. In contrast, ATR FT-IR surface depth profiling experiments near the F-A interfaces clearly demonstrate nonhomogeneity in the direction perpendicular to the film plane. Thus, the presence of two separate T_g values results from stratification near the F-A interface. It should be noted that there are numerous studies dealing with the phase separation in polymers; however, to our best knowledge, this is the first approach actually showing where, with respect to the rest of the film, the phase separation occurs.

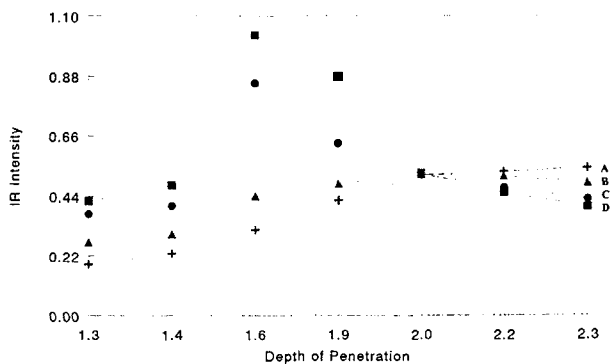


Figure 5 Relative intensities of the 700 cm^{-1} band at the F-A interface (TE polarization) at various surface depths as a function of time. (A) 24 h, (B) 40 h, (C) 56 h, (D) 72 h.

The above data demonstrate that the 50/50 p-BA/p-Sty latex film is a nonuniform composite of soft and hard particles near the F-A interface, and hydrophobic and hydrophilic particles of the composite latex will facilitate different interactions of the individual components. Therefore, the ability of water uptake can be used as a means of altering these interactions. For this reason, we exposed coalesced 50/50 p-Sty/p-BA latex films at 100% RH for 72 h. Figure 6 illustrates a series of the ATR FT-IR spectra recorded with TM polarization from the surface depths ranging from 1.3 to 2.3 μm . A comparison of the results for the latex exposed to 100% RH (Fig. 6), with the data shown in Figure 1 (40% RH), indicates that, on exposure to humidity, the bands of 1,046 and 1,056 cm^{-1} , characteristic of SDOSS, are not detected. Furthermore, the band due to p-Sty at 700 cm^{-1} appears to be significantly weaker (Fig. 7, Traces A-E). Furthermore, under 100% RH, this band reaches its maximum intensity at approximately 2.3 μm from the F-A interface (Fig. 7, Trace E). As we recall, a maximum intensity of 40% RH was detected near 1.6 μm for the F-A interface.

On the basis of these experiments, it is obvious that when the latex films are exposed to 100% humidity, water uptake occurs. Furthermore, because

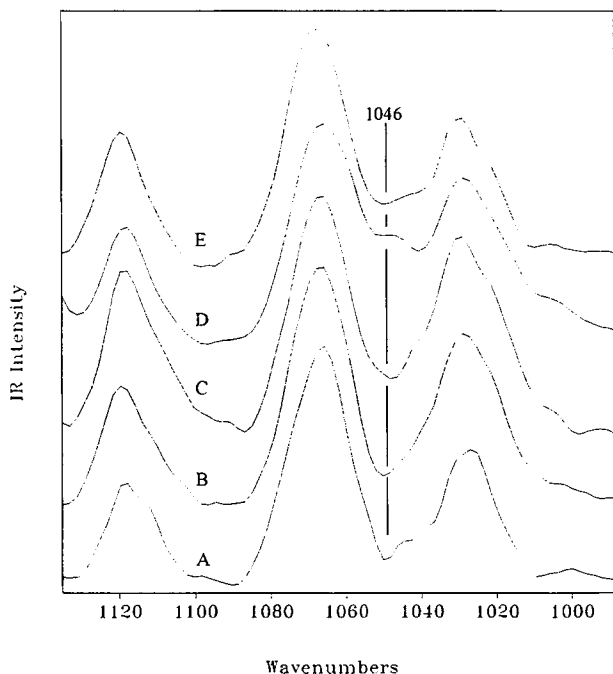


Figure 6 ATR FTIR spectra in the 950–1,150 cm^{-1} region, recorded at the F-A interface (TM polarization) of a 50/50 p-Sty/p-BA latex film coalesced under 100% humidity, at various angles of incidence. (A) 1.3 μm , (B) 1.4 μm , (C) 1.6 μm , (D) 1.9 μm , (E) 2.3 μm .

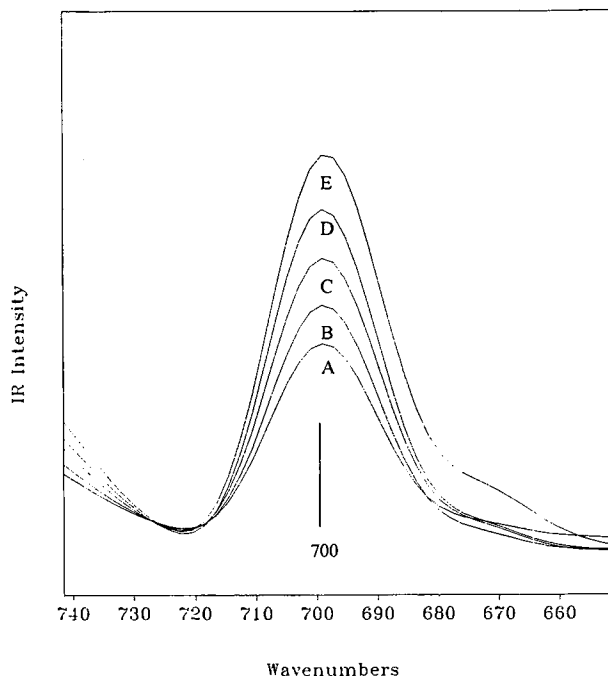


Figure 7 ATR FTIR spectra in the 650–750 cm^{-1} region, recorded at the F-A interface (TM polarization) of a 50/50 p-Sty/p-BA latex film coalesced under 100% humidity, at various angles of incidence. (A) 1.3 μm , (B) 1.4 μm , (C) 1.6 μm , (D) 1.9 μm , (E) 2.3 μm .

surfactant molecules are water soluble, their removal from the surface is attributed to the fact that water penetrates the network, thus allowing SDOSS molecules to diffuse into it. This process is facilitated by an excess of the free volume at the temperature of the experiment (27°C), because the T_g of the p-BA phase is -52°C and the T_g of the p-Sty phase is 98°C . Because p-BA has substantially greater amounts of the free volume, it is a medium for water uptake and, subsequently, enhanced diffusion of SDOSS molecules. While this behavior of SDOSS under given conditions is anticipated, the diminished intensity of the 700 cm^{-1} band due to the p-Sty phase is somewhat surprising. However, when water diffuses into the film, the top p-BA surface layer can be plasticized by water, which results in swelling it. Thus, the effective thickness of the p-BA layer increases as the result of water intake, and this phenomenon is believed to be responsible for the hydrophobic p-Sty phase being detected at greater depths. While Figure 4(A) schematically depicts a stratification of the p-Sty phase near the F-A interface, Figure 4(B) illustrates the case of the top p-BA layer being swelled by H_2O . When such a latex film is exposed to 100% RH, the top layer becomes thicker. This is shown in Figure 4(B).

At this point, it is appropriate to mention that, in contrast to our previous studies on 50/50 p-Sty/p-BA copolymer,¹² not a mixture of homopolymers, there was no stratification of polystyrene near the F-A interface. Furthermore, there were no intensity changes of the 700 cm⁻¹ band for the TM and TE polarizations and no intensity differences between various penetration depths. As one would anticipate, the DMTA data showed the presence of a single T_g at 16°C. Thus, the results on the p-Sty/p-BA copolymer indicated no phase separation, which was also accompanied by no preferential orientation of the polystyrene rings near the surface. In addition, only the 1,046 cm⁻¹ band characteristic of the SO₃⁻Na⁺-H₂O interactions near the F-A interface was detected. However, the 1,056 cm⁻¹ band was not present,¹² indicating that the SO₃⁻Na⁺-HOOC surfactant-latex interactions are not detected. Thus, there are significant differences in the latex surface and interfacial properties, depending on the latex makeup. When latex particles are made up of a copolymer, the latex particles are able to coalesce uniformly, thus giving a single-phase latex film. In a latex film composed of homopolymers, hard p-Sty and soft p-BA particles display a phase separation, but the separation occurs near the F-A interface and stratification of the p-Sty layers are detected. It should be noted that although DMTA is capable of detecting phase separation in polymers, it is unable to determine that the phase separation may occur nonuniformly across the film thickness, such as is demonstrated for the p-Sty/*n*-BA mixture. As a result of the stratified phase separation between the homopolymers during film formation, the mobility and orientation changes of SDOSS within the latex film will be also affected.

CONCLUSIONS

In this study, stratification processes that occur during the film formation and their effect on the distribution of SDOSS surfactant molecules within the latex film were examined. The phase separation of blended p-BA and p-Sty homopolymers occurs near the F-A interface. After coalescence, the p-Sty phase of the latex exhibits a significant degree of stratification at approximately 1.6 μm from the F-A interface. At that depth, polystyrene rings take on a preferentially parallel orientation to the film surface. At the same time, the hydrophilic ends of the SDOSS (SO₃⁻Na⁺) are oriented preferentially parallel to the surface. This behavior is associated

with the film formation and the fact that an excess of p-Sty molecules can be found at 1.6 μm from the film surface. Because water plays a significant role in surfactant distribution, RH will also influence the stratification process. Under 100% RH, water diffuses into the film and swells the p-BA surface layers, causing their expansion. As a result, the hydrophobic p-Sty phase is detected at approximately 2.3 μm. The polystyrene rings maintain their preferential parallel orientation to the film surface. However, the hydrophilic groups of SDOSS diffuse into the bulk with water uptake by the latex. As a result, they are not present at the film surface.

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