

# Surface and Interfacial FTIR Spectroscopic Studies of Latexes. IX. The Effect of Homopolymer and Copolymer Structures on Surfactant Mobility in Sty/BA Latices

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## SYNOPSIS

The effects of homopolymer and copolymer compositions and structures in styrene/*n*-butyl acrylate (Sty/BA) latices on sodium dioctyl sulfosuccinate (SDOSS) surfactant mobility and its preferential concentration at the film–air (F–A) and film–substrate (F–S) interfaces were examined using attenuated total reflectance Fourier transform infrared (ATR FTIR) spectroscopy. It appears that the SDOSS concentration at the F–S interface is highest when the Sty/BA feed ratio is 50/50, and the excess of Sty results in migration of SDOSS surfactant to the F–A interface. This behavior is attributed to the increased glass transition temperature and diminished compatibility between surfactant molecules and copolymer latex. This study also shows that the primary factors that influence exudation to either F–A or F–S interfaces are surface tension of the substrate, glass transition temperature, water flux during coalescence, and compatibility between latex components. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Our recent studies indicated that the distribution of surfactants in latex films may depend upon many factors, among which surfactant–latex compatibility, interfacial latex–substrate surface tension, temperature, and the rate of water evaporation during latex coalescence appear to play a key role.<sup>1–5</sup> Whereas these factors primarily affect mobility and orientation of surfactants at the film–air (F–A) and film–substrate (F–S) interfaces,<sup>6,7</sup> the nature of the F–A and F–S interfaces also depends upon surfactant orientation and distribution. Although there are other variables that may influence surfactant distribution, latex copolymer composition may be particularly important. As a matter of fact, our initial studies indicated that surfactant molecules show significantly different behavior in styrene/butyl acrylate (Sty/BA) than in butyl acrylate/methacrylic acid (BA/MAA) latex environments. This stimulated our next attempt, to address the issue of how

sodium dioctyl sulfosuccinate (SDOSS) surfactant may behave in various compositions of Sty/BA latex copolymers deposited on polytetrafluoroethylene (PTFE) substrate. Attenuated total reflectance Fourier transform infrared (ATR FTIR) spectroscopy, along with the recently developed quantitative spectral analysis,<sup>8,9</sup> will be used to determine the extent of the surfactant exudation to the F–A and F–S interfaces.

## EXPERIMENTAL

### Latex Preparation

Styrene (Sty), butyl acrylate (BA), and methacrylic acid monomers (Aldrich Chemical Co.) were copolymerized by a semicontinuous emulsion polymerization process in a glass four-neck breakaway reaction vessel equipped with a mechanical stirrer, addition funnel, thermometer, condenser, and nitrogen inlet tube. A typical recipe based on a total weight formulation included: double deionized (DDI) water 53.9% w/w; (styrene/butyl acrylate) 42.7% w/w (97% based on total monomer wt.); methacrylic acid, 1.3% w/w (3% based on total monomer wt.);

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sodium dioctyl sulfosuccinate (SDOSS, Aldrich Chemical Company), 1.8% w/w (4% based on total monomer wt.); and potassium persulfate (Aldrich Chemical Company), 0.26% w/w (0.6% based on total monomer wt.). The monomers were mixed together thoroughly and placed in the addition funnel. The reaction vessel was purged for 20 min with nitrogen; then water, SDOSS, and initiator were added. The mixture was stirred for 5 minutes while heating. At 40°C, 20% of the monomer mixture was slowly added while stirring over a 5-min period. When the temperature reached 70°C, it was held constant until a white, milky emulsion was observed; then monomer was slowly added over a 3-h period. After that, the temperature was raised to 80°C and held constant for 3 h or until no monomer odor could be detected. The final product contained 45% solids.

### Film Preparation

Liquid latex was deposited on the substrate, which is polytetrafluoroethylene (PTFE) film, to air-dry for 72 h at room temperature. All films were prepared to maintain an approximate film thickness of 200  $\mu\text{m}$ .

### Spectroscopic Measurements

ATR FTIR spectroscopy was used to monitor latex films at film-air (F-A) and film-substrate (F-S) interfaces. ATR FTIR spectra were collected on a Digilab FTS-20 instrument equipped with an ATR cell (Spectra Tech) containing a KRS-5 crystal. In a typical experiment, 200 scans at a resolution of 4  $\text{cm}^{-1}$  with a 90° (TE) polarizer filter were collected. The rectangular ATR attachment (Digilab Instrument) was equipped with a KRS-5 crystal aligned to give an incident beam angle of 45 degrees. All spectra were transferred to an AT-compatible computer for further spectral analysis utilizing Spectra Calc software (Galactic, Inc.). The spectra were corrected for optical effects using recently developed algorithms.<sup>9,10</sup>

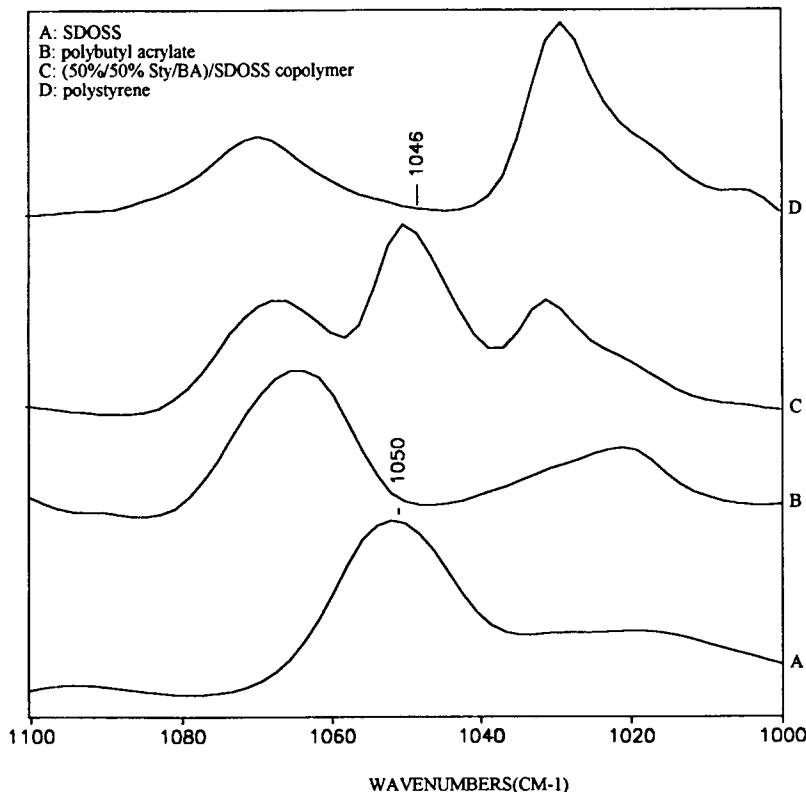
## RESULTS AND DISCUSSION

Before we begin analysis of the ATR FTIR spectra recorded from the F-A and F-S interfaces of Sty/BA latex films, it is essential to establish the origin of infrared bands and provide proper normalization procedures for the analyzed spectra. Although the first step in this analysis is to correct all raw ATR spectra for optical effects using recently developed ATR algorithms,<sup>9,10,11</sup> it is also necessary to find a

band which will not be affected by the latex suspension composition changes. Figure 1 shows the ATR FTIR spectra of SDOSS surfactant (Trace A), polybutyl acrylate (Trace B), SDOSS containing Sty/BA latex copolymer (Trace C), and polystyrene (Trace D). While the band assignments for these species are listed in Table I, here we will focus on the bands characteristic of the hydrophilic ends of SDOSS in the 1050  $\text{cm}^{-1}$  region. The band at 1050  $\text{cm}^{-1}$  of the SDOSS spectrum (Trace A) is due to the S—O stretching modes in the  $-\text{SO}_3\text{Na}^+$  groups. As our earlier studies on ethyl acrylate/methacrylic acid (EA/MAA) have shown,<sup>4,5</sup> the hydrophilic  $-\text{SO}_3\text{Na}^+$  end of the surfactant molecule can associate with the acid groups of the EA/MAA latex copolymer in the presence of water. These interactions result in the splitting of the 1050  $\text{cm}^{-1}$  band to two bands at 1056 and 1046  $\text{cm}^{-1}$ . In the case of Sty/BA, ATR FTIR spectra in the 1100–1000  $\text{cm}^{-1}$  region for 50%/50% Sty/BA (Trace A), pure Sty/BA copolymer (Trace B), the difference spectrum obtained by a subtraction of the latex and copolymer spectra (Trace C), and SDOSS surfactant (Trace D), are shown in Figure 2. As illustrated in Trace C, there is only one band at 1046  $\text{cm}^{-1}$  and no splitting of the 1050  $\text{cm}^{-1}$  band. For reference, the SDOSS surfactant spectrum is shown in Figure 2, Trace D.

In an effort to establish whether the SDOSS concentration changes as a function of the latex composition, latex containing Sty/BA ratios ranging from a 50%/50% Sty/BA feed ratio to pure BA were synthesized and examined. Figure 3, Traces A through F, illustrate a series of spectra for latex compositions ranging from 100% BA to 50%/50% Sty/BA. As illustrated by the decreasing band at 1046  $\text{cm}^{-1}$  in Figure 3, (weak in Trace A and stronger in Trace F), the higher styrene content, higher  $-\text{SO}_3\text{Na}^+$  groups of the surfactant are detected at the F-S interface. Although this observation may be interpreted in various ways, it should be kept in mind that the copolymer ratio also affects spectral features because the Sty/BA ratio changes. As illustrated in Figure 3, the band intensities due to poly(butyl acrylate) at 1167, 961, 942, and 740  $\text{cm}^{-1}$  decrease as the amount of BA monomer decreases, whereas the bands at 1602, 1494, 762, and 700  $\text{cm}^{-1}$  due to polystyrene increase as more styrene monomer is present in the Sty/BA latex composition.

To compensate for the spectral changes resulting from the compositional differences between the samples, and to determine concentrations of SDOSS at the F-S and F-A interfaces for different Sty/BA



**Figure 1** ATR FTIR spectra of: A, SDOSS surfactant; B, poly(butyl acrylate); C, SDOSS containing 50%/50% Sty/BA copolymer; D, polystyrene.

ratios, it is necessary to find a reference band. Ideally, the most suitable band would be the one that is characteristic for both BA and Sty components and, more importantly, that would change at the same rate as the monomer feed ratio changes. As a result, the intensity of this reference band would be independent upon the Sty/BA ratio. With this in mind, let us consider the band at  $841\text{ cm}^{-1}$ , which is due to the C—C skeletal modes of the C—C copolymer main chain. Since this band is present in the spectra of poly(butyl acrylate), polystyrene, and Sty/BA copolymer, it appears to be the most suitable candidate for reference purposes.

To examine this band's suitability as an internal standard reference, Figure 4 was constructed. It represents a plot of the IR band intensities, recorded in a transmission mode, as a function of the copolymer weight for different Sty/BA compositions. It appears that linear relationships between the band absorbances and wt % of copolymer are obtained. Whereas line A represents the experimental and calculated values obtained for the  $841\text{ cm}^{-1}$  band intensity for pure BA, styrene, and Sty/BA copol-

ymers, lines B and C are the experimental values obtained for the  $1167$  and  $700\text{ cm}^{-1}$  bands, due to BA and styrene groups, respectively. It appears that the absorbance of polyBA, polystyrene, and Sty/BA copolymers are almost identical (lines marked A, in Figure 4). A blowup of this part of the figure shows only slight slope variations, designated as: A<sub>1</sub>, pure polystyrene (experimental value); A<sub>2</sub>, 50%/50% Sty/BA (experimental value); A<sub>3</sub>, 50%/50% Sty/BA (calculated value); A<sub>4</sub>, 40%/60% Sty/BA (experimental value); A<sub>5</sub>, 40%/60% Sty/BA (calculated value); A<sub>6</sub>, 10%/90% Sty/BA (experimental value); A<sub>7</sub>, 10%/90% Sty/BA (calculated value); and A<sub>8</sub>, pure polybutyl acrylate (experimental value). Their magnitudes are certainly within an experimental error. To further examine whether the  $841\text{ cm}^{-1}$  absorption coefficient changes with Sty/BA concentration, plots of the relative intensities of the  $1167\text{ cm}^{-1}$  band (line A, Figure 5), which is due to the normal vibrational modes of the —COC ester groups of butyl acrylate copolymer segments, and the  $762$  and  $1494\text{ cm}^{-1}$  bands due to =C—H out-of-plane and C=C stretching of styrene (lines B

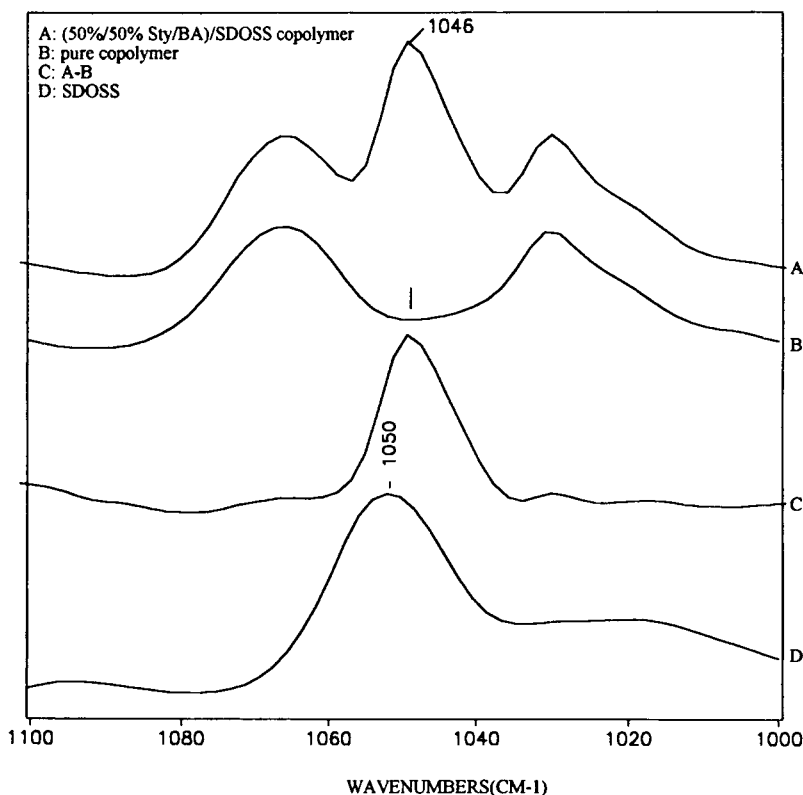
**Table I Tentative Band Assignments for Poly(butyl Acrylate), Polystyrene, Poly(styrene/butyl acrylate) Copolymer, and SDOSS.**

Poly(BA)	Poly(Sty)	Poly(Sty/BA)	SDOSS	Assignment
WAVENUMBER (CM <sup>-1</sup> )				
	3084	3084		
	3060	3060		$\nu_{as}^*$ , C—H, (=C—H)
	3027	3027		
2960		2960	2960	$\nu_{as}$ , C—H(CH <sub>3</sub> )
2935	2933	2931	2934	$\nu_{as}$ , C—H(CH <sub>2</sub> )
2875		2873	2879	$\nu_s^*$ , C—H(CH <sub>3</sub> )
	2865	2861		$\nu_{as}$ , C—H(C—H)
1730		1727	1735	$\nu$ , C=O
	1602	1602		p-sub. Arom.
	1584	1584		C=C, Arom
	1494	1494		
1457		1453	1464	C—H, def
			1461	CH <sub>2</sub> , scissor
1396		1396	1393	$\delta^*$ , CH <sub>2</sub>
1380		1380		$\gamma^*$ , C—H, (CH <sub>3</sub> )
1300	1272	1300	1314	$\gamma$ , CH <sub>2</sub>
1243		1240	1240	$\nu_{as}$ , C—O—C
			1216	$\nu_{as}$ , S—O, (SO <sub>3</sub> )
1160		1158	1175	$\nu$ , C—O—C
1117		1119		C—C, skel. vib.
1067	1070	1065		C—C, skel. vib. main chain
		1056	1050	$\nu$ , S—O, (SO <sub>3</sub> )
		1046		
1024	1030	1030	1025	C—C, skel. vib.
961		961		C—C, skel. vib.
942		942		<i>n</i> -butyl
	907	907		=C—H, out-of plane (5H)
841	841	841	857	C—C, skel. vib.
	755	760		=C—H, out-of-plane def.
740		740	730	$\tau^*$ , —(CH <sub>2</sub> ) <sub><i>n</i></sub> — ( <i>n</i> > 3)
	700	697		out-of-plane ring def.
		654	652	$\delta$ , S—O, (SO <sub>3</sub> )
	622			in-plane ring def.
			581	SO <sub>2</sub> , scissor
		680		—OCO, in-plane vib. mode

\*  $\nu_{as}$ -asymmetric stretching mode  
 $\nu_s$ -symmetric stretching mode  
 $\delta$ -bending mode  
 $\gamma$ -wagging mode  
 $\tau$ -twisting mode

and C, respectively), were constructed. As shown in Figure 5, the absorbance of line A decreases linearly with the increasing styrene concentration, whereas absorbances shown in plots B and C increase linearly with the styrene concentration increase. In contrast, however, the 841 cm<sup>-1</sup> band absorbance (line D) remains constant, substantiating our previous conclusions that this band can be used for normalization purposes.

Let us go back to a main theme and, using the above normalization procedures, analyze the intensity changes of the 1046 and 1056 cm<sup>-1</sup> bands. Again, these bands will be used as a probe for monitoring the SDOSS migration to the F-S or F-A interfaces. Figures 6 and 7 illustrate the S—O stretching region of the ATR FTIR spectra for a 0/100% ratio (Trace A), 10%/90% (Trace B), 20%/80% (Trace C), 30%/70% (Trace D), 40%/60% (Trace E), and 50%/50%

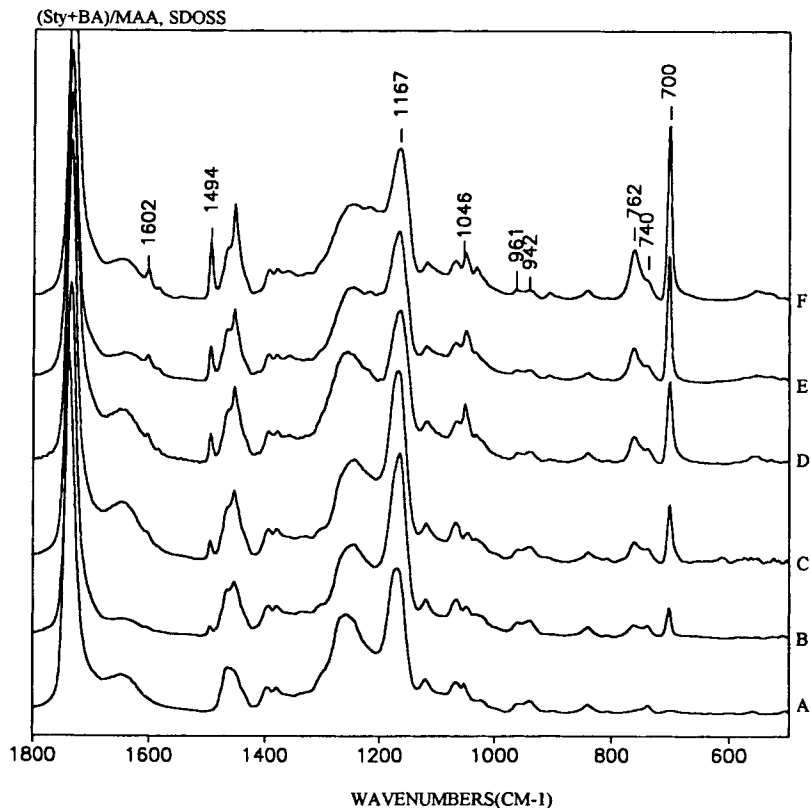


**Figure 2** ATR FTIR spectra of: A, 50%/50% Sty/BA latex copolymer; B, 50%/50% Sty/BA copolymer without surfactant; C, subtracted spectra, A minus B; D, SDOSS surfactant.

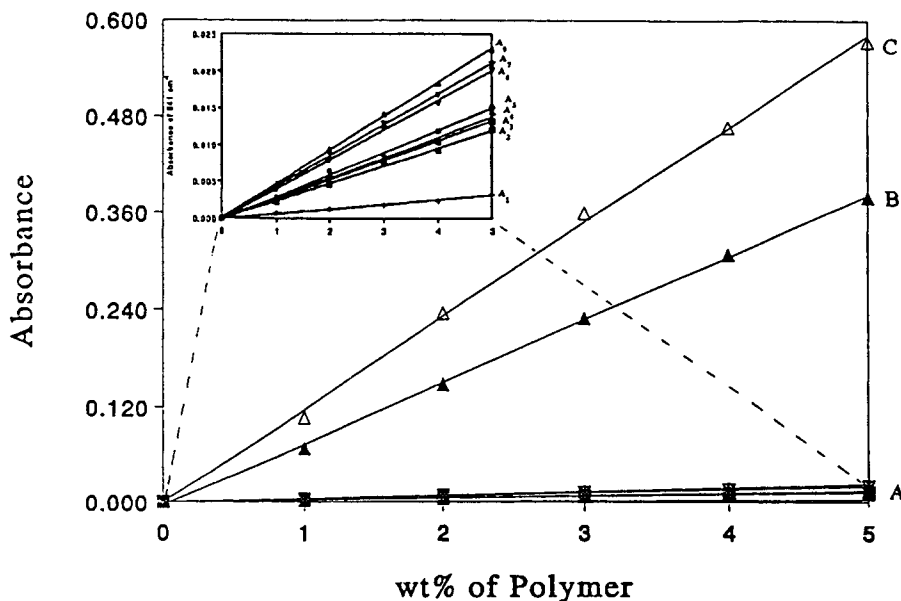
Sty/BA (Trace F) at the F-S and F-A interfaces, respectively. If we use the  $1046\text{ cm}^{-1}$  band intensity changes shown in Figure 6 as a measure of surfactant molecules at a given interface, it appears that for pure BA latex (Trace A), the lowest concentration of SDOSS is detected at the F-S interface. The band increases gradually, and as the styrene concentration increases its intensity becomes the highest for 50%/50% Sty/BA latex (Trace F). Because hydrophobic styrene is a part of latex copolymer, incompatibility between surfactant molecules and latex copolymer increases, expelling surfactant molecules toward the F-S interface. An additional driving force is surface tension between latex copolymers and substrate. Furthermore, the  $1046\text{ cm}^{-1}$  increase occurs when the Sty/BA ratio exceeds 20%/80%. This observation indicates that the surfactant molecules are expelled when a higher content of styrene near the Sty/BA particle surface exists, again supporting the presence of a core-shell-like situation within the latex particles. Because Sty exhibits a higher reactivity ratio, it is likely that the particles consist of a polystyrene core which increases in size as the styrene concentration is higher in the initial monomer mixture.

The results for the F-A interface, illustrated in Figure 7, indicate similar trends; namely, the  $1046\text{ cm}^{-1}$  band for a 50%/50% Sty/BA composition is the most pronounced feature in the spectra. The band decreases gradually as the styrene concentration decreases, and its intensity becomes virtually nondetectable for pure BA latex. This observation indicates that a certain amount of SDOSS exists at the F-A interface. Neglecting temporarily the surface tension effect of the substrate on the mobility of surfactant molecules, water flux is one of the driving forces to carry surfactant toward the F-A interface during latex coalescence. Since SDOSS surfactant is water soluble, it will preferentially stay in an aqueous phase and its mobility in a noncoalesced latex suspension will be similar to that of water.

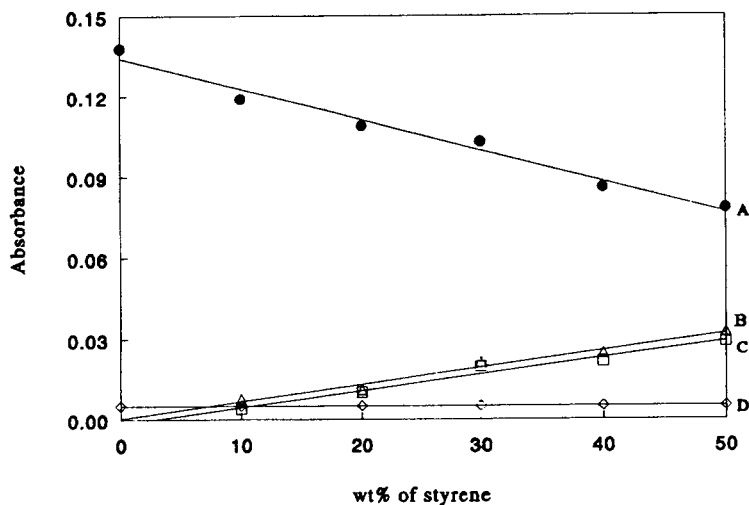
So far we have considered the effect of Sty/BA ratio on the mobility of SDOSS surfactant molecules to F-S and F-A interfaces. One issue that was temporarily ignored, however, was the effect of glass transition temperature ( $T_g$ ). After all, changing the Sty/BA ratio alters the  $T_g$  of the latex film. Figure 8, curve A, illustrates the relationship between the latex composition and  $T_g$ . As one would expect, lower



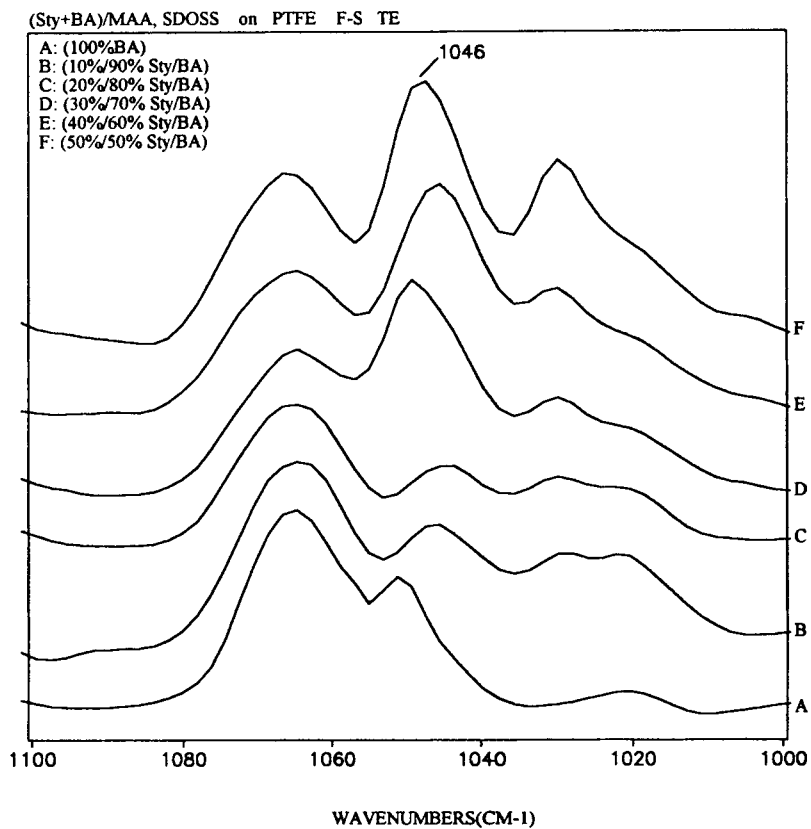
**Figure 3** ATR FTIR spectra of Sty/BA latex copolymers: A, 100% BA; B, 10%/90% Sty/BA; C, 20%/80% Sty/BA; D, 30%/70% Sty/BA; E, 40%/60% Sty/BA; F, 50%/50% Sty/BA.



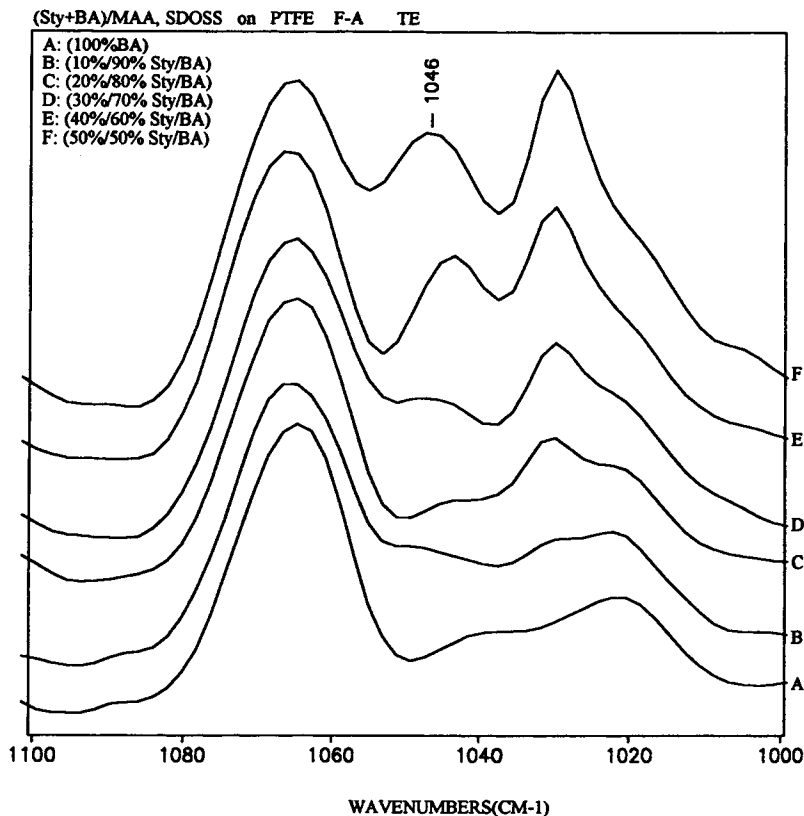
**Figure 4** Absorbance vs concentration of Sty/BA copolymers: A, absorbance of  $841\text{ cm}^{-1}$ ; B, absorbance of  $1169\text{ cm}^{-1}$ ; C, absorbance of  $700\text{ cm}^{-1}$ . ( $A_1$ , pure polystyrene, experimental value;  $A_2$ , 50%/50% Sty/BA, experimental value;  $A_3$ , 50%/50% Sty/BA, calculated value;  $A_4$ , 40%/60% Sty/BA, experimental value;  $A_5$ , 40%/60% Sty/BA, calculated value;  $A_6$ , 10%/90% Sty/BA, experimental value;  $A_7$ , 10%/90% Sty/BA, calculated value; and  $A_8$ , pure poly(butyl acrylate), experimental value.



**Figure 5** Relative intensities of different bands vs. wt % of styrene at F-S interface: A,  $1167\text{ cm}^{-1}$ ; B,  $762\text{ cm}^{-1}$ ; C,  $1494\text{ cm}^{-1}$ ; D,  $841\text{ cm}^{-1}$ .



**Figure 6** ATR FTIR spectra of Sty/BA latex copolymers at F-S interface: A, 100% BA; B, 10%/90% Sty/BA; C, 20%/80% Sty/BA; D, 30%/70% Sty/BA; E, 40%/60% Sty/BA; F, 50%/50% Sty/BA.

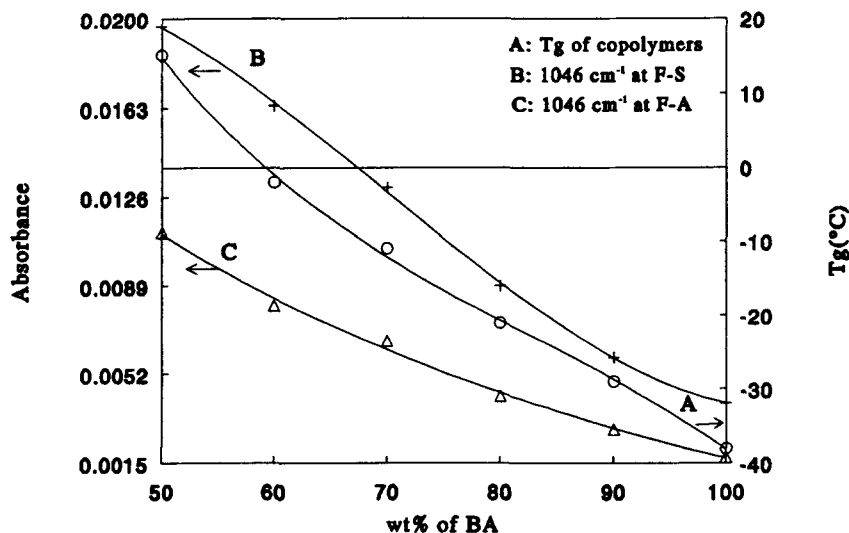


**Figure 7** ATR FTIR spectra of Sty/BA latex copolymers at F-A interface: A, 100% BA; B, 10%/90% Sty/BA; C, 20%/80% Sty/BA; D, 30%/70% Sty/BA; E, 40%/60% Sty/BA; F, 50%/50% Sty/BA.

Sty content will diminish  $T_g$ . Figure 8, curves B and C, illustrate the  $1046\text{ cm}^{-1}$  band intensity changes at F-S and F-A interfaces, both plotted as functions of the latex composition. The band intensities used to construct these plots were obtained from the spectra that were corrected for optical effects using recently developed algorithms,<sup>9,10</sup> and thus they can be used for quantitative purposes. As shown in Figure 8, curve B, for the F-S interface, the  $1046\text{ cm}^{-1}$  band is stronger than its counterpart at the F-A interface (curve C). If one assumes that latex coalescence parallels the evaporation of water, surfactant is initially carried to the F-A interface, followed by its slow diffusion towards the F-S interface, in order to respond to the interfacial surface tension between latex film and PTFE substrate. As a result, SDOSS concentration at the F-S interface is greater than that at the F-A interface. In order to understand the relationship between  $T_g$  and distribution of SDOSS surfactant molecules at F-S and F-A interfaces, it is necessary to consider the dynamics of the process. During coalescence, external factors govern distribution of SDOSS molecules: the most

effective ones are water flux to the F-A interface and surface tension of the substrate. During coalescence, as water molecules diffuse out of the latex, they carry SDOSS molecules to the F-A interface. However, when the interfacial surface tension difference between substrate and liquid latex is high, SDOSS will be driven to the F-S interface. If one of these effects is stronger, it will dominate the process. During coalescence, however,  $T_g$  increases and, if the  $T_g$  increase is fast, the SDOSS molecules may become trapped and diffusion to either interface will be inhibited. The glass transition changes during coalescence, along with the water flux and the surface tension of the substrate, are the major factors affecting exudation of the SDOSS surfactant during latex coalescence. For PTFE with a relatively low surface tension ( $18\text{ mN/m}$ ), the surfactant molecules are driven to the F-S interface in order to lower the interfacial surface tension difference between the PTFE substrate and the latex copolymer. This process, however, competes with the changing during coalescence film-air interfacial tension, water flux, and the changing glass transition temperature. Fur-





**Figure 8** A,  $T_g$  as a function of Sty/BA composition; B,  $1046\text{ cm}^{-1}$  intensity at F-S interface plotted as a function of Sty/BA composition; C,  $1046\text{ cm}^{-1}$  intensity at F-A interface plotted as a function of Sty/BA composition.

thermore, the fact that water did evaporate from the latex film does not imply that the coalescence process is complete. Free volume is still sufficient to allow surfactant molecules to be driven through the network.

## CONCLUSIONS

ATR FTIR spectroscopy was used to study the effect of homopolymer and copolymer structures on SDOSS surfactant mobility in Sty/BA latex films. This study shows that the factors that influence exudation of SDOSS are interfacial surface tension, glass transition temperature of the copolymer, water flux during coalescence, and compatibility of the latex components. Concentration of SDOSS is higher at the F-S interface for 50%/50% Sty/BA latex, whereas the addition of styrene monomer to Sty/BA copolymer latex results in a migration of the surfactant molecules to the F-A interface. This behavior is due to the increased glass transition temperature and diminished compatibility between the surfactant molecules and the copolymer latex composition.

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