

# Mobility of SDOSS Powered by Ionic Interactions in Sty/*n*-BA/MAA Core–Shell Latex Films. 21. A Spectroscopic Study<sup>†</sup>

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Received April 29, 2000. In Final Form: August 23, 2000

While molecular level interactions between sulfonate groups of sodium dioctylsulfosuccinate (SDOSS) and COOH groups in styrene/*n*-butyl acrylate/methacrylate acid (Sty/*n*-BA/MAA) copolymer particles have been the subject of our earlier studies, the main focus of this work is to establish how MAA groups affixed to polymer latex particle surfaces will affect SDOSS mobility in Sty/*n*-BA/MAA latex films. The ultimate objective is to develop a series of model systems simulating the degree of neutralization of polymer surfaces and how it may alter polymer contractions and release of entropically attached molecules to interfacial regions. These studies show that the release of SDOSS molecules from MAA containing Sty/*n*-BA particles is attributed to two factors: (1) entropic effect due to increased compatibility resulting from surfactant penetration into latex particle surfaces and (2) enhanced particle out-layer glass transition temperature ( $T_g$ ). The SDOSS release is inhibited when surface neutralization levels are 0–25%, but at higher degrees of neutralization (50–100%), excessive SDOSS exudation to the film–air (F–A) interface of a film is observed. This behavior is attributed to the displacement of SDOSS molecules from MAA-containing latex particles during film formation as a result of the conversion of potential surface energy into mechanical movement when ionic bonds are broken. Thus, the simultaneous presence of *p*-MAA and SDOSS at the particle surfaces make them act as polyelectrolytes, responding to chemical changes, and during film formation, ionomeric species containing  $\text{SO}_3^-\text{Na}^+-\text{COO}^-\text{Na}^+$  entities near the F–A interface are formed.

## Introduction

It is well established that carboxyl-containing species, such as acrylics or derivatives of methacrylic acid (MAA), when incorporated onto surfaces, significantly affect numerous properties.<sup>1,2</sup> While one of the traditional functions of these entities is to provide additional cross-linking sites, there are other relatively unexplored opportunities for these groups to perform. For example, one can envision that by varying the degree of neutralization near latex particle surfaces, chain conformations of surface molecules will be altered as a result of the imbalance between osmotic and entropic forces. Although this behavior is known for polyelectrolyte gels,<sup>3,4</sup> latex particles have not been studied in this context. However, when latex particles contain MAA groups, they store the energy by the electrostatic repulsion between charged particle surfaces, and an introduction of neutralizing ions may result in the release of surface ionic species. As a result, potential energy is released during conformational changes resulting from a cleavage of certain bonds, and mechanical motion of molecular segments is anticipated. With this background in mind this study focuses on the effect of MAA concentration and neutralization of latex particle surfaces on the mobility and stratification of small molecules and their interactions with active and nonactive functional groups. Furthermore, once particle surface molecules are released and the latex suspension is allowed

to coalesce, they may stratify and many factors may affect this process.

For the purpose of these model studies we prepared precisely controlled latex particles that contain a polystyrene (*p*-Sty)/(poly *n*-butyl acrylate) (*p*-*n*-BA) core surrounded by a MAA shell. This choice was dictated by the fact that the presence of MAA groups on particle surfaces may alter particle interdiffusion during latex film formation as well as interactions with sodium dioctylsulfosuccinate (SDOSS) molecules used to stabilize the particles in an aqueous environment.<sup>5</sup> Furthermore, such prepared particle surfaces can be neutralized and one could anticipate the formation of ionic aggregates, perhaps analogous to conventional ionomers<sup>6</sup> that may form heterogeneous areas on latex particles as well as after coalescence.<sup>5–9</sup> Although one could draw an analogy between the behavior of true ionomeric polymers and ionic species present in latex suspensions, if SDOSS and MAA groups form organized structures during latex film formation, potential similarities are possible. In this context, the presence of neutralized and nonneutralized acid groups plays an important role on mobility of  $\text{SO}_3^-\text{Na}^+$  containing SDOSS.

Previous studies on latex films indicated that the mobility of SDOSS molecules was affected by the compatibility of SDOSS with a polymer matrix,<sup>5–12</sup> coalescence

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<sup>†</sup> Parts 1–20 were published in *Macromolecules* and *J. Appl. Polym. Sci.* (1991–2000).

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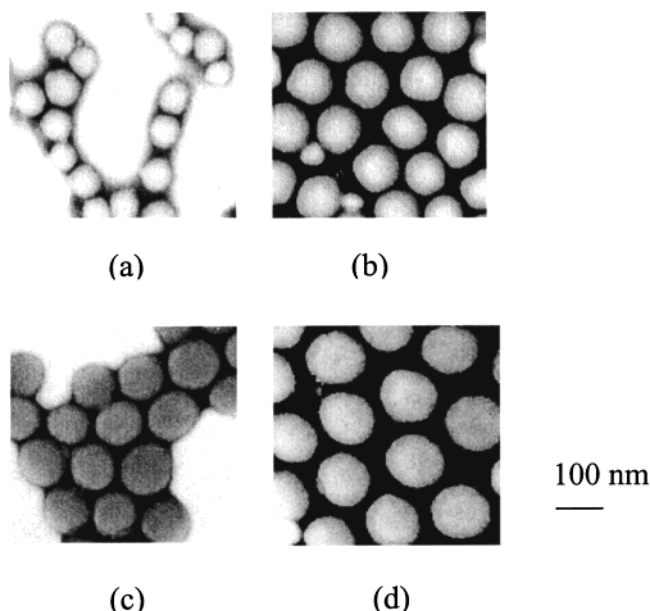
**Table 1. P(Sty/*n*-BA) Seed Recipe and P(Sty/*n*-BA/MAA) Latexes**

components	seed (Sty/ <i>n</i> -BA)	second stage Sty/ <i>n</i> -BA/MAA (47.5/45/5%)	second stage Sty/ <i>n</i> -BA/MAA (45/45/10%)
pSty/ <i>n</i> -BA seed (35% w/w solids)	—	48.48	48.87
DDI (% w/w)	65.36	33.23	33.23
styrene (% w/w)	16.55	8.13	7.70
<i>n</i> -butyl acrylate (% w/w)	16.55	8.13	7.70
methacrylic acid (% w/w)	—	0.86	1.71
SDOSS (% w/w)	1.35	0.68	0.68
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (% w/w)	0.195	0.101	0.101

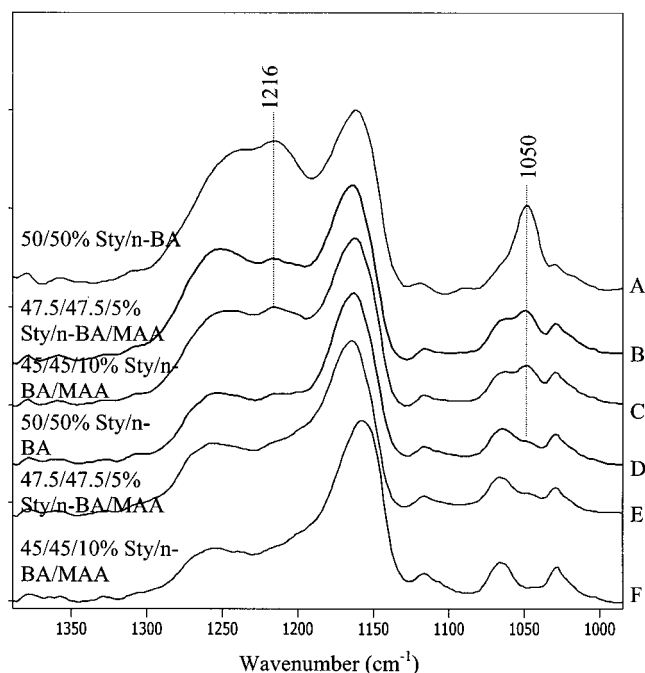
temperature ( $T_c$ ),<sup>13</sup> and glass transition temperature ( $T_g$ ).<sup>14</sup> However, such factors as latex particle surface hydrophilicity, that not only influence distribution of individual components, but may also significantly affect film formation and the formation of ordered surfactant structures, are important. In an effort to address this issue, this study focuses on synthesis and molecular level understanding of interactions in latexes containing controllable and well-defined quantities of styrene (Sty), *n*-butyl acrylate (*n*-BA), and methacrylic acid (MAA) moieties, that are copolymerized into a core-shell architecture. As previous studies indicated,<sup>9–11</sup> numerous factors affect particle coalescence, and very often minute molecular level changes dictate significant macroscopic property developments. Thus, the simultaneous presence of MAA and SDOSS on latex particle surfaces creates an opportunity for modeling a motion of controllable arrangements of ionic entities. In an effort to determine sodium dioctylsulfosuccinate (SDOSS) surfactant behavior in Sty/*n*-BA/MAA copolymer latex films, we will utilize molecular level probes that, in addition to surface sensitivity and selectivity, also allow us to perform surface microanalysis. While attenuated total reflectance (ATR) FTIR probes depths up to 3  $\mu$ m, and quantitative information can be retrieved,<sup>15</sup> chemical changes resulting in different surface morphologies can be analyzed using FTIR microscopy.

### Experimental Section

**Latex Synthesis and Film Preparation.** Styrene (Sty), *n*-butyl acrylate (*n*-BA), methacrylic acid (MAA), sodium dioctylsulfosuccinate (SDOSS), and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), were purchased from Aldrich Chemical Co. 50/50% sty/*n*-BA copolymer latex was synthesized by a semicontinuous emulsion polymerization, as described in previous publications.<sup>15</sup> Latexes formulated with Sty, *n*-BA, and MAA were synthesized in two stages: seed latex particles were synthesized by feeding a 50/50 w/w% Sty/*n*-BA mixture, followed by the addition of MAA monomer in a subsequent polymerization stage. To obtain 2.5–5 w/w% MAA content on Sty/*n*-BA seed particle surfaces, at the final stages of polymerization 5–10 w/w% of MAA was added. A chemical makeup of the starting materials utilized in the synthesis is summarized in Table 1. Polymerization of poly(Sty/*n*-BA) seeds was conducted using a conventional batch emulsion polymerization process, which was carried out in a 500 mL glass reactor equipped with a reflux condenser, a stirrer, and a thermometer. The reactor was charged with deionized H<sub>2</sub>O (DDI), SDOSS, Sty, and *n*-BA, heated to 70 °C, and purged with N<sub>2</sub> for 60 min. At this point, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> initiator solution was added, and the reactions continued for 4 h while temperature was maintained at 75 °C. This process generates uniform poly(Sty/*n*-BA) seeds with an average diameter of 69  $\pm$  10 nm which were analyzed using transmission electron microscopy (TEM) (JEM-100S, JEOL) and micrographs are shown in Figure 1 (a). Sty/*n*-BA/



**Figure 1.** TEM micrographs of latex particles: (a) 50/50 Sty/*n*-BA seeds; (b) 50/50/0% Sty/*n*-BA/MAA latex particles; (c) Latex particles containing 47.5/47.5/5% Sty/*n*-BA/MAA core/shell structure; (d) Latex particles containing 45/45/10% Sty/*n*-BA/MAA core/shell structure.

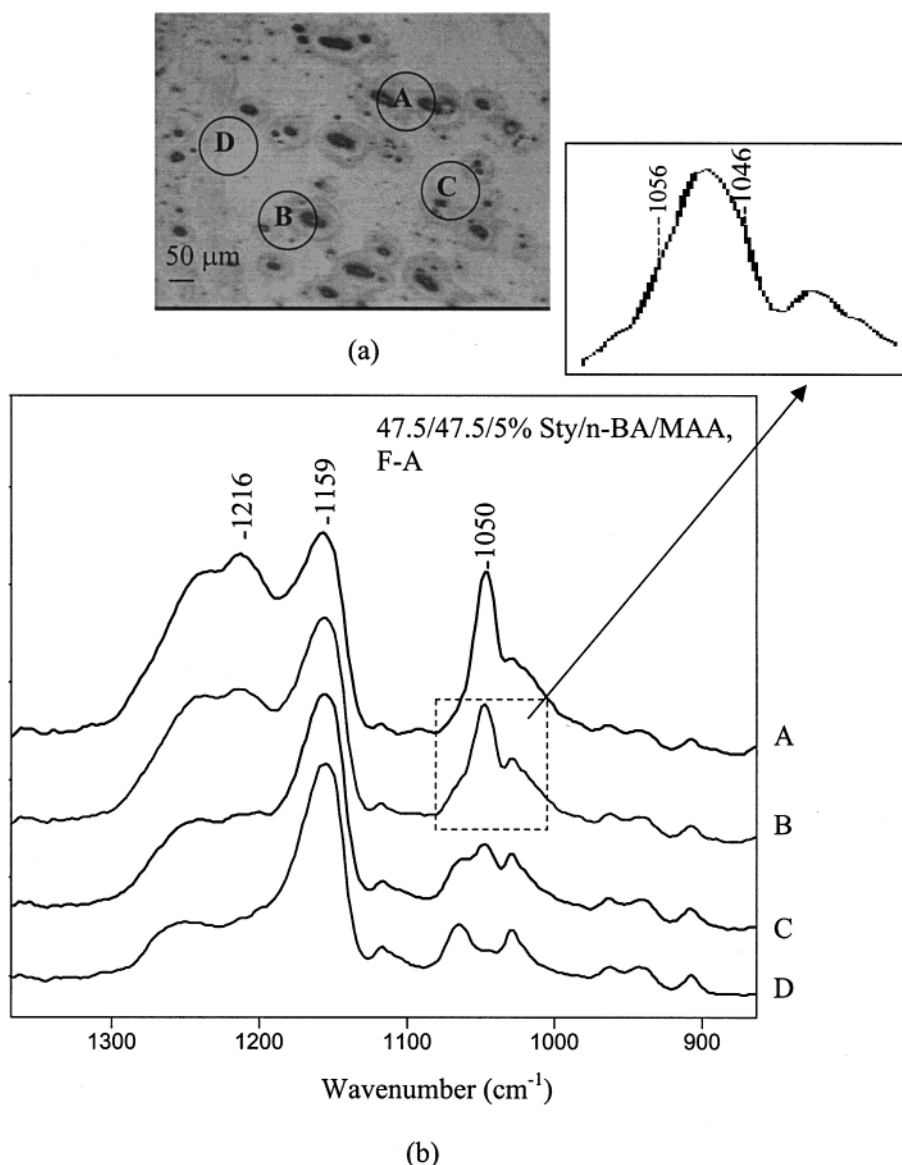


**Figure 2.** ATR FTIR spectra in the 1390–980  $\text{cm}^{-1}$  region of Sty/*n*-BA/MAA copolymer latexes: A – 50/50/0%, F–A interface; B – 47.5/47.5/5%, F–A interface; C – 45/45/10%, F–A; D – 50/50/0%, F–S interface; E – 47.5/47.5/5%, F–S interface; F – 45/45/10%, F–S (Coalescence time: 5 days, RH = 20%).

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(15) The average depth thickness was determined in the following equation:  $d_p = \lambda_o / (2\pi\eta_1 (\sin^2 \theta - \eta_{21}^2)^{1/2})$  where  $\lambda_o$  is wavelength of light,  $\eta_1$  is the refractive index of crystal,  $\theta$  is the angle of incidence, and  $\eta_{21}$  is the refractive index ratio of the sample and crystal. All spectra were corrected using the Urban–Huang algorithm<sup>16</sup> to remove spectral distortions resulting from refractive index changes.



**Figure 3.** (a) Optical images of 50/50/0% Sty/*n*-BA/MAA copolymer latex at the F–A interface; (b) ATR FTIR spectra in the 1340–870  $\text{cm}^{-1}$  region of Sty/*n*-BA/MAA copolymer latex F–A interface; Traces A, B, C, and D were recorded from areas A, B, C, and D of the optical image in Figure 3 (a), (Coalescence time: 5 days, RH = 20%).

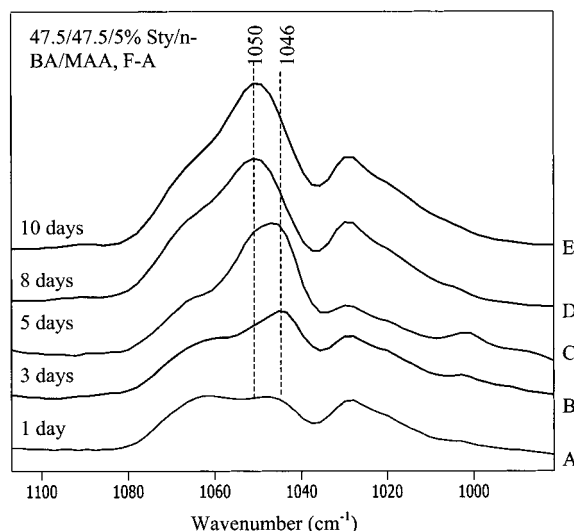
MAA particles were obtained by a polymerization process conducted using a semibatch process in which water and seed were first charged into the reactor, and then heated to 70 °C under  $\text{N}_2$ . At this point, the initiator solution was charged, and a monomer preemulsion mixture of Sty, *n*-BA, MAA, SDOSS, and  $\text{H}_2\text{O}$  were added. Addition rates of the preemulsion and initiator were controlled by a REGLO 100 pump and a universal syringe pump (model 575, Valley Science Co.), respectively. Upon addition of preemulsion and initiator, reaction temperature was kept at 75 °C for 3 h. Particle size and particle size distribution of Sty/*n*-BA/MAA latexes were examined using TEM (JEM-100S, JEOL), and for shell compositions containing 50/50/0%, 47.5/47.5/5%, and 45/45/10% Sty/*n*-BA/MAA, and the average particle sizes were  $94 \pm 15$ ,  $112 \pm 10$ , and  $132 \pm 10$  nm, respectively. Particle micrographs for all latexes are shown in Figure 1b–d.

Such prepared latexes (35 w/w % solids) were cast on a poly-(tetrafluoroethylene) (PTFE) substrate and allowed to coalesce in air at 20% relative humidity (RH) for 3 days at room temperature. An approximate film thickness of dry films was 100  $\mu\text{m}$ .

**Latex Surface Cleaning, Carboxylic Acid Content and Particle Neutralization.** Before the content of COOH groups on the particle surfaces was determined, ion-exchange experi-

ments were carried out<sup>5</sup> to remove potentially present water soluble residues of surfactant and/or initiator, which may be present in an aqueous phase. AG-501-X8 ion-exchange resin supplied by Bio-Rad was washed with hot deionized water (>80 °C), methanol, and again deionized water. In a typical experiment, the ion-exchange resin was used in a 2:1 ratio with respect to w/w% latex solids. This prepared mixture was stirred at room temperature for 2 h and the resin was removed by a slow vacuum filtration process. This procedure was repeated three times. In an effort to determine the COOH content of the latex particle surfaces, a freshly filtered latex solution was subjected to conductometric titration,<sup>7</sup> which was accomplished by adding an excess of 0.1 M NaOH to a 2.5 w/w% of latex solution, followed by a reverse titration with a 0.05 M HCl solution. The mass balance of the amount of MAA present on the surface of latex particles or in the serum accounted for an average of  $100 \pm 2\%$  of the acid charged into the reactor. To determine if water soluble polymers were present in a latex suspension, latex serums were titrated after the sedimentation of latex particles which was accomplished by centrifuging the latex suspension. Analysis on the aqueous phase showed that only 5% of the initial acid charged into the reactor was detected, indicating that the majority of MAA groups are present on the latex particle surfaces. Latex particle neutralization was conducted by slow addition of 0.1 M





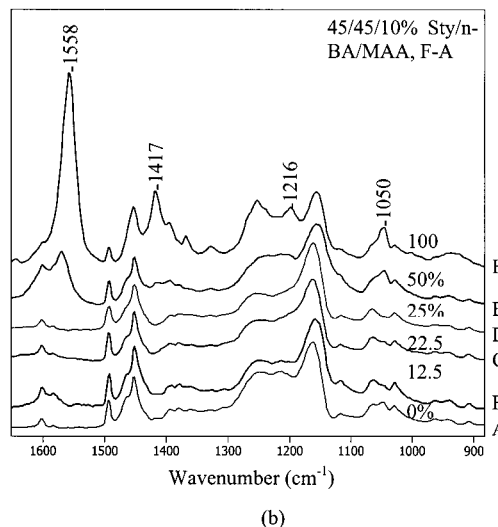
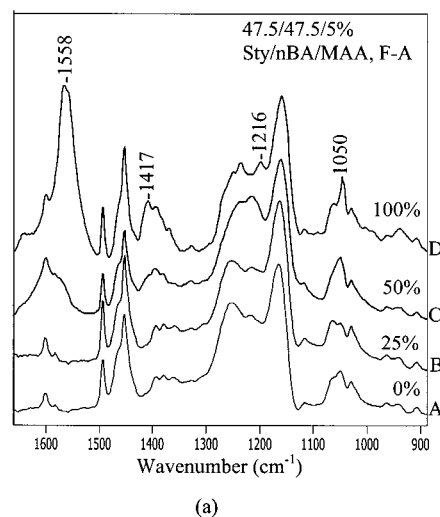
**Figure 4.** ATR FTIR spectra in the 1120–990  $\text{cm}^{-1}$  region of 50/50/0% Sty/*n*-BA/MAA copolymer latex at the F–A interface: Coalescence times: A – 1 day; B – 3 days; C – 5 days; D – 8 days; E – 10 days.

NaOH solution to 47.5/47.5/5% and 45/45/10% Sty/*n*-BA/MAA latexes while stirring. The degree of neutralization was determined based on the COOH:NaOH ratios.

**Spectroscopic Measurements.** ATR FTIR spectra were collected on a Nicolet Magna-850 FTIR single beam spectrometer at 4  $\text{cm}^{-1}$  resolution and a mirror speed of 0.1581  $\text{cm s}^{-1}$ . A KRS-5 crystal with a 45° angle  $50 \times 20 \times 3$  mm was used. Each spectrum represents 200 coadded scans ratioed to 200 scans collected on an empty ATR cell. All spectra were corrected for spectral distortions and optical effects using Q-ATR software.<sup>15</sup> Microscopic ATR FTIR spectra were collected using IR $\mu$ s/Nic-Plan molecular microanalysis system (Nicolet Instruments, Inc.). Latex samples were analyzed using an ATR objective in a reflectance mode equipped with a ZnSe crystal. Surfaces were mapped using a constant contact pressure between the ZnSe crystal and latex specimens. Each spectrum was recorded at 4  $\text{cm}^{-1}$  resolution, and 200 scans were coadded using a 3.2 mm circular aperture. In a typical experiment, an ATR probe analyzes approximately 50–100  $\mu\text{m}$  surface area and the source of an ATR signal comes from about 3  $\mu\text{m}$  below the surface.<sup>15</sup>

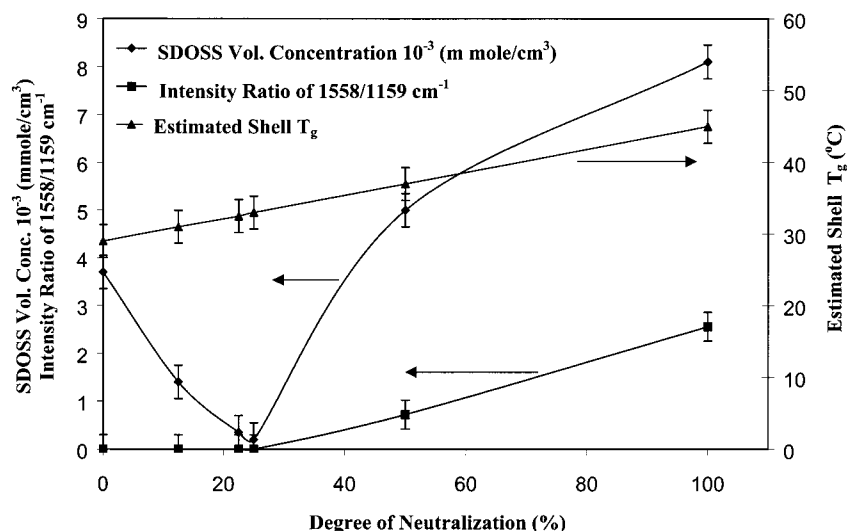
## Results and Discussion

As indicated in the Introduction section, the objective of this study is to elucidate the origin of SDOSS aggregation/stratification in the presence of MAA on latex particles. It should be realized that the presence of MAA groups on the latex particle surface does not necessarily imply that the same groups will exist after film formation at the film–air (F–A) interface. Although previously detected COOH–SDOSS and  $\text{H}_2\text{O}$ –SDOSS interactions appear to suggest that this is the case, the presence of core–shell particles provides an opportunity for controlling particle surface behavior. With this in mind, let us analyze the F–A interfaces of latexes containing various amounts of COOH groups on particle surfaces. While ATR FTIR spectra in the 1340–970  $\text{cm}^{-1}$  region of 50/50/0%, 47.5/47.5/5%, and 45/45/10% Sty/*n*-BA/MAA coalesced copolymer latex films recorded from the F–A interfaces are shown in Figure 2, Traces A, B, and C, the spectra recorded from the F–S interfaces are depicted as Traces E, D, and F, respectively. In both cases the spectra were recorded from an average depth of 1.9  $\mu\text{m}$  from the respective interface.<sup>15</sup> Comparison of the spectra recorded from the F–A (Traces A, B, and C) and the F–S (Traces E, D, and F) interfaces shows that the 1050 and 1216  $\text{cm}^{-1}$  bands are present at the F–A interface. Since both bands are



**Figure 5.** (a) ATR FT-IR spectra in the 1690–890  $\text{cm}^{-1}$  region recorded from the F–A interface of 47.5/47.5/5% Sty/*n*-BA/MAA copolymer. Degrees of neutralization: A – 0%; B – 25%; C – 50%; D – 100%. (b) ATR FTIR spectra in the 1690–890  $\text{cm}^{-1}$  region recorded from the F–A interface of 45/45/10% Sty/*n*-BA/MAA copolymer latex. Degrees of neutralization: A – 0%; B – 12.5%; C – 22.5%; D – 25%; E – 50%; F – 100% (Coalescence time: 5 days, RH = 20%).

attributed to the S–O stretching vibrations<sup>10–12</sup> of SDOSS, their presence results from the SDOSS exudation to the F–A interface. These bands not only exhibit higher intensities for the latex films not containing MAA groups on the particle surfaces (Trace A), but the fact that the 1050  $\text{cm}^{-1}$  band does not split to 1046 and 1056  $\text{cm}^{-1}$  indicates that  $\text{SO}_3^- \text{Na}^+$  groups are not affected by the presence of the MAA shell. Furthermore, this behavior indicates that the presence of hydrophilic MAA shells on latex particles diminishes SDOSS exudation to the F–A interface. Although these results may seem to contradict our previous studies,<sup>13</sup> more hydrophilic acid containing particles exhibit higher compatibility with SDOSS, thus preventing SDOSS migration to the F–A interface. Let us now determine the distribution of SDOSS molecules at the F–A interface. Figure 3 (a) shows optical images obtained from the F–A interface of the 47.5/47.5/5% Sty/*n*-BA/MAA copolymer latex. As seen, aggregates are detected at the F–A interface and in an effort to determine their composition, ATR microanalysis was performed, which was accomplished by recording IR spectra using an ATR crystal from the surface area of 50–100  $\mu\text{m}$ . While



**Figure 6.** SDOSS volume concentration changes near the F–A interface, relative COO $^-$ Na $^+$  concentration changes (intensity ratio of 1558/1159 cm $^{-1}$ ) and the estimated shell  $T_g$  for 45/45/10% Sty/*n*-BA/MAA latexes plotted as a function of the degree of neutralization. The vertical size of an arrow indicates the error bar.

circles marked in Figure 3 (a) indicate spectral acquisition areas at the F–A interface, Figure 3 (b) illustrates a series of spectra that correspond to points A, B, C, and D of Figure 3 (a). The band at 1159 cm $^{-1}$  due to the C–O–C stretching modes of *p*-*n*-BA does not change in intensity, but the bands at 1050 and 1216 cm $^{-1}$  due to SDOSS decrease while moving IR beam from points A to D, thus illustrating that the observed aggregates in Figure 3 (a) are mainly composed of water soluble SDOSS islands. It should be noted that the presence of the 1216 and 1050 cm $^{-1}$  bands also indicates that, when latex films are coalesced at 20% RH for 5 days, SO $_3^-$ Na $^+$ ...H $_2$ O and SO $_3^-$ Na $^+$ ...COOH interactions<sup>10–12</sup> appear to be weak, as demonstrated by the blowup of the 1050 cm $^{-1}$  band (Figure 3(b), Trace B), with the presence of the 1056 and 1046 cm $^{-1}$  shoulders resulting from SO $_3^-$ Na $^+$ ...COOH and SO $_3^-$ Na $^+$ ...H $_2$ O interactions.<sup>16</sup> This observation is somewhat surprising because these associations are present under 80% RH film formation conditions.<sup>13</sup>

Because the dynamics of water evaporation may affect these interactions, SDOSS exudation to the F–A interface during the 50/50/5% Sty/*n*-BA/MAA copolymer latex film formation process was examined using ATR FTIR and the spectra were recorded from the F–A interface as a function of time. The results are shown in Figure 4, Traces A, B, C, D, and E and the spectra were recorded from the F–A interface after 1, 3, 5, 8, and 10 days of coalescence, respectively. As seen, when coalescence times are extended to 1, 3, and 5 days, the band at 1046 cm $^{-1}$  due to S–O symmetric stretching modes resulting from the SO $_3^-$ Na $^+$ ...H $_2$ O interactions is detected (Traces A, B, and C), respectively. However, the band at 1050 cm $^{-1}$  due to free SO $_3^-$ Na $^+$  groups of SDOSS increases when coalescence times extend to 8 days and beyond, indicating that the SO $_3^-$ Na $^+$ ...H $_2$ O interactions are diminished at extended times under 20% RH, and water was removed from the film.

At this point it is appropriate to examine the effect of an MAA shell on SDOSS exudation. As shown in Figure 1 (a), the *p*-(Sty/*n*-BA) seed has an average particle size of 69 ± 10 nm. As copolymerization progresses, the particle

size increases to 94 ± 15 nm (Figure 1 (b)), 112 ± 10 nm (Figure 1 (c)), and 132 ± 10 nm (Figure 1 (d)) for 50/50/0%, 47.5/47.5/5%, and 45/45/10% sty/*n*-BA/MAA latexes, respectively, and over 90% of acid groups are titratable on latex particle surfaces. As shown in Figure 2, the presence of MAA on latex surfaces diminishes the exudation of SDOSS that most likely results from the increased hydrophilicity of the particle surfaces. In an effort to justify this hypothesis, a 47.5/47.5/5% Sty/*n*-BA/MAA copolymer latex suspension was neutralized with a NaOH solution and the degree of neutralization was determined based on the NaOH/COOH ratios. The resulting ATR FTIR spectra recorded from the F–A interface of coalesced films are illustrated in Figure 5 (a) Traces A, B, C, and D, respectively. As seen, when going from 0 to 100% neutralization, the 1050 cm $^{-1}$  band due to free SO $_3^-$ Na $^+$  groups decreases, followed by its increase when the degrees of neutralization reach 50% and 100% (Figure 5 (a), Traces C and D). At the same time, the bands at 1558 and 1417 cm $^{-1}$  are detected, and are attributed to symmetric and asymmetric C–O stretching modes of COO $^-$ Na $^+$  groups.<sup>17</sup> The same results are shown in Figure 5 (b) for 45/45/10% Sty/*n*-BA/MAA copolymer latex films and Traces A, B, C, D, E, and F are ATR FTIR spectra recorded from the F–A interfaces of 45/45/10% Sty/*n*-BA/MAA copolymer latexes. As seen, the primary difference between latexes containing 5% and 10% MAA is the magnitude of the 1050 cm $^{-1}$  band at different degrees of neutralization.

Previous studies<sup>18,19</sup> concerned with the SDOSS migration in ethyl acrylate/methacrylate acid latexes indicated that SDOSS mobility is controlled by neutralization, and these results confirm that for Sty/*n*-BA this is also the case. However, the main differences between these two systems is the effect of the  $T_g$  of latexes which results from neutralization of the latex particle surface acid groups, thus causing an increase of the  $T_g$  of the particle outer layer. Due to the fact that the empirical  $T_g$  determination of the core/shell particles is troublesome, the  $T_g$  of Sty/*n*-BA copolymer was estimated using the Fox equation.<sup>20</sup> Furthermore, the Eisenberg empirical ap-

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**Table 2. Glass Transition Temperature and  $T_g$  Increments of Copolymers**

polymer	$T_g$ (K)	$T_g$ (°C)
<i>p</i> (Sty/ <i>n</i> -BA)	279 <sup>a</sup>	6
PMAA	458 <sup>b</sup>	185
PMAA-Na <sup>+</sup>	583 <sup>b</sup>	310

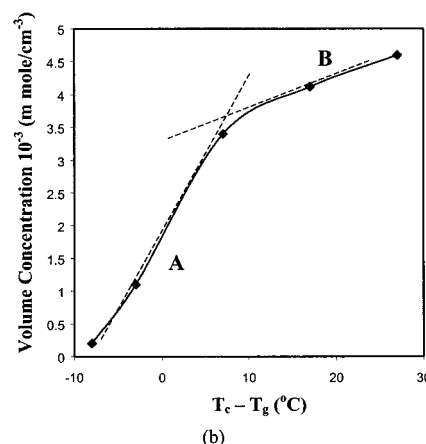
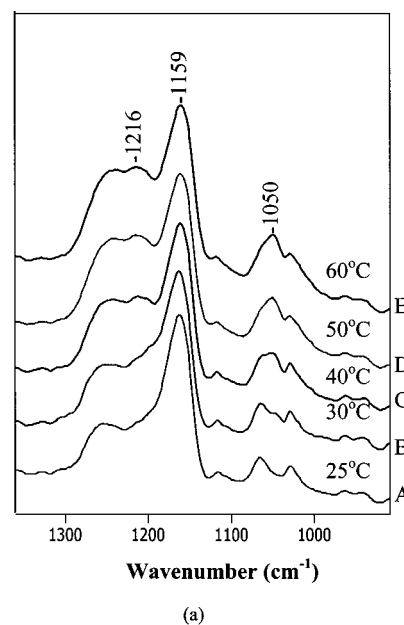
  

polymer	$\partial T_g / \partial c$ (°C/mol %)
<i>p</i> (Sty/ <i>n</i> -BA)-PMAA	1.79 <sup>c</sup>
<i>p</i> (Sty/ <i>n</i> -BA)-PMAA(Na <sup>+</sup> )	3.04 <sup>c</sup>

<sup>a</sup> Ref 20. <sup>b</sup> Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989. <sup>c</sup> Ref 5.

proach<sup>21</sup> was utilized for the core/shell Sty/*n*-BA/MAA neutralized latexes, which postulates that  $T_g$  increases linearly with the increase of ionic group content. This is expressed by  $T_g = cq/a$ , where:  $c$  is the mole fraction of acid or ionic groups in the copolymer,  $q$  is the ionic charge, and  $a$  is the characteristic distance representing the center-to-center separation of the cationic and anionic pairs. The values of  $\partial T_g / \partial c$  calculated for *p*(Sty/*n*-BA)-P-MAA and *p*(Sty/*n*-BA)-*p*-MAA(Na<sup>+</sup>) are 1.79 °C/mol % and 3.04 °C/mol %, respectively.<sup>5</sup> The  $T_g$  of *p*(Sty/*n*-BA) (50/50 w/w%) copolymer latex obtained from the Flory–Fox equation and the  $T_g$  of ionomers estimated using the Eisenberg approach<sup>21</sup> are listed in Tables 2 and 3, respectively. To correlate the SDOSS volume concentration changes near the F–A interface, the 1558/1159  $\text{cm}^{-1}$  band intensity ratio, the degree of neutralization, and the outer layer  $T_g$  of the copolymer latexes were correlated and are plotted in Figure 6. It should be noted that the 1558/1159  $\text{cm}^{-1}$  ratio represents the relative amount of COO<sup>−</sup>Na<sup>+</sup> groups on the latex film surface, and the SDOSS volume concentration was determined using the previously developed ATR FTIR quantitative approach.<sup>22</sup> It is quite apparent that the COO<sup>−</sup>Na<sup>+</sup> groups are detected when a 50% of neutralization is reached, and their concentration levels increase for completely neutralized latex particles. The  $T_g$  of the outer copolymer layer increases from 29 to 45 °C when the degree of neutralization reaches 100%. At the same time, the SDOSS volume concentration decreases from  $3.7 \times 10^{-3}$  to  $2 \times 10^{-4}$  mmol/ $\text{cm}^3$  when the  $T_g$  changes from 29 to 33 °C. However, when the  $T_g$  is further increased by the increased degree of neutralization from 50 to 100%, the migration of SDOSS is enhanced, and SDOSS concentration levels increase to  $5 \times 10^{-3}$  and  $8.1 \times 10^{-3}$  mmol/ $\text{cm}^3$  for 50 and 100% neutralization, respectively. Analysis of the results shown in Figure 6 indicates that a minimum of the SDOSS volume concentration near the F–A interface occurs at about 20–30% of neutralization. These results show that by synthetic modification of latex particle surfaces, it is possible to control surfactant release to the interfacial regions, in this case to the F–A interface. Furthermore, depending upon the degree of neutralization, latex coalescence mechanisms may be governed by different processes that are affected by the outer most outer particle layer.

One of the important aspects of latex coalescence is the temperature difference between the coalescence temperature  $T_c$  and the actual  $T_g$  of latex particles. As we already established, this difference plays an important role not



**Figure 7.** (a) ATR FTIR spectra in the 1650–900  $\text{cm}^{-1}$  region recorded from the F–A interface of 45/45/10% Sty/*n*-BA/MAA latex neutralized at 25% and coalesced at: A – 25 °C; B – 30 °C; C – 40 °C; D – 50 °C; E – 60 °C; (b) A plot of SDOSS volume concentration at the F–A interface as a function of  $T_c - T_g$ .

only on the mobility of latex components, but on latex coalescence. Therefore, to further understand the  $T_c - T_g$  significance on SDOSS migration, latex films were coalesced at 25, 30, 40, 50, and 60 °C for 2 h, followed by cooling to 25 °C, and ATR FTIR spectra were recorded from the F–A interface. While Figure 7 (a) shows the resulting spectra, with the 1050  $\text{cm}^{-1}$  band due to SDOSS increasing at higher  $T_c$ , a plot of the amount of SDOSS migration to the F–A interface as a function of  $T_c - T_g$  is shown in Figure 7 (b). It is quite apparent that when  $T_c - T_g$  is negative ( $T_c < T_g$ ), concentration levels of SDOSS increase at higher rates; this is represented by the slope of line A. When  $T_c - T_g$  crosses the point where  $T_c = T_g$ , and becomes positive ( $T_c > T_g$ ), the slope changes and the rate at which SDOSS migrates to the F–A interface is slow, but the amount of SDOSS is high.

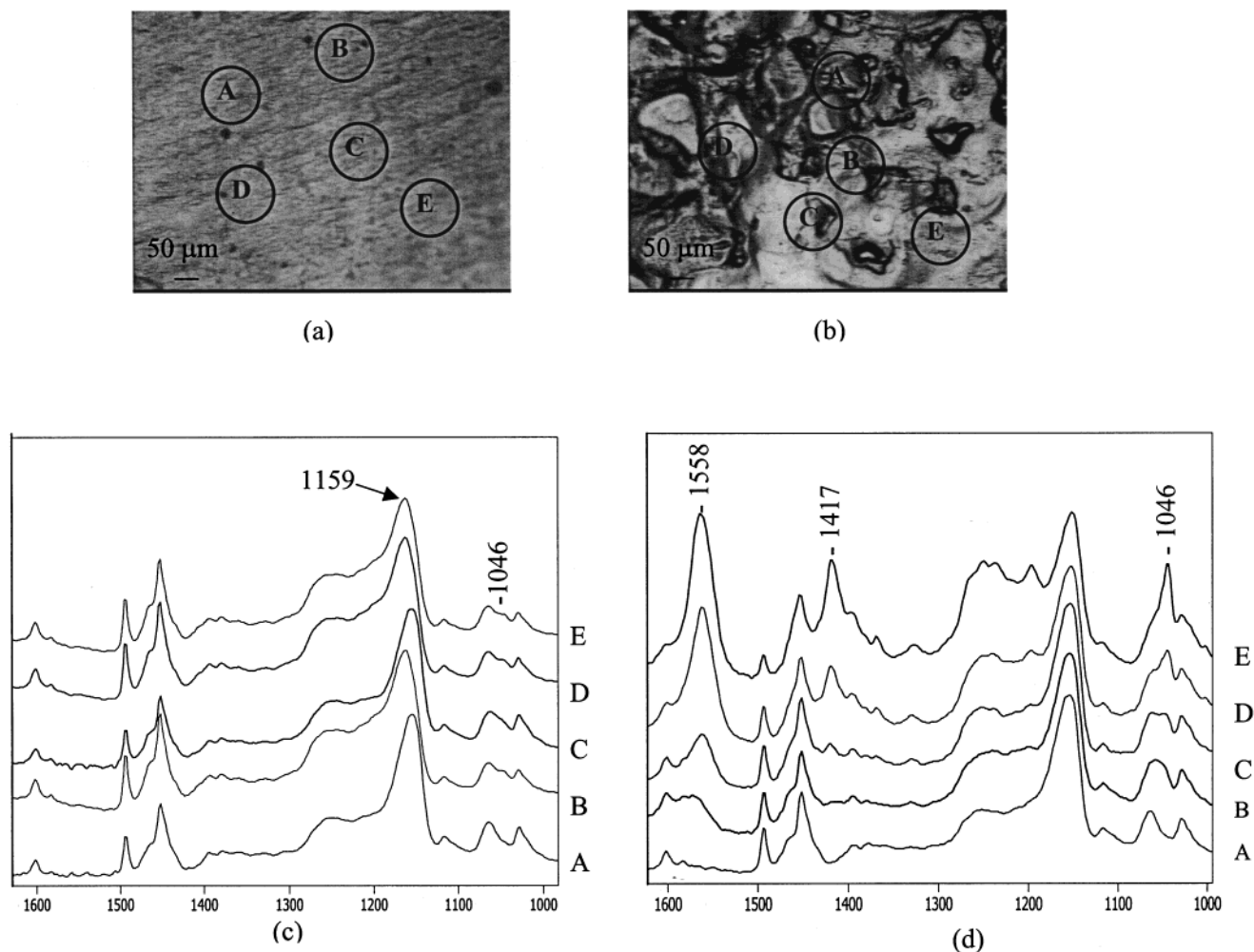
The results shown in Figure 7 are somewhat surprising because if the  $T_g$  of the latex and compatibility among its components are the main factors that affect SDOSS migration, one would expect that, with the increased degree of neutralization, the  $T_g$  increases and the compatibility between polar ends of SDOSS and MAA shell will also increase because latex surfaces become more

(20) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(21) Eisenberg, A. *Macromolecules* **1976**, *1*, 126–128.

(22) The extinction coefficient of the 1046  $\text{cm}^{-1}$  band was obtained using Circle ATR FTIR, using double KKT approach,<sup>16</sup> it is possible to determine SDOSS volume concentration at various degrees of neutralization. It should be noted that the extinction coefficient determined at the 1046  $\text{cm}^{-1}$  band due to SDOSS···H<sub>2</sub>O, we assumed that the extinction coefficient of the SDOSS band at 1050  $\text{cm}^{-1}$  is similar.





**Figure 8.** (a) and (b) Optical images recorded from the F–A interface of 45/45/10% Sty/*n*-BA/MAA copolymer: (a) – 25% neutralization; (b) – 100% neutralization. (c) and (d) ATR FTIR spectra in the 1640–990  $\text{cm}^{-1}$  region recorded from the F–A interface of Sty/*n*-BA/MAA: (c) 25% neutralization; (d) 100% neutralization. Traces A, B, C, D, and E represent the spectra recorded from areas marked A, B, C, D, and E of (a) and (b) (Coalescence time: 3 days, RH = 20%).

**Table 3. Composition and Estimated  $T_g$  Values Using Eisenberg Empirical Approach for the Shell Phase of Latex Particles<sup>a</sup>**

latexes	% neutralization	PMAA (mol %)	PMAA–Na <sup>+</sup> (mol %)	$T_g$ (K) ( $\pm 2$ )	$T_g$ ( $^{\circ}\text{C}$ ) ( $\pm 2$ )
47.5/47.5/5% Sty/ <i>n</i> -BA/MAA	0	6.56	0	290	17
	25	4.92	1.64	293	20
	50	3.28	3.28	295	22
	100	0	6.56	299	26
45/45/10% Sty/ <i>n</i> -BA/MAA	0	12.9	0	302	29
	12.5	11.29	1.61	304	31
	22.5	10.48	2.42	305	32
	25	9.67	3.23	306	33
	50	6.45	6.45	310	37
	100	0	12.9	318	45

<sup>a</sup> Ref 21.

hydrophilic. If this is indeed the case, one would anticipate that at a 50–100% degree of neutralization, SDOSS migration should be further inhibited. However, our data clearly indicate that enhanced SDOSS migration is observed at 50–100% degrees of neutralization, thus suggesting that there are other factors governing SDOSS release. For example, the neutralization of the acid surface functionalities may result in the swelling of the latex particles by water due to the increased solubility brought on by the formation of carboxylate groups. As a result, the viscosity of the resulting emulsion may increase with the increase of pH due to the larger hydrodynamic volume of

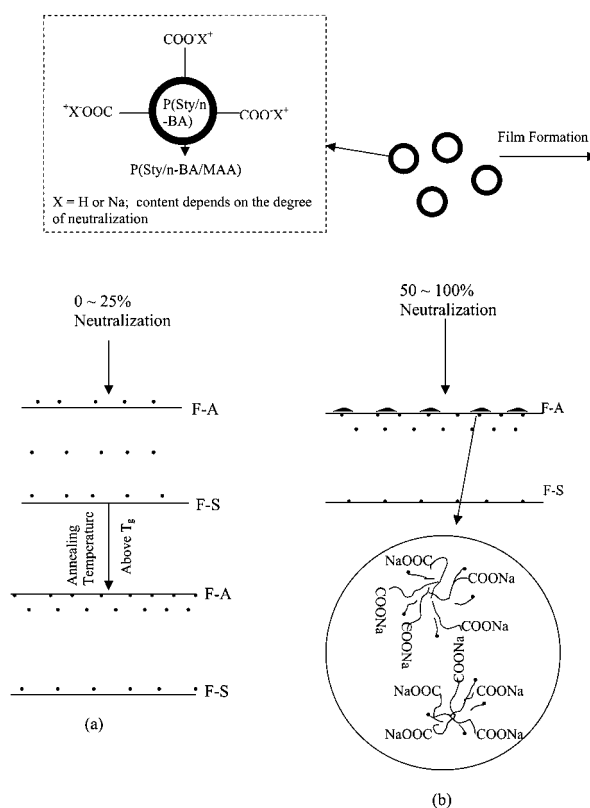
the particles caused by chain extension.<sup>23</sup> Therefore, hydrophobic *n*-butyl groups pendant on the copolymer chain will be pushed out into the aqueous phase and attract residual nonadsorbed surfactant molecules present in an aqueous phase to form solubilized polymer–surfactant complexes through hydrophobic interactions.<sup>19</sup> On the contrary, if the neutralization process leads to the displacement of surfactant molecules from the particle surfaces into an aqueous phase, the enhanced surfactant migration would be observed since surfactant molecules

(23) Okubo, M.; Xu, D. H.; Kanai, K.; Matsumoto, T. *Coll. Polym. Sci.* **1987**, 265, 246.

would be capable of diffusing through the latex film with the water flux out of the film. At lower degrees of neutralization, SDOSS molecules are not displaced from particle surfaces as demonstrated by the lack of SDOSS enrichment near the F–A interface. When the degree of neutralization is high, SDOSS is forced from the particle surface into the aqueous phase and migrates to the F–A interface with the flux of water during the initial stages of film formation. Thus, latex particles containing MAA act as polyelectrolyte particle surfaces releasing or accepting ionic surfactants depending on the pH of the surface layer.

In an effort to examine how latex surface morphology changes due to SDOSS migration, we also utilized microscopic FTIR imaging. This allows us to detect not only surface homogeneity, but also chemical entities responsible for morphological changes. Optical images obtained from the F–A interface of these films are shown in Figure 8 (a) and (b) and their corresponding ATR FTIR spectra are plotted in Figure 8 (c) and (d). As seen, for the 25% neutralized latex (Figure 8a), the image is uniform, and analysis of ATR FTIR spectra (Figure 8 (c) Traces A to E) show that the  $1050\text{ cm}^{-1}$  band due to SDOSS is not detected. Therefore, SDOSS stratification does not occur during latex film formation process. However, when the latex is 100% neutralized, the surface of the latex film is nonuniform (Figure 8 (b)), which is demonstrated by the formation of aggregates. In an effort to identify the origin of aggregates, microscopic ATR FTIR experiments were conducted by recording the spectra using an ATR crystal on the surface area of  $50\text{--}100\text{ }\mu\text{m}$ . While the circles marked in Figure 8 (b) indicate spectral acquisition areas at the F–A interface, Figure 8 (d) illustrates a series of spectra that correspond to points A, B, C, D, and E of Figure 8 (b). The band at  $1159\text{ cm}^{-1}$  due to the C–O–C stretching modes of *p*-*n*-BA does not change its intensity, but the intensities of the  $1050\text{ cm}^{-1}$  bands due to S–O stretching modes in SDOSS, and the  $1558$  and  $1417\text{ cm}^{-1}$  bands due to symmetric and asymmetric C–O stretching vibrations of  $\text{COO}^-\text{Na}^+$  groups resulting from neutralization, increase while moving IR beam from points A through E. These results show that the observed aggregates in Figure 8 (d) are mainly composed of SDOSS and carboxylate groups. Furthermore, for fully neutralized latex films (Figure 8 (d)), higher intensities of the  $1558$  and  $1417\text{ cm}^{-1}$  bands are always associated with the enhanced intensity of the  $1046\text{ cm}^{-1}$  band, indicating that  $\text{SO}_3^-\text{Na}^+$  entities of SDOSS parallel the presence of  $\text{COO}^-\text{Na}^+$  groups.

These data indicate that morphological and chemical changes near the F–A interface are a function of the latex particle composition. Therefore, we are in a position to identify processes that occur during core/shell latex coalescence. The latex system examined in this study can be depicted as a particle suspension stabilized by a layer of *p*-MAA and SDOSS that, in the presence of water, forms polyelectrolyte particle surfaces sensitive to the acid/base character of an aqueous environment. When the degree of neutralization is in the 0–25% range, no ionic aggregates are detected. As soon as acid groups are 50–100% neutralized, the latex particle surface releases SDOSS to an aqueous phase. Some SDOSS is carried to the F–A interface during film formation, and some is dispersed in the polymer matrix. Thus, the presence of  $\text{SO}_3^-\text{Na}^+$  and  $\text{COO}^-\text{Na}^+$  entities results in the conversion of potential energy into mechanical movement when ionic bonds are broken. One can envision that when these species are attached to a longer polymer chain, chemically



**Figure 9.** Schematic diagram of latex film formation mechanisms and its relationship to the SDOSS mobility in Sty/*n*-BA/MAA latexes: (a) 0–25% neutralization; (b) 50–100% neutralization.

induced conformational changes along a polymer backbone result in macromolecular motions.

In summary, polyelectrolyte-containing latex particle surfaces, initially dispersed in an aqueous phase, upon the loss of water undergo a transition to form a solid film. A schematic representation of these processes is illustrated in Figure 9, (a) and (b), where the degree of neutralization is the deciding factor on the magnitude of SDOSS migration and subsequent ionic domain formation. Similar to conventional ionomers with unique solid state and solution properties, such as increased  $T_g$ , higher modulus, and melting viscosity,<sup>24–26</sup> Sty/*n*-BA/MAA films exhibit similar behavior due to the presence of outer layers of MAA and SDOSS.

## Conclusions

When MAA is affixed to the surface of Sty/*n*-BA/MAA particles, SDOSS migration can be controlled not only by the increase of compatibility between SDOSS and latex copolymer, but also by adjusting neutralization levels. When neutralization levels are low (0–25%), Sty/*n*-BA/MAA latex particle surfaces exhibit polyelectrolyte-like behavior, which inhibit SDOSS migration due to the increase of hydrophobic interactions between SDOSS and copolymer and the  $T_g$  of the latex copolymer. For  $T_c - T_g > 0$ , SDOSS migration to the F–A interface is enhanced. However, at greater degrees of neutralization, SDOSS

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can be released during latex coalescence to form ionomers near the F–A interface and SDOSS~COO<sup>-</sup>Na<sup>+</sup> hydrophilic associations dominate these clusters. Although the majority of studies on movement and motion were conducted on biological movements,<sup>27</sup> this study attempts to correlate not only chemical changes with mobility in manmade polymers, but also addresses the issue of how

compatibility among individual components may affect their mobility.

**Acknowledgment.** The authors are thankful to the National Science Foundation I/UCRC Program (Grant No. EEC 0002775) for supporting these studies.

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