Surface and Interfacial FTIR Spectroscopic Studies of Latexes. I. Surfactant–Copolymer Interactions

KEVIN W. EVANSON and MAREK W. URBAN*

Department of Polymers and Coatings, North Dakota State University, Fargo, North Dakota 58105

SYNOPSIS

Molecular level interactions between surfactants and copolymers as well as transient effects during latex film formation play an important role in latex technology. Photoacoustic (PA) and attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy were utilized for the characterization of interactions between sodium dioctylsulfosuccinate and ethyl acrylate/methacrylic acid (SDOSS/EA/MAA) copolymer in latex films at both the film–air and film–substrate interfaces. It is shown that the splitting of the asymmetric S—O stretching normal vibrations of the SO_3^- groups in the presence of Na^+ counterions occurs only when weak —COOH acid groups of latex are present. The absence of the COOH groups either by neutralization of latex or intentional synthesis eliminates the S—O$\cdots$H—O— associations that are the primary source of the symmetry changes resulting in the splitting of the S—O symmetric mode at 1050 cm^{-1} to two bands at 1046 and 1056 cm^{-1}.

INTRODUCTION

Although polymer latices and their technology have been established many years ago, there is an extensive effort underway to develop novel modes of preparation, techniques for cleaning, and methods for determining their surface or bulk characteristics. A particular emphasis has been given to the potential applications of polymer latices as model colloids.[1] In spite of the fact that typical formulations of styrene consisting of monomer, water, water soluble initiator, and emulsifier result in a polydisperse latex, several approaches including seed growth,[2] controlled emulsifier concentrations,[3,4] and combinations of ionic and nonionic surfactants[5] have been employed to achieve monodispersity. Such monodisperse latices can be easily reproduced, but the detailed surface characterization remains an elusive goal. Following the definition of La Mer,[6] latices are considered to be "monodispersive" when the vari-

ation of the mean diameter is less than 10%. The techniques that may be employed to determine average particle diameters include electron microscopy,[7,8] light scattering,[9–11] ultracentrifugation,[10] small angle X-ray scattering,[12] soap titration,[13] and photon correlation spectroscopy.[14] Transmission electron microscopy is the technique most frequently utilized since it allows a visual assessment of the size, shape, and the size distribution of particles. The capability of visual assessments has enabled the observation of interparticle bridge formation,[15] anomalous particle morphology,[16] and the presence of a fraction of small particles resulting from secondary nucleation.[17]

Although monodispersity and the particle-size diameter are essential factors determining film properties, it is also important to establish interactions between individual latex components. In this case, spectroscopic techniques are usually employed since information on the molecular level is sought. Among spectroscopic techniques, Fourier transform infrared spectroscopy (FTIR) had found only limited application to latex systems in the past, mainly because of the strong absorbance of water in the infrared region.

Recently, Zhao et al.[18] demonstrated the kinetics of surfactant exhudation in latex films containing anionic surfactants by ATR FTIR. Surfactant enrichment at both the film–air and film–substrate interface was observed. The enrichment was dependent upon the nature of the surfactant, the interface involved, the global concentration of surfactant, and the coalescence time. The concentration of surfactant at the film–air interface was higher than at the substrate interface, and the distribution was mostly established after 3 h. However, analysis of surfactant exhudation in the early stages of coalescence as well as interactions between polymer and other components of the latex system have not been reported.

Since the properties of latex films may be influenced by the surface activity of surfactants, determination of the distribution of surfactant throughout the latex film is essential and plays a significant role in the film properties such as adhesion and other physical properties. Especially, the latex composition at the film–substrate and the film–air interfaces is of particular interest. These reasons motivated further investigation into the distribution of surfactants throughout latex films during film formation. This is the first paper of a series focusing on latex film–air and film–substrate interfaces as monitored by the surface FTIR techniques.

The present study is concerned with an SDOSS/EA/MAA (sodium dioctylsulfosuccinate/ethyl acrylate/methacrylic acid) latex system in which the polarity of the system was modified by the addition of a small fraction of acid monomer. In most latices, a small percentage of acid monomer[19] is incorporated to improve adhesion, increase stability of the latex particles, control viscosity, and provide cross-linking sites for interparticle thermosetting reactions. ATR, Circle ATR, and photoacoustic FTIR techniques will be employed to the analysis of latex films at the film–substrate and film–air interfaces. Circle ATR was originally developed for the analysis of aqueous solutions that are difficult to analyze due to strong water absorbance in transmission measurements.[20] Using Circle ATR, the distribution of surfactant at the substrate interface can be monitored immediately after application and throughout the early stages of film formation. Hence, Circle ATR is well suited for the analysis of film composition near the substrate and gives a significantly improved signal-to-noise ratio over that of the traditional ATR technique.[21] Photoacoustic FTIR allows the detection of the air–film interface[22–26] during the early stages of film formation; thus, both techniques complement each other.

EXPERIMENTAL

Latex Preparation

Ethyl acrylate 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 upon total formulation weight included double deionized (DDI) water, 53.4%; ethyl acrylate, 42.1% (95.8% based upon total monomer weight); methacrylic acid, 1.9% (4.2% based upon total monomer weight); sodium dioctylsulfosuccinate (SDOSS, Aerosol OT; American Cyanamide), 2.3% (4.0% based on total monomer weight); and ammonium persulfate (Aldrich Chemical Co.), 0.26% (0.60% based on total monomer weight). The monomers were mixed together thoroughly and placed in the addition funnel. The reaction vessel was purged for 20 min with nitrogen, then all the water, SDOSS, and initiator were added and allowed to stir for 5 min while heating. At 40°C, 20% of the monomer mixture was slowly added with stirring over a 5 min period. At this point, the temperature was raised to 70°C and held constant until a white milky emulsion was observed, followed by slow monomer addition over a 3 h period. The temperature was then raised to 85°C and held for 3 h or until no monomer odor could be detected. The final product contained 46% solids. The preparation of the pure copolymer studied was carried out using a procedure reported earlier.[27]

Neutralization of the Latex

Sodium hydroxide (Aldrich Chemical Co.) was used to prepare a 0.075 molar NaOH solution. Neutralization was carried out on a 1 : 1 ratio of COOH : NaOH based on theoretical equivalents of acid in the latex.

Film Preparation and Properties

All films were prepared to maintain the film thickness between 100 and 150 μm. Upon deposition, the films were all air-dried for 72 h (unless otherwise specified) at 23°C. For the PAS measurements, the films were prepared by direct deposition of a predetermined amount of latex on an aluminum photoacoustic sample cup. A typical thickness of dry films was approximately 100 μm. The films studied

by Circle ATR were applied directly to the ATR crystal to yield films approximately 75 μm thick. The films prepared on other substrates such as polyethylene, polytetrafluoroethylene (PTFE), and mercury were prepared in a similar manner.

The glass transition temperature of the latex films (−5°C) was determined from the average of three runs on a DuPont Instruments 910 differential scanning calorimeter equipped with a DuPont Thermal Analyzer 2000. The temperature range was from −50 to 250°C at a heating rate of 20°C/min.

Spectral Measurements

Transmission, attenuated total reflectance (ATR), Circle ATR, and photoacoustic (PA) FTIR techniques were used to monitor latex films. Transmission, Circle ATR, and rectangular ATR FTIR spectra were collected on a Mattson Cygnus 25 instrument equipped with a single beam spectrometer (Sirius 100). In a typical experiment, 200 scans at a resolution of 4 cm⁻¹ were collected. Temperature transmission spectra were obtained in the same manner with the use of a Spectra Tech model 0019-020 heated IR cell equipped with a model 4001 KC temperature controller (Omega Engineering Inc.). Circle ATR spectra were obtained using a cylindrical internal reflection accessory with a ZnSe circular crystal at an average angle of incidence of 45° (Spectra Tech Inc.). Latex films were prepared directly on the ZnSe crystal to provide spectra of the film–substrate interface collected as a function of time. Latex film–air interface spectra were collected using a procedure previously described.[21] The rectangular ATR attachment (Mattson Instruments) was equipped with a KRS-5 crystal aligned to give an incident beam angle of 45 degrees.

Photoacoustic FTIR spectra were recorded on a Digilab FTS-10M equipped with a photoacoustic cell (Digilab). Four hundred single-beam spectra were signal averaged at a resolution of 4 cm⁻¹ and ratioed against a carbon black reference. Each sample was purged with helium for 5 min prior to the spectral collection. Both FTIR instruments were purged continuously with purified air (Balston filter system).

Spectral Analysis

All spectra were transferred to an AT compatible computer for further spectral analysis utilizing Spectra Calc software (Galactic Ind.). The maximum entropy restoration algorithm (Spectra Calc;

Galactic Ind.) was used to isolate heavily overlaying bands in the carbonyl region of the spectra.

Particle-size Analysis

Latex particle-size analysis was performed on a Coulter submicron particle analyzer model N4-SD using 200 scans at a light angle of 90°, a temperature of 20°C, and a refractive index of 1.33. The latex average particle diameter was determined to be 224 nm.

RESULTS AND DISCUSSION

Before we begin the analysis of the surface infrared spectra of ethyl acrylate–methacrylic acid copolymer latex, let us set the stage by defining the relevant features in the infrared spectra of all individual components of the latex. Figure 1 illustrates photoacoustic FTIR spectra of sodium dioctylsulfosuccinate (trace A), ethyl acrylate/methacrylic acid copolymer only (trace B), and the corresponding ethyl acrylate–methacrylic acid copolymer latex (trace C). Although all three spectra exhibit a strong carbonyl band due to alkyl ester groups centered at 1735 cm⁻¹, the shoulder at 1703 cm⁻¹ appears only in the spectra of the solution copolymer acrylic (trace B) and the latex (trace C). The 1703 cm⁻¹ band is characteristic of carboxylic acid dimers that
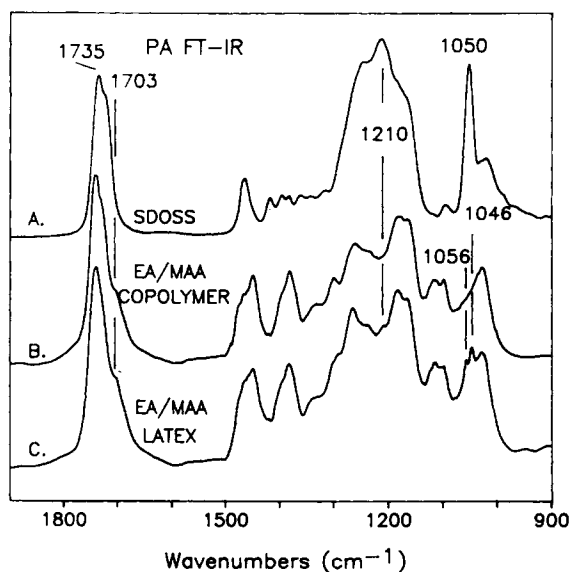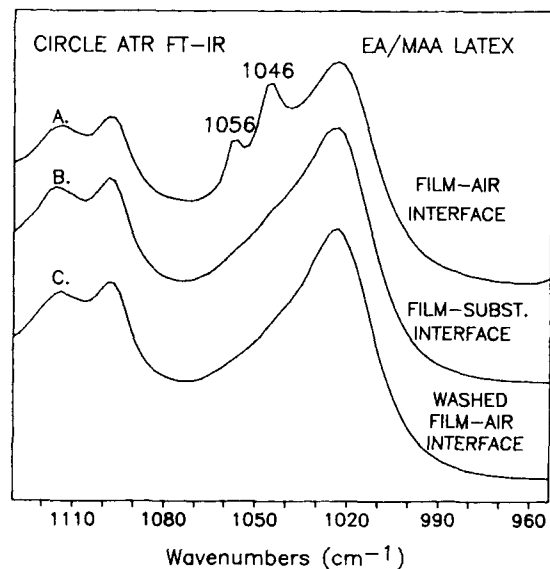

Figure 1 PA FTIR spectra in the 1900 to 900 cm⁻¹ region: (A) SDOSS (surfactant only); (B) EA/MAA copolymer; (C) EA/MAA latex.

have a tendency to form strong intermolecular hydrogen bonding.[28] The presence of SO_3^- groups in the surfactant is manifested by the strong band at 1050 cm^{-1} (trace A), attributed to the symmetric S$-$O stretching vibrations of the sodium sulfonate groups.[29] The asymmetric S$-$O stretching mode appears at 1210 cm^{-1}. A closer examination of the latex spectrum (trace C) indicates, however, the presence of two bands at 1056 and 1046 cm^{-1}.

Postponing temporarily the evaluation of the differences between these three spectra until later on, let us focus on the C$-$H stretching region of the surfactant (trace A), EA/MAA copolymer only (trace B), and the latex (trace C). They are shown in Figure 2. The spectra of the latex and the copolymer exhibit the band at 2981 cm^{-1}, which are attributed to the asymmetric C$-$H stretching normal vibrations of the CH$_3$ units, and the bands at 2960 and 2934 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of the CH$_2$ groups, respectively. Relative to the spectrum of the EA/MAA copolymer only (trace B), the spectrum of the latex (trace C) indicates a marked increase of the relative intensity of the bands at 2981 and 2934 cm^{-1}. Since photoacoustic FTIR spectroscopy is a surface-sensitive technique, and these bands are attributed to the C$-$H normal vibrational modes of the surfactant, such an observation may suggest a greater concentration of the surfactant (SDOSS) on the latex surface. This, in turn, would indicate that the
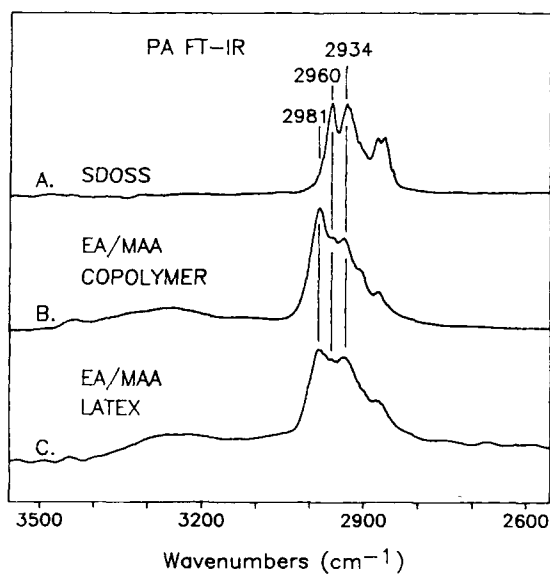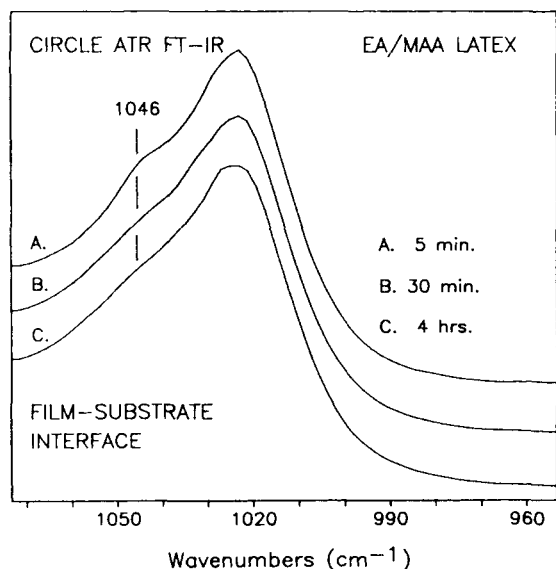

Figure 3 Circle ATR FTIR spectra of EA/MAA latex in the 1130 to 950 cm^{-1} region: (A) film–air interface; (B) film–substrate interface; (C) film–air interface washed with MeOH/DDI H$_2$O solution.

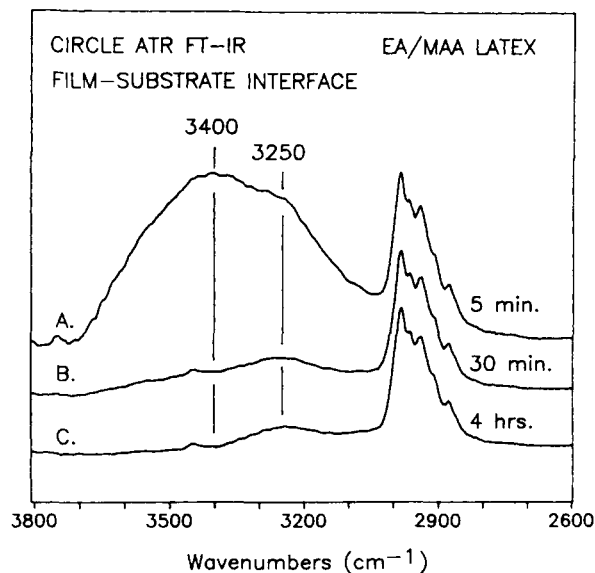surfactant exudes to the film–air interface during its coalescence.

In an effort to establish if indeed the exudation process occurs, the latex film infrared spectra at the film–air and film–substrate interface were recorded using Circle ATR FTIR spectroscopy. While the experimental section provides all the necessary details relevant to the use of Circle ATR, Figure 3 illustrates a series of ATR FTIR spectra recorded at the film–air (trace A) and film–substrate (trace B) interfaces. Similarly to the PA FTIR results, the spectrum of the film–air interface indicates the presence of the bands at 1056 and 1046 cm^{-1}. Changing the configuration of the sample with respect to the Circle ATR crystal allows us to establish the composition of the film-substrate interface. Trace B of Figure 3 illustrates the results of this analysis. It appears that both the 1056 and 1046 cm^{-1} bands are not detected, indicating that during coalescence the surfactant* exhudates to the film–air interface. To further substantiate the observed phenomenon, and taking advantage of the fact that the surfactant is water soluble, the film–air interface was washed with DDI water–MeOH (80 : 20 v/v). Such a surface modified sample was analyzed again at the film–air interface, and the resulting spectrum is shown in Figure 3, trace C. It is apparent that the bands at 1056 and 1046 cm^{-1} are absent, such as that seen in trace B, since the excess of surfactant was washed away from the film–air interface.

Figure 2 PA FTIR spectra in the 3550 to 2550 cm^{-1} region: (A) SDOSS; (B) EA/MAA copolymer; (C) EA/MAA latex.

Since exudation of the surfactant away from the film–substrate interface occurs during the latex film formation, the process can be monitored using Circle ATR. Figure 4 illustrates infrared spectra recorded as a function of time. Trace A exhibits a shoulder at 1046 cm^{-1} assigned to the S—O asymmetric stretching mode of the SO$_3^-$ groups. As the film formation proceeds, the 1046 cm^{-1} band diminishes as illustrated by traces A (5 min), B (30 min), and C (4 h). After 4 h, the film is completely transparent, indicating a continuous phase, and the shoulder at 1046 cm^{-1} is no longer present. Although the concentration gradient of the surfactant across the latex film has been reported earlier,[18] it is apparent that during the early stages only one band at 1046 cm^{-1} is detected, whereas the film–air interface exhibits an additional band at 1056 cm^{-1}.

The transient intensity changes of the 1046 cm^{-1} band are associated with and parallel the disappearance of a broad band around 3400 cm^{-1} attributed to water evaporating from the film. This is demonstrated in Figure 5. Because the surfactant is water soluble, during the initial stages of film formation, the concentration of the surfactant diminishes at the film–substrate interface as water evaporates from the system. It should also be noted that the spectrum obtained by subtracting out contributions of water from a 0.05 M aqueous solution of SDOSS reveals the spectrum of SDOSS with a


Figure 5   Circle ATR FTIR spectra in the 3800 to 2600 cm^{-1} region collected as a function of time for the EA/MAA latex as it coalesces: (A) 5 min; (B) 30 min; (C) 4 h.

strong band centered at 1046 cm^{-1}, shown in Figure 6(A). This observation indicates that the band at 1046 cm^{-1} of the latex spectrum (Fig. 1, trace C) is a result of hydration of the sulfonate group of the surfactant since these groups tend to be highly hydrophilic. In contrast, when the surfactant is dissolved in ethanol, the S—O stretching band appears

Figure 4   Circle ATR FTIR spectra in the 1070 to 960 cm^{-1} region collected as a function of time for the EA/MAA latex as it coalesces: (A) 5 min; (B) 30 min; (C) 4 h.
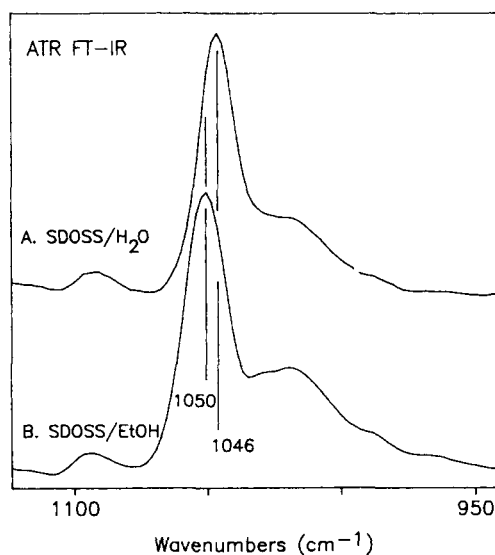
Figure 6   Transmission FTIR spectra of SDOSS after being dissolved in (A) H$_2$O and (B) ethanol, followed by solvent evaporation.

at 1050 cm^{-1} [Fig. 6(B)]. Although the observed frequency shift is only 4 cm^{-1}, this comparison indicates that the presence of water does affect the surfactant environment.

Vanderhoff [30] reported that surfactants may become insoluble in the polymer film and are then forced to the film–air interface due to incompatibility. Expanding this approach and going far beyond it, as a result of surface tension and surface tension differentials, surfactants may accumulate at the colloid interface in order to lower the high surface tension present between the polymer and the air. Such water soluble surfactants may be carried to the film–air interface during coalescence [18] by the water flux that passes between latex particles during film formation. This effect would be most pronounced in the very early stages of film formation when the concentration of water is the highest. As the water diffuses out of the film and away from the substrate, one would expect weaker bands due to surfactant. Indeed, the spectra (not shown) collected at the film–air interface for the case where a second layer of latex was prepared over a preexisting latex film resulted in very pronounced increases in the bands due to surfactant, indicating that the excess surfactant may relatively easily move with the water flux through the film.

To understand the origin of the surface surfactant–copolymer interactions, we will focus on the two bands at 1056 and 1046 cm^{-1} since they appear to be sensitive to the SO$_3^-$Na$^+$ environments. Both bands originate from the symmetric S—O stretching vibrations of the SO$_3^-$ groups, and because the copolymer contains carboxylic acid groups, hydrogen bonding between the carboxylic acid groups and the sulfonate groups or ionic interactions are most likely responsible for the occurrence of the two infrared bands in this region.

In an effort to establish the effect of hydrogen bonding, the spectra of the latex and the EA/MAA copolymer only were recorded as a function of temperature. It is well established that dissociation of the hydrogen-bonded species can be achieved at elevated temperatures, such as demonstrated in numerous studies on polymer blends.[28,31,32] In this case, we have utilized transmission FTIR measurements as the most convenient means to perform temperature studies. Since the 1056 and 1046 cm^{-1} bands are most pronounced on the latex surface, we will utilize digital subtraction as one of the spectral processing operations widely used in polymer analysis permitting the detection of subtle differences between spectra.[33] Being fully aware that the elevated temperatures may result in band distortions or

spectral broadening, the spectra of the ethyl acrylate–methacrylic acid copolymer at a given temperature were subtracted from the spectra of the ethyl acrylate–methacrylic acid copolymer latex recorded at the same temperature. This approach effectively eliminates contributions to the spectra from the band-broadening effects and enhances the changes as a result of higher temperatures. Trace A of Figure 7 shows the room temperature (25°C) subtraction spectrum that exhibits well-resolved bands at 1046 and 1056 cm^{-1} and complete elimination of the 1025 cm^{-1} band due to the —O—CH$_2$ stretching mode of the ester side chain groups. The latter was used as a reference in the digital subtraction. As the temperature is increased to 105° (trace B), there are no apparent changes in the appearance of both bands. However, when the temperature reaches 145°C (trace C), there is a marked decrease in the intensity of the 1056 cm^{-1} band. As the temperature is increased further to 185°C (trace D), the band at 1056 cm^{-1} is greatly diminished. This observation suggests that the 1056 cm^{-1} band is a result of interactions between the sulfonate group and the copolymer. It should be noted that it is possible to partially reverse the process upon cooling, though the effect is not as strong as prior to heating because of anhydride formation. Although these observations may indicate that at elevated temperatures the — — —SO$_3^-$ · · · HO— — — bonding dissociates freeing the SO$_3^-$ and COOH groups, there is an ap-
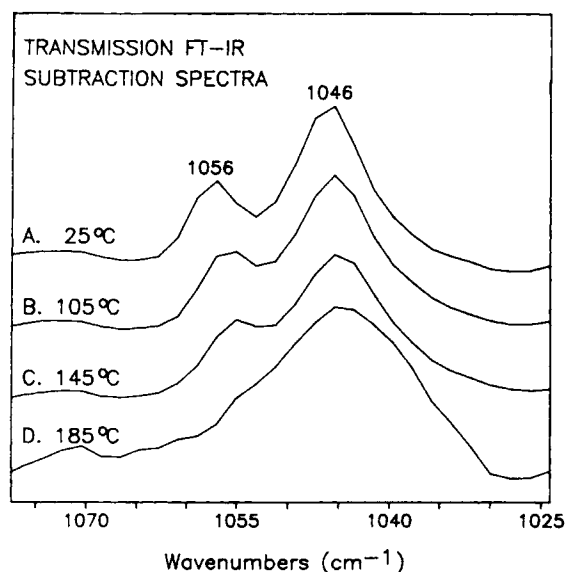
Figure 7 Transmission FTIR subtraction spectra of the EA/MAA latex in the 1075 to 1025 cm^{-1} region, collected as a function of temperature: (A) 25°C; (B) 105°C; (C) 145°C; (D) 165°C.

parent controversy as to the exact origin of these interactions. This is because usually the dissociation of hydrogen-bonded species occurs at lower temperatures and, moreover, using analogy of C=O···H—O associations in polymer blends, it is well established that the carbonyl normal vibrations will occur at higher wavenumbers when no hydrogen bonding occurs. In view of the above considerations, the 1046 cm^{-1} band would be more sensitive to the temperature changes. It should also be noted that both the 1056 and 1046 cm^{-1} bands are relatively weak in the original transmission spectra, because this mode of detection does not differentiate between the concentrations of the surface and the bulk species. This reinforces our earlier findings that the concentration of the species responsible for the appearance of the 1056 and 1046 cm^{-1} bands is much greater at the surface than in the bulk. Therefore, it is primarily a surface phenomenon.

In an effort to determine how temperature changes may affect acid groups of the latex, the carbonyl region of the spectra will be examined. If the interactions due to hydrogen bonding occur, one would anticipate observing changes in this region as a result of elevated temperatures and the presence of sodium ions in the surfactant. In addition, carboxylic acid groups have a strong tendency to form hydrogen bonds with each other, leading to the
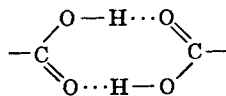
associations. These associations are reflected in the carbonyl vibrational frequency shifts by approximately 20–30 cm^{-1}. Figure 8(a) illustrates the carbonyl region of the EA—MAA copolymer latex as a function of temperature. Trace A (25°C) exhibits a weak shoulder at 1703 cm^{-1}, which has been previously assigned to the C=O stretching normal vibrations of hydrogen-bonded carboxylic acid dimer groups.[29] As the temperature increases, a slight decrease of the intensity of the 1703 cm^{-1} band is observed. This is illustrated in Figure 8(a), traces B, C, and D. At the same time, one would expect to see an increase of the 1760 cm^{-1} band due to "free" carboxylic acid groups liberated as a result of breaking hydrogen bonds at higher temperatures. Because these changes are very subtle, we have utilized the maximum entropy restoration algorithm to resolve heavily overlaying bands. This technique has several advantages[34] over other deconvolution techniques, such as a sound statistical background and no need
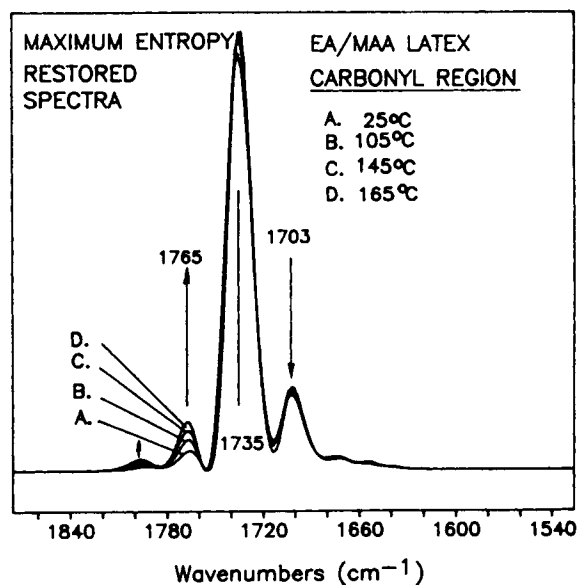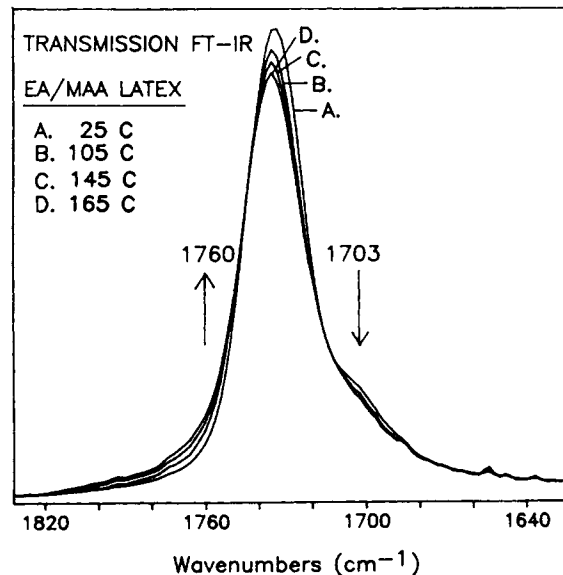

Figure 8 (a) Transmission FTIR spectra recorded as a function of temperature for the EA/MAA latex in the 1830 to 1630 cm^{-1} region: (A) 25°C; (B) 105°C; (C) 145°C; (D) 165°C (arrows point to the direction of intensity changes). (b) Maximum entropy restored spectra at various temperatures for the EA/MAA latex in the 1860 to 1530 cm^{-1} region: (A) 25°C; (B) 105°C; (C) 145°C; (D) 165°C.

to guess the number of overlaying bands in the spectrum. Figure 8(b) illustrates the restored bands of the carbonyl region recorded as a function of temperature. As the temperature increases [traces A, B, C, and D of Fig. 8(b), respectively], the band at 1703 cm^{-1} decreases slightly, indicating a lesser

amount of the hydrogen-bonded acid groups. These changes are accompanied by the intensity increase of the bands at 1760 and 1800 cm^{-1} assigned to "free" or monomeric carboxylic acid groups and cyclic anhydride groups, respectively.[28] The formation of cyclic anhydrides makes the process not fully reversible, as was demonstrated in Figure 7.

It is well known that at temperatures near 140°C carboxylic acids may form linear and cyclic anhydrides.[28] This is illustrated by the increasing intensity of the 1800 cm^{-1} band. A closer analysis reveals that there is no change of the intensity at 1703 cm^{-1} when the temperature is raised from 105 to 145°C. Instead, the band at 1760 cm^{-1} increases, indicating the greater concentration of "free" carboxylic acid species in this temperature range. Therefore, only a fraction of the carboxylic acid groups are involved in the hydrogen-bonding interactions with other carboxylic acid species. This observation is further substantiated by the decrease of the 1735 cm^{-1} band intensity that results from the breaking of interactions that lead to the formation of free[28,31,35] carbonyl groups of the acid functionality. Although hydrogen bonding between sulfonates and hydrogen donors has been previously reported,[36] no systematic spectroscopic data is available; therefore, it is essential to examine all other possible interactions before one concludes that the functional group participating in such associations is the sulfonate group of the SDOSS surfactant.
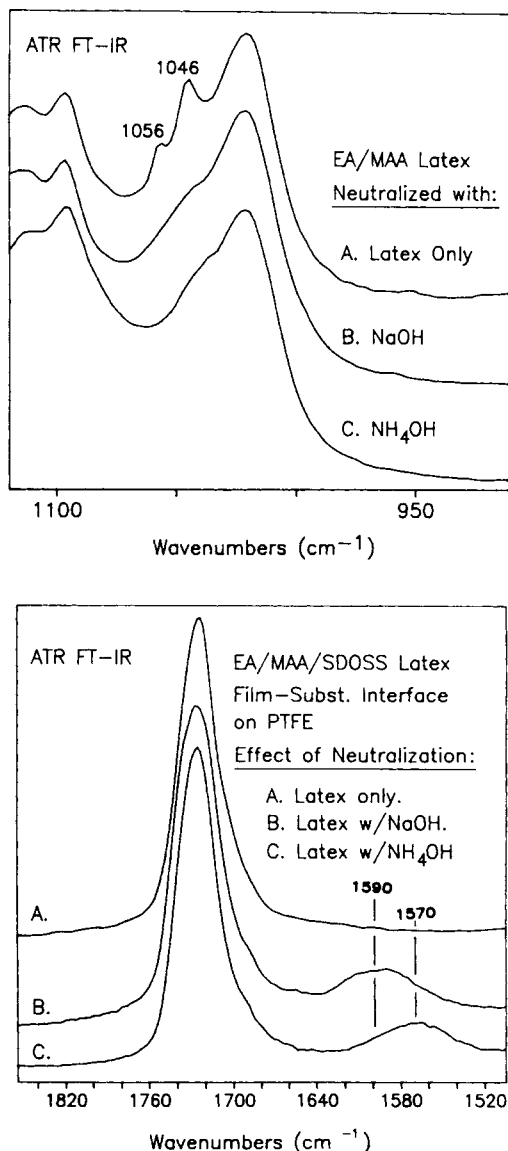
For that reason, ethyl acrylate/methyl methacrylate (EA/MMA) copolymer latex was prepared to provide further evidence that the presence of COOH groups is responsible for the observed splitting of the 1050 cm^{-1} sulfonate band to 1056 and 1046 cm^{-1}. The spectra are presented in Figure 9. Trace B shows the spectrum of an ethyl acrylate/methyl methacrylate (EA/MMA) latex copolymer, which lacks carboxylic acid functionality or other hydrogen donors available for hydrogen bonding. Although it appears that there is no significant difference between the spectra, a single band centered at 1050 cm^{-1} corresponding to the previously assigned symmetric S—O stretching vibrations of the sodium sulfonate groups of the surfactant is detected. For comparison, trace A of Figure 9 illustrates the spectrum of the EA–MAA copolymer latex obtained in the same manner, with the bands at 1056 and 1046 cm^{-1}. Thus, the simultaneous presence of both SO$_3^-$ groups of the surfactant and COOH groups of the copolymer backbone is responsible for the local symmetry changes around the sodium sulfonate end of the surfactant that causes splitting of the S—O normal stretching vibrations.
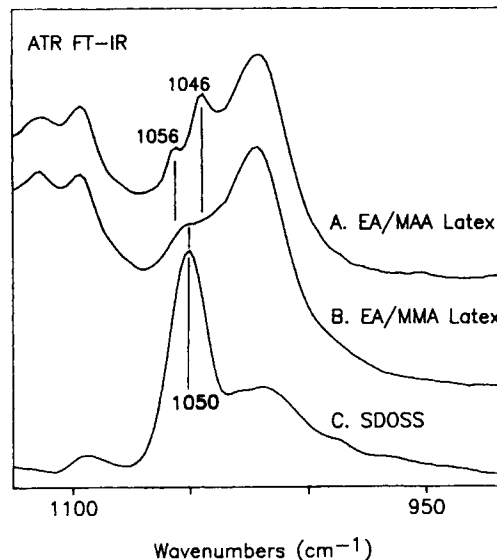

Figure 9 ATR spectra in the 1110–950 cm^{-1} region: (A) EA/MAA latex; (B) EA/MMA latex; (C) SDOSS surfactant.

Before we attempt to interpret the above results and eventually establish the nature of interactions between acid and sulfonate groups, let us consider the results of the experiment involving neutralizing the latex carboxylic acid groups with a base. Although by introducing a strong base to the system the carboxylic acid will be converted to a carboxylic acid salt, our intention is to determine how such a disturbance of the COOH environment will affect the interactions between the SO$_3^-$ groups of the surfactant and the COO$^-$ neutralized group of the acid. For that reason, stoichiometric amounts of base (based on the initial copolymer acid groups) were added to the EA–MAA latex. The results of spectroscopic analysis of the latex neutralized with NaOH and NH$_4$OH are presented in Figure 10(a). Whereas trace A illustrates ATR FTIR spectrum of latex and traces B and C are the spectra of neutralized latex with NaOH and NH$_4$OH. The two bases were chosen to investigate the influence of different cations on the observed frequency shifts. Whereas the nonneutralized latex spectrum (trace A) shows the familiar bands at 1046 and 1056 cm^{-1}, the spectra of neutralized films indicate the presence of a single band at 1046 cm^{-1}. Because of the surface selectivity of ATR and PA FTIR spectroscopy, the intensity of the bands is strong enough that there was no need for a spectral subtraction, such as in the case of transmission spectra presented in Figure 7. Based on these data, two conclusions can be drawn: First, the strength of ionic bonding does not
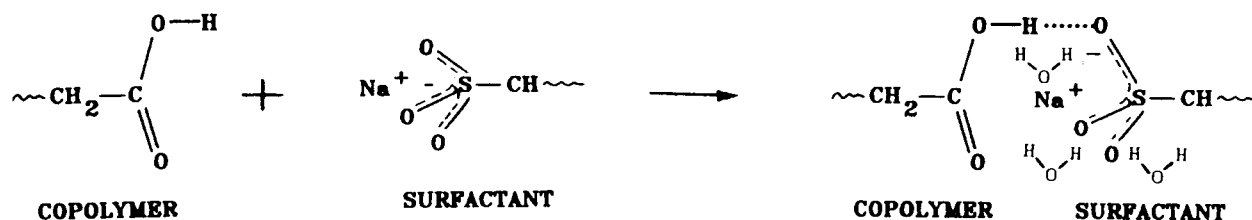
affect the S—O stretching mode at 1046 cm^{-1}, attributed to the hydration of SO_3^- Na^+ ion pairs, and, second, neutralization of acid groups of the copolymer latex leads to the disappearance of the 1056 cm^{-1} band. However, the presence of base neutralizes the acid groups of the latex copolymer, which is reflected by the appearance of the C—O stretching modes due to the COO^-Na^+ or $COO^-NH_4^+$ salt formation. As illustrated in Figure 10(b), indeed, the bands at 1590 cm^{-1} (COO^-Na^+) and 1570 cm^{-1} ($COO^-NH_4^+$) are observed in the spectra B and C, respectively. The frequency shifts are attributed to the differences in the strength of ion-pair bonding.

At this point, we are in a position to establish the scenario for the origin of the 1056 cm^{-1} band. The terminal $-SO_3^- - Na^+$ ion pair of surfactant is associated with the COOH acid groups through hydrogen. Upon neutralization, however, weak COOH acid groups form salts, COO^-Na^+ with H_2O, which break apart $-S-O \cdots H-O-C=O$ associations, resulting in elimination of the 1056 cm^{-1} band. This is schematically depicted in Figure 11. Without the base, hydrogen of the COOH group approaches the $-SO_3^-Na^+$ hydrophilic head. With a coordination number of four, there are four possible local symmetries of the $-SO_3^-$ group that need consideration: tetrahedral arrangement (T_d), tetragonal plane (D_{4h}), tetragonal pyramidal (C_{4v}), and an irregular tetrahedral arrangement (C_{3v}). According to the reduction tables[37] and keeping in mind that the heterogeneous atoms surround the central sulfur atom (three oxygens and carbon), only tetragonal pyramidal structure with the dp^3 and d^3p orbital configurations or irregular tetrahedral arrangement with the dp^3, d^3p, and d^2sp orbital configurations are possible. While the tetragonal pyramid structure exists in the nonhydrated surfactant [Fig. 11(A)] manifested by the presence of the 1050 cm^{-1} band, the presence of weak acid disturbs the $SO_3^-Na^+$ environment by the formation of partial Π double bond between sulfur and oxygen, induced by hydrogen bonding. This is schematically illustrated in Figure 11(B).

Figure 10 (a) ATR FTIR spectra in the 1100–950 cm^{-1} region of (A) EA/MAA latex; (B) EA/MAA latex neutralized with NaOH; (C) EA/MAA latex neutralized with NH$_4$OH. (b) ATR FTIR spectra in the 1800–1520 cm^{-1} region of (A) EA/MAA latex; (B) EA/MAA latex neutralized with NaOH; (C) EA/MAA latex neutralized with NH$_4$OH.

Figure 11 Schematic representation of the surfactant–weak acid interactions.

CONCLUSIONS

The primary and strong interactions between the sulfonate (SO_3^-) groups of ionic surfactant and the COOH groups of the copolymer latex in the presence of counterions and water lead to splitting of the S—O stretching mode at 1050 cm^{-1}. Apparently, it is under these circumstances that the formation of hydrogen bonding and hydration of the SO_3^- groups become significant at these latex surfaces.

REFERENCES

1. J. W. Vanderhoff, *ACS Div. Org. Coat. Plast. Prepr.*, **24**, 223 (1964).
2. E. A. Willson, J. R. Miller, and E. H. Rowe, *J. Phys. Coll. Chem.*, **53**, 357 (1969).
3. B. M. E. Van der Hoff, *J. Polym. Sci.*, **33**, 487 (1958).
4. C. P. Roe and P. D. Brass, *J. Polym. Sci.*, **24**, 401 (1953).
5. M. E. Woods, J. S. Dodge, I. M. Krieger, and P. E. Pierce, *J. Paint Tech.*, **40**, 541 (1968).
6. R. E. Wachtel and V. K. LaMer, *J. Colloid Interface Sci.*, **17**, 531 (1962).
7. E. B. Bradford and J. W. Vanderhoff, *J. Appl. Phys.*, **36**, 864 (1955).
8. J. A. Davidson and H. S. Haller, *J. Colloid Interface Sci.*, **47**, 459 (1974).
9. D. H. Napper and R. H. Ottewill, *J. Colloid Interface Sci.*, **19**, 72 (1964).
10. H. J. Van der Hul and J. W. Vanderhoff, in *Polymer Colloids*, R. M. Fitch, Ed., Plenum, New York, 1971.
11. A. M. Wims and M. E. Meyers, *J. Colloid Interface Sci.*, **39**, 447 (1972).
12. B. L. Henke and J. W. M. du Mond, *J. Appl. Phys.*, **26**, 903 (1955).
13. S. H. Mason, M. E. Elder, and I. N. Ulevitch, *J. Colloid Interface Sci.*, **9**, 83 (1954).
14. D. Munro and K. Randle, *Photo Correlation Spectroscopy and Velocimetry*, NATO Adv. Study Inst. Series B, Plenum, New York, 1977, Vol. 23, p. 537.
15. M. C. Wilkinson, R. Ellis, and C. K. Callaway, *Microscope*, **22**(3), 229 (1974).
16. A. R. Goodall, M. C. Wilkinson, and J. Hearn, *J. Colloid Interface Sci.*, **53**(2), (1975).
17. J. Hearn, Ph.D. Thesis, University of Bristol, 1971.
18. C. L. Zhao, Y. Holl, T. Pith, and M. Lambla, *Coll. Polym. Sci.*, **265**, 823–829 (1987).
19. D. R. Bassett, E. J. Derderian, J. E. Johnston, and T. B. MacRury, ACS Symp. Ser. 165, American Chemical Society, Washington, DC, 1980, pp. 263–278.
20. E. G. Bartick and R. G. Messerschmidt, *Am. Lab.*, **Nov.** (1984).
21. A. M. Tiefenthaler and M. W. Urban, *Appl. Spectr.*, **42**(1), 163 (1988).
22. M. W. Urban and E. Salazar-Rojas, *Macromolecules*, **21**, 372 (1988).
23. M. W. Urban and E. Salazar-Rojas, *J. Polym. Sci.*, to appear.
24. E. Salazar-Rojas and M. W. Urban, *Prog. Org. Coat.*, **16**(4), 371–386 (1989).
25. M. W. Urban, *J. Coat. Technol.*, **59**(745), 29 and references therein (1987).
26. M. W. Urban, *Prog. Org. Coat.*, **16**(4), 321–353 (1989).
27. C. L. Zhao, Y. Holl, T. Pith, and M. Lambla, *Br. Poly. J.*, **21**, 155–160 (1989).
28. Y. J. Lee, P. C. Painter, and M. M. Coleman, *Macromolecules*, **21**, 346–354 (1988).
29. G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley, New York, 1980.
30. J. W. Vanderhoff, *Br. Polym. J.*, **2**, 161–173 (1970).
31. J. Y. Lee, P. C. Painter, and M. M. Coleman, *Macromolecules*, **21**, 954–960 (1988).
32. M. M. Coleman, D. J. Skrovanek, S. E. Howe, and P. C. Painter, *Macromolecules*, **18**, 301–302 (1985).
33. J. L. Koenig, *Appl. Spectros.*, **29**, 293 (1975).
34. R. Frieden, *J. Opt. Soc. Am.*, **73**(7), 927–938 (1983).
35. A. M. Lichkus, P. C. Painter, and M. M. Coleman, *Macromolecules*, **21**, 2636–2641 (1988).
36. V. B. Kartha, R. N. Jones, and R. E. Robertson, in *Proceedings of the Indian Academy of Sciences*, 1963, Vol. 58A, pp. 216–228.
37. F. A. Cotton, *Chemical Applications of Group Theory*, 2nd ed., Wiley-Interscience, New York, 1971.