

# Synthesis and Characterization of Core/Shell Ionomeric Latexes. II. Surface Analysis by X-Ray Photoelectron Spectroscopy

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## SYNOPSIS

It is generally accepted that conductometric titration is a time-dependent technique in the case of highly carboxylated latexes because of the changes in the structure of the particle surface resulting from the neutralization and the alkali swellability imparted by the carboxyl groups when titrated with an alkali. At high levels of neutralization, the diffusion of the hydroxyl groups into the shell will be much faster than at the lower levels of neutralization. Due to this changing rate of the diffusion of the hydroxyl groups into the highly alkali-swellable copolymer shell, the assignment of the carboxyl groups to the different sublevels inside the particle shell can, at best, be arbitrary. To overcome this handicap, x-ray photoelectron spectroscopy (XPS or ESCA) was used to obtain the depth profile of methacrylic acid near the surface of the particles. It is expected that by accurately characterizing the surface loading of the carboxyl groups, it will be possible to control the microphase separation process of the system. Considering the high concentration of the carboxyl groups on the surface of the core/shell latexes prepared in this study, XPS experiments were conducted to obtain the depth profile of the carboxyl groups. Angle-dependent XPS studies were performed on films derived from the core/shell latexes with different amounts of methacrylic acid in the shell layer in order to determine the compositional heterogeneities between the surface and subsurface layers. In addition, x-ray photoelectron spectroscopy was used to study the changes in the surface composition of solvent-cast core/shell latex films prepared in this study upon treatment with alkali solution. It was discovered that a large-scale migration of the carboxyl groups could occur as a result of coulombic interactions. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It was mentioned in Part I of this two-part series that the distribution of carboxyl groups in the core/shell latex particles is a major area of interest. Upon neutralization with a metal cation, ion pairs participate in the ionic aggregate formation and introduce physical crosslinking into the system, especially in the interphase region between the shell copolymer between adjacent latex particles that come in contact

during the latex film formation process. In order to understand the structure–property relationship for the ionomeric latex polymer films after the formation of the ionic bonds, it is imperative to characterize the distribution of the carboxylic functionality incorporated into the latex particles. This article will discuss the determination of the distribution of carboxyl groups in the core/shell latex particles using x-ray photoelectron spectroscopy (XPS).

The surface composition of latex particles to a great extent governs the colloidal properties of a latex. First of all, the type and amount of surface charge is important. The study of surface charge has been the subject of numerous articles in the past decade.<sup>1,2</sup> In most of the studies, conductometry and

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potentiometry were used as the main experimental techniques. It was previously discussed in Part I that conductometric titrations could not provide any specific information about the distribution of methacrylic acid in the case of the highly carboxylated core/shell latexes prepared in this study. It was then decided to apply the x-ray photoelectron spectroscopy (XPS) technique to determine the surface composition of the core/shell latexes more accurately.

The characteristics of XPS and its applications in the polymer field have been reviewed adequately.<sup>3,4</sup> Stone-Masui and Stone<sup>5,6</sup> used XPS to study the sulfate groups at the surface of polystyrene latex particles. Pipjers and Donners<sup>7</sup> used XPS on acrylate copolymer latexes of known compositions. It was shown that the XPS technique is well suited for the quantitative determination of the polymer composition at the latex polymer surfaces, which makes it possible to use this method in systems in which the composition of the particle surface differs from the bulk composition because of the difference in the reactivity ratios of the monomers, nonuniform-feed techniques, or differences in the degree of hydrophilicity of the comonomers.

### Principle of X-Ray Photoelectron Spectroscopy

X-Ray photoelectron spectroscopy (XPS or ESCA) is a powerful tool for the identification of all the elements in the periodic table and also permits the determination of the oxidation state of an element and the type of species to which it is bonded. In XPS, the specimen is exposed to a monochromatic x-ray source, and the kinetic energy of the photoelectrons emitted from the specimen is recorded. The spectrum, thus, consists of a plot of the number of emitted photoelectrons as a function of the energy of the emitted photoelectrons. Each element possesses a characteristic value of the binding energy of the photoelectrons, and thus, the XPS spectrum provides a means of qualitative and quantitative identification of the elements present in the specimen. Because of the poor penetrating power of the photoelectrons, XPS provides information about solids that is restricted largely to a surface layer 20–100 Å thick. Some of the most important and valuable current applications of XPS are the determination of the surface chemistry of solids such as metals, alloys, semiconductors, polymers, and heterogeneous catalysts.

### Depth Profiling Using Angle-Dependent XPS

The method of depth profiling using angle-dependent photoelectron spectroscopy is based on the

principle of surface sensitivity enhancement at grazing electron emission angles. In XPS, the effective sampling depth corresponds to the regions from which the photoelectrons can escape without inelastic scattering. The flux of photoelectrons,  $I(x)$ , originating at a depth  $x$  below the surface, and emerging at an angle  $\theta$  relative to the surface<sup>8</sup> is given by:

$$I(x) = I_o(x) \exp\left(-\frac{x}{\lambda \sin \theta}\right) \quad (1)$$

where  $I_o(x)$  is the flux at depth  $x$ ,  $\lambda$  is the inelastic mean free path, and  $\theta$  is the emission angle. Approximately 95% of the total photoelectron peak intensity originates from depths equal to  $3\lambda \sin \theta$ . Hence, the depth of the material actually sampled is equal to  $3\lambda \sin \theta$ . The inelastic mean free path is a function of the electron energy and the material. So, it is possible to vary the effective analyzed depth by varying the factor  $3\lambda \sin \theta$ . This might be accomplished by varying the value of the mean free path (by changing the photon energy) or, more simply, by varying the angle of emission  $\theta$ . The basic principle and some applications of the x-ray photoelectron angular distributions have been reviewed by Fadley et al.<sup>9</sup>

### Model for Angular Dependent XPS

The model is based on the predictions of the general flat surface intensity model first utilized by Henke,<sup>8</sup> extended by Fadley et al.,<sup>9</sup> and routinely used in quantitative XPS analysis. The model has been discussed in detail by Fadley.<sup>10</sup> The major assumptions are: (1) both x-rays and electrons are assumed to be attenuated exponentially, (2) the surface of the sample is atomically flat, (3) the effects of diffraction of emitted electrons are neglected, and (4) the effects of the elastic electron scattering and the reflection and refraction of x-rays and electrons are neglected.

If the maximum sampling depth of the sample is divided into  $n$  equal and parallel layers, then the current,  $I_A(\theta)$ , of the photoelectrons excited from the atoms,  $A$ , measured in the direction  $\theta$ , can be expressed as the sum of the intensities due to each layer modulated by the attenuation in the upper layers:

$$I_A(\theta) = \sigma_A k(\theta) \sum_{j=1}^n \left[ N_A(j) \left[ 1 - \exp\left[-\frac{x_0}{\lambda(j) \sin \theta}\right] \right] \times \prod_{k=1, j \geq 2}^{j-1} \exp\left[-\frac{x_0}{\lambda(k) \sin \theta}\right] \right] \quad (2)$$

In this equation,  $N_A(j)$  is the number density of atoms  $A$  in the  $j$ th layer,  $\sigma_A$  is the photoelectron cross-section of the subshell considered,  $k(\theta)$  is an instrumental factor, depending on the x-ray flux and the sample-analyzer geometry,  $x_o$  is the thickness of the layer, and  $\lambda(j)$  is the inelastic mean free path in the  $j$ th layer for the photoelectrons considered. The above-mentioned model can be used to calculate the wt % of the intensity contribution of each layer to the total intensity at different emission angles.

According to Fadley,<sup>10</sup> electron refraction occurs mostly at very low emission angles, typically 5–10 degrees for the XPS kinetic range, and can be neglected for angles greater than 10–15 degrees. Keeping this in mind, XPS studies were carried out at two electron emission angles, i.e., 90 and 20 degrees, to distinguish between the surface and subsurface compositions.

## EXPERIMENTAL

### Distribution of Surface Composition by X-Ray Photoelectron Spectroscopy (XPS)

The two series of core/shell latexes studied using XPS analysis were prepared by semicontinuous emulsion polymerization as discussed previously in Part I. The latexes had a solids content of about 20% w/w and contained 15% or 30% w/w methacrylic acid in the shell. Before the XPS analysis was carried out, the latexes were diluted to a solids content <5% and cleaned by serum replacement<sup>11</sup> to remove all adsorbed emulsifier. Some preliminary XPS studies carried out with latexes cleaned using serum replacement, ion-exchange resin, or ultracentrifugation as a cleaning method, indicated that serum replacement gave the best results. Films for the XPS measurements were obtained by putting a few drops of the cleaned latex on a copper plate (1 × 1 cm), followed by drying at room temperature in a vacuum oven for 72 h. The films obtained after drying the core/shell latexes were flaky in appearance due to the presence of a glassy polystyrene core. The use of the copper substrate contributed to the adhesion of the film to the plate due to the presence of carboxyl groups and also improved the surface roughness of the film. Angle-dependent studies of the dried latex polymer films were carried out at two electron emission angles, i.e., 90 and 20 degrees, to distinguish between the surface and subsurface layers. The copper plates used for film deposition were cleaned beforehand by etching in concentrated nitric acid followed by a thorough rinsing with distilled-

deionized water. The samples were then stored in a desiccator until the XPS tests were performed. A Scienta ESCA-300 was used for the XPS analysis.

### Surface Restructuring of Core/Shell Latex Films

The core/shell latex with a shell composition of 14/56/30 (wt) styrene (Sty)/*n*-butyl acrylate (*n*-BA)/methacrylic acid (MAA) was used in this study. The cleaned latex in its acid form was dried at room temperature and dissolved in tetrahydrofuran (THF). A film was cast from the resulting solution and dried under vacuum at room temperature. The surface properties of the following films were studied: (1) solvent-cast film, (2) solvent-cast film treated with NaOH solution for 72 h at 20°C, and (3) solvent-cast film treated with NaOH solution for 72 h at 70°C.

## RESULTS AND DISCUSSION

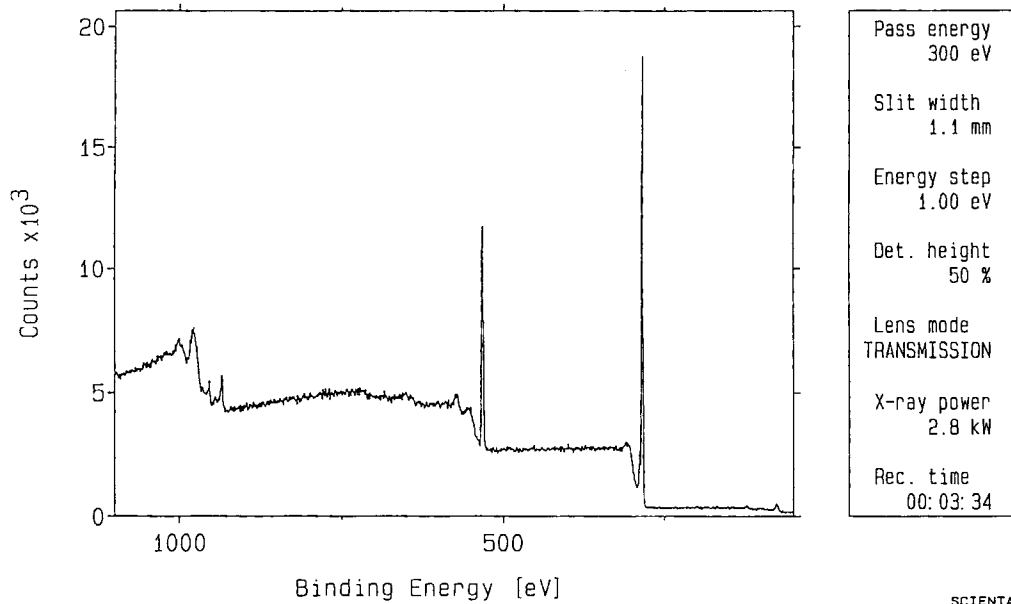
### XPS Analysis

#### Survey Scan Spectra

The survey scan spectrum of the core/shell latex with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, at an emission angle of 90 degrees, is shown in Figure 1. It can be seen from Figure 1 that the spectrum consists of two major peaks at 530 eV and 285 eV, which result from the presence of the oxygen and carbon atoms, respectively. The small peaks near 1000 eV are a result of the presence of copper, which was used as the substrate for the core/shell latex film. The survey spectrum does not exhibit any other peaks, which suggests that the sample is free of contamination.

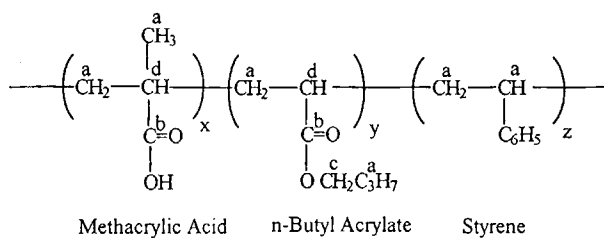
#### High Resolution C(1s) Spectrum

It is known that the presence of oxygen atoms has a profound effect on the binding energies of the respective carbon atoms, and hence, the C(1s) signal in the XPS spectrum changes dramatically with polymer composition. The structure of the Sty/*n*-BA/MAA terpolymer prepared in this study is shown in Figure 2. It can be seen from Figure 2 that there are three main types of carbon atoms present in the system. The backbone carbon atom is represented as  $C^a$  and has a binding energy of 285 eV. The COO carbon atom, present in both methacrylic acid and butyl acrylate, is represented as  $C^b$  and has a binding energy of 289 eV. The CO carbon atom, present in butyl acrylate only, is represented as  $C^c$



**Figure 1** Survey scan XPS spectrum for the core/shell latex with a polystyrene core and a shell composition of 29/56/15 (wt) styrene/*n*-butyl acrylate/methacrylic acid; core/shell ratio = 1; at 90° emission angle.

and possesses a binding energy of 287 eV. In the literature,<sup>12</sup> generally four contributions to the C(1s) signal of the carbon-oxygen compounds are described (Table I). Thus, in the Sty/*n*-BA/MAA terpolymer C(1s) spectrum, three peaks with relative shifts of 0.0, 1.6, and 4.0 eV are expected. Keeping this in mind, the high resolution C(1s) spectrum of the core/shell latex film with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA, was resolved into three peaks with binding energies of 285 eV, 286.6 eV, and 289 eV and is shown in Figure 3. However, as a further refinement, the C(1s) signal was split into four peaks for the core/shell latex with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA. The four-peak fit procedure was used to incorporate a secondary chemical shift of 0.7 eV by the COO oxygen atoms on the backbone carbon atoms,<sup>7</sup> which

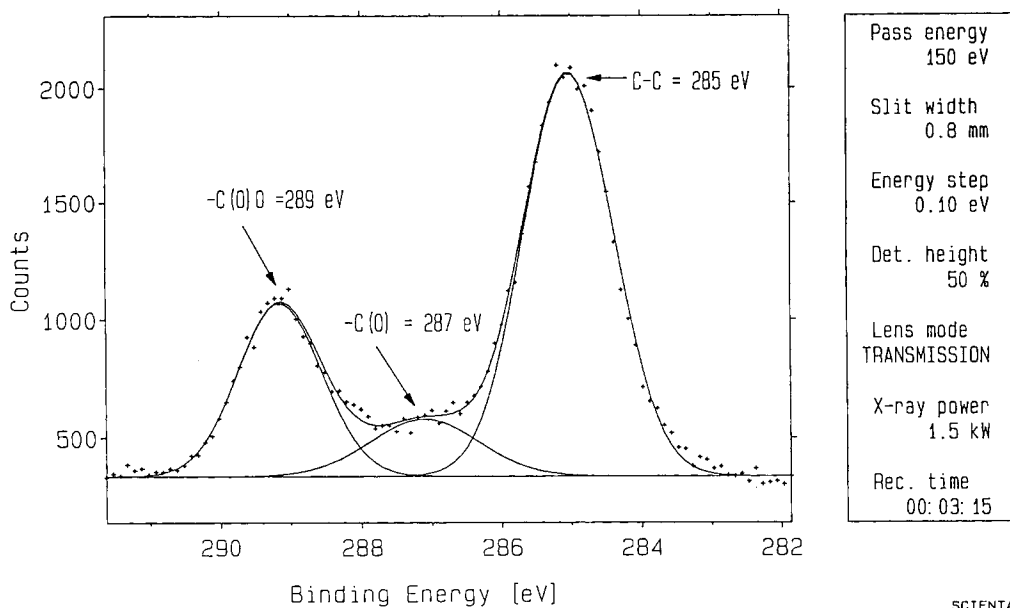


**Figure 2** Structure of the styrene/*n*-butyl acrylate/methacrylic acid copolymer depicting the different types of carbon atoms present in the polymer.

are represented as C<sup>d</sup> in Figure 2. Thus, the C(1s) peak was split into four peaks with relative chemical shifts of 0.0, 0.7, 1.7, and 4.0 eV. It would be pertinent here to comment on the curve fitting and peak integration procedure using the Scienta ESCA 300 software. The values of the binding energies and the peak widths of the expected peaks in the XPS spectrum have to be defined before carrying out the curve fitting procedure, which is then followed by an iterative curve fitting process. The iterative procedure determines the best fit to the experimental data by shifting the peaks along the binding energy axis and by adjusting the peak widths. It was discovered that the goodness of the fit improved slightly after adopting the four-peak fitting procedure. The high resolution C(1s) spectrum of the core/shell latex with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA, is shown in Figure 4. On comparing the C(1s) spectra of the two latexes (see Figs. 3 and 4),

**Table I** Contributions to the C(1s) Signal in Carbon-Oxygen Compounds

| C Type                          | Relative Shift in Binding Energy (eV) |
|---------------------------------|---------------------------------------|
| (CH <sub>2</sub> ) <sub>n</sub> | 0.0                                   |
| C—O                             | 1.6 ± 0.2                             |
| C=O                             | 2.8 ± 0.2                             |
| COO                             | 4.0 ± 0.2                             |



**Figure 3** Results of the C(1s) peak analysis for the core/shell latex with a shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid. Points represent the experimental data after x-ray satellite and background removal, and solid lines represent the calculated curves for the various components and the fitted envelope that results.

it can be seen that the agreement between the experimental data (represented by points) and the fitted envelope (solid line), has slightly improved after adopting the four-peak fitting procedure.

#### XPS Spectra at Different Emission Angles

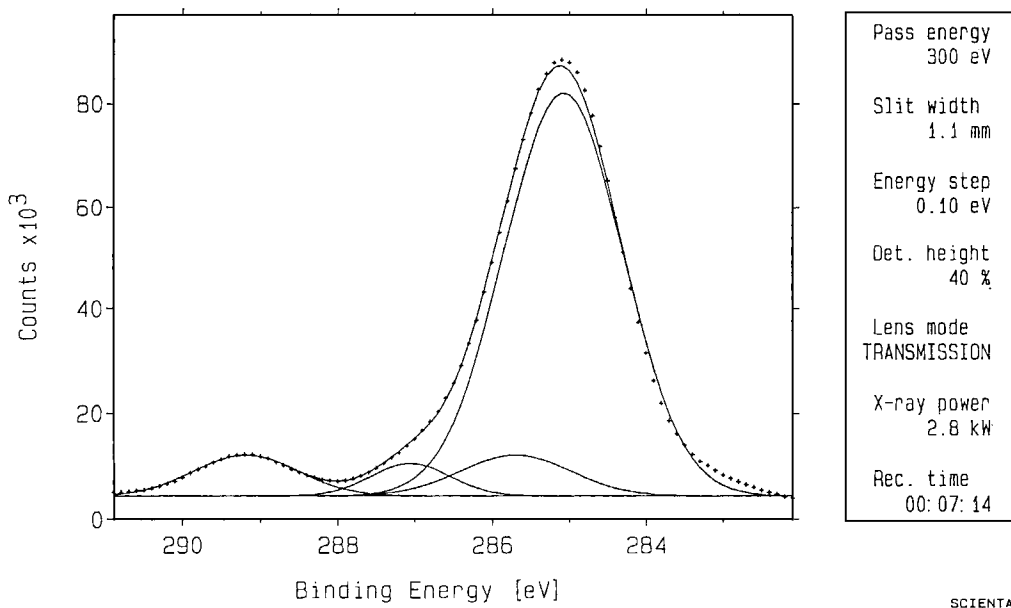
Utilizing the same principle of surface sensitivity enhancement at lower emission angles, XPS spectra of the core/shell latexes with shell compositions of 29/56/15 (wt) and 14/56/30 (wt) Sty/*n*-BA/MAA, respectively, were taken at emission angles of 20 degrees and 90 degrees to differentiate between the surface and subsurface compositions. The XPS spectra obtained for these two core/shell latexes are shown in Figures 5 and 6.

It can be seen from Figures 5 and 6 that there are significant differences between the XPS spectra of the two core/shell latexes. In the core/shell latex with the shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA (Figure 6), the contribution of the COO carbon atom (289 eV), present in both methacrylic acid and butyl acrylate, is larger at 20 degrees than its relative contribution at 90 degrees. This suggests that there is a greater concentration of methacrylic acid at the surface of these core/shell latex particles. It can be seen from Figure 5 that this difference is much smaller in the case of the 29/56/15 Sty/*n*-BA/MAA core/shell latex.

#### Depth Profiles of Core/Shell Latexes

The relative contributions of the different carbon atoms derived from peak integration analysis of the XPS spectra obtained at 20 and 90 degree emission angles for the two core/shell latexes were applied to the model for the depth profiling discussed earlier, to yield two sets of equations with two unknowns, similar to eq. 2, for each spectrum. These sets of simultaneous equations were solved to obtain the number density of COO (289 eV) and CO (287 eV) carbon atoms at depth levels of 25 Å and 75 Å corresponding to the emission angles of 20 and 90 degrees, respectively. The value of  $\lambda$  for the polymer was assumed to be 25 Å. After the determination of the number density of COO and CO carbon atoms, the MAA/*n*-BA ratio was calculated at the two depth levels. The depth profiles relating the MAA/*n*-BA ratio at the two depth levels for the two core/shell latexes are shown in Table II.

On comparing the depth profiles of the two core/shell latexes, it can be noted that both the core/shell latexes have compositional differences between the surface and subsurface levels, although the degree of heterogeneity is different in each case. The core/shell latex with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA has a very high MAA/*n*-BA ratio in the first layer (0–25 Å) with the MAA/*n*-BA ratio in the second layer (25–75 Å) still being a little

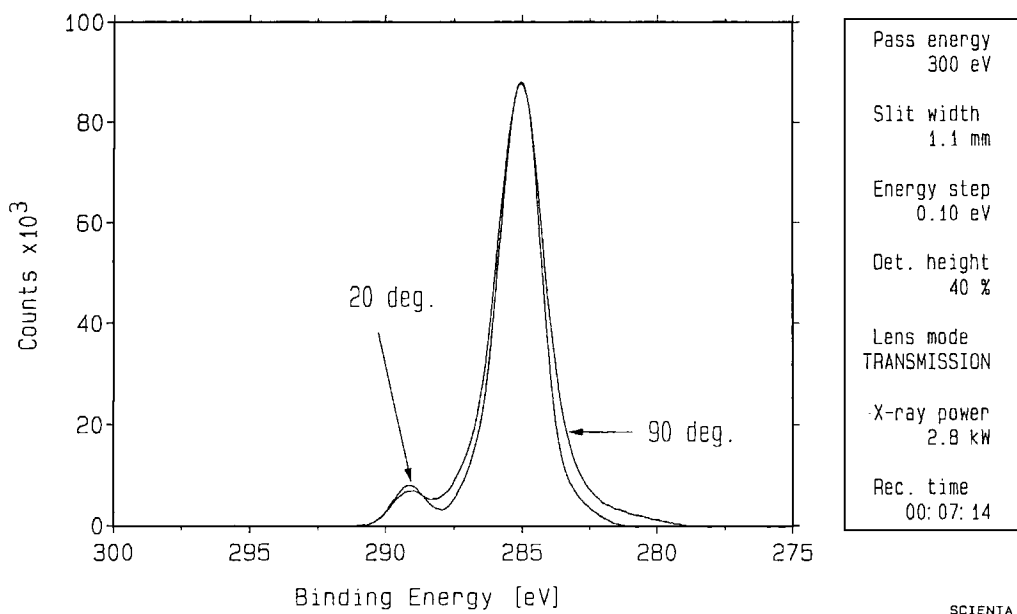


**Figure 4** Results of the C(1s) peak analysis for the core/shell latex with a shell composition of 29/56/15 (wt) styrene/*n*-butyl acrylate/methacrylic acid. Points represent the experimental data after x-ray satellite and background removal, and solid lines represent the calculated curves for the various components and the fitted envelope that results.

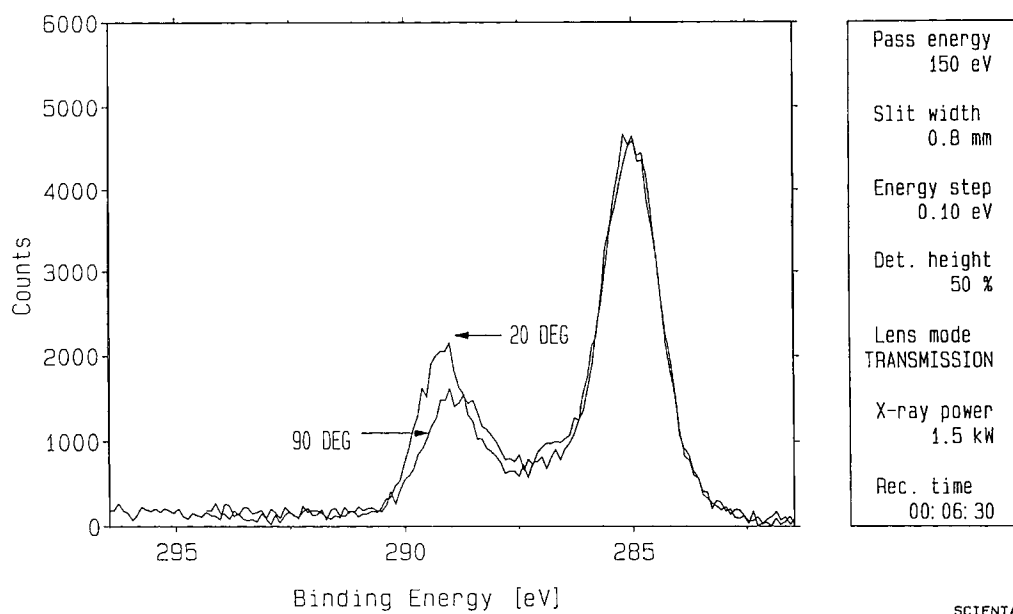
higher than that expected from the recipe. On the other hand, the core/shell latex with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA also has a high MAA/BA ratio in the first layer (0–25 Å), which is approximately three times that predicted from the recipe. However, the subsequent layer (25–

75 Å) has a MAA/BA ratio approximately equal to that expected from the recipe.

It is worth noting that although both of the core/shell latexes exhibit a high MAA/*n*-BA ratio in the first layer (0–25 Å), which is approximately three times the ratio expected from the respective recipes,



**Figure 5** XPS spectra of the core/shell latex with a shell composition of 29/56/15 (wt) styrene/*n*-butyl acrylate/methacrylic acid at emission angles of 20 and 90°.



**Figure 6** XPS spectra of the core/shell latex with a shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid at emission angles of 20 and 90°.

the core/shell latex with a shell composition of 14/56/30 (wt) Sty/*n*-BA/MAA exhibits a bigger difference in the XPS spectra at 20 and 90 degree emission angles than the core/shell latex with a shell composition of 29/56/15 (wt) Sty/*n*-BA/MAA. This can be explained by considering the absolute MAA/*n*-BA ratios in the both cases. In the core/shell latex with 30 wt % MAA in the shell, the MAA/*n*-BA ratio in the shell is approximately 1.7, whereas in the core/shell latex with 15 wt % MAA in the shell, this ratio is only 0.6.

#### Surface Restructuring of Core/Shell Latex Films

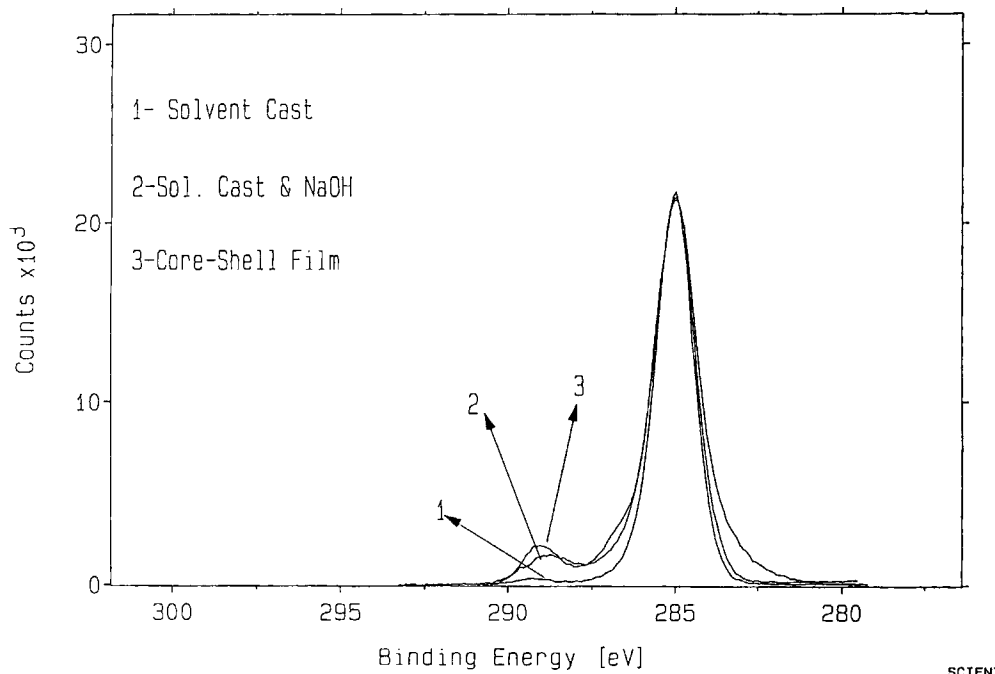
Polymers provide a wide variety of useful chemical and physical properties. The choice of a polymer is governed by the particular application and, in some cases, the polymer is specifically chosen for its surface characteristics. Most often, however, a polymer is chosen for its bulk properties. Whatever may be the reason for its selection, the polymer must be compatible with its surroundings. Since a given

polymer always interfaces with its surroundings via its surface, the structure of the surface and its compositional differences from the bulk material become very important. This is also of great relevance in the case of colloidal particles. Generally, colloidal polymer particles of specific surface properties can be synthesized, but most often on solvent casting, the functional groups tend to diffuse away from the surface in order to minimize the interfacial free energy. In this context, the concept of restructuring the surface of the solvent-cast polymer film to mimic the surface characteristics of the original colloidal particles provides interesting possibilities.

It was previously discussed in Part I that the core/shell latexes prepared in this study exhibit heterogeneity in terms of the methacrylic acid (i.e., carboxyl group) distribution. Upon neutralization with an alkali, there is ionic aggregate formation due to the coulombic interactions between the metal cations and the carboxylate anions. Although a major portion of this research work concentrates on understanding the structure-property relationships

**Table II** Depth Profiles of Core/Shell Latexes

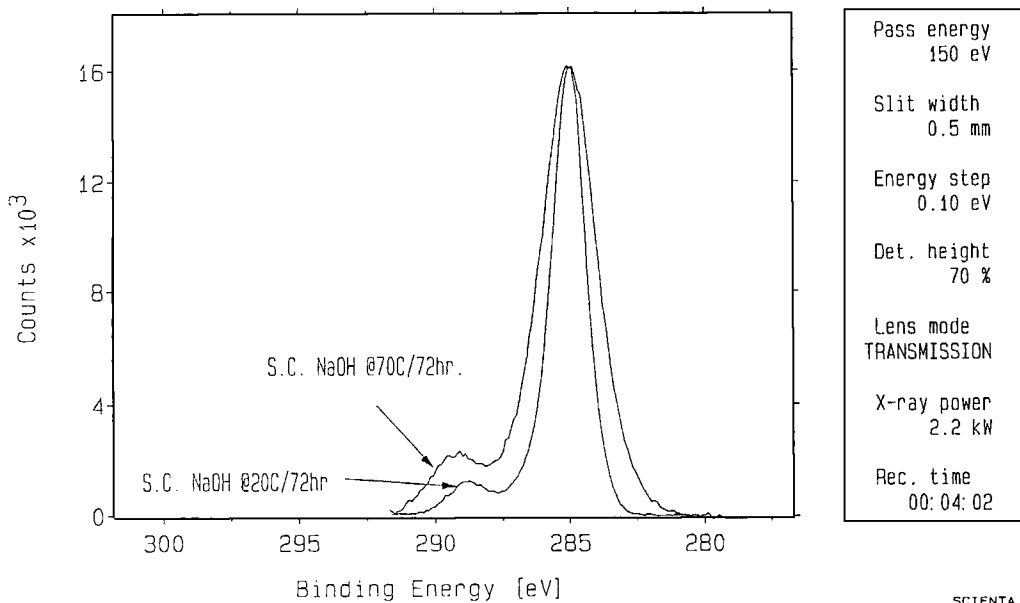
| Core/Shell Latex               | MAA/ <i>n</i> -BA Ratio |                     |                       |
|--------------------------------|-------------------------|---------------------|-----------------------|
|                                | 1st Layer (0–25 Å)      | 2nd Layer (25–75 Å) | Predicted From Recipe |
| 29/56/15 Sty/ <i>n</i> -BA/MAA | 0.64                    | 0.24                | 0.27                  |
| 14/56/30 Sty/ <i>n</i> -BA/MAA | 1.69                    | 0.70                | 0.54                  |



**Figure 7** Comparison of the XPS spectra of the solvent (THF)-cast film derived from the core/shell latex with a shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid, without any treatment and the solvent-cast film treated with NaOH solution for 72 h at 20°C; all at 90° emission angle.

due to ionic aggregate formation, the utilization of these coulombic interactions to restructure the surface of the solvent-cast films of the core/shell latexes

presented interesting opportunities, especially after the successful demonstration of the potential of the XPS technique in exploring the heterogeneity in the



**Figure 8** Comparison of the XPS spectra of the solvent (THF)-cast film derived from the core/shell latex with shell composition of 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid, treated with NaOH solution for 72 h at 20°C and 70°C at 90° emission angle.



surface composition of the core/shell latexes prepared in this study.

There have been some studies dealing with the reorientation of the functional groups involving the surface oxidation of polyethylene films.<sup>13</sup> A preliminary investigation was carried out in this research work to observe the migration of the carboxyl groups in the solvent (THF)-cast films of the core/shell latex prepared in this study.

The XPS spectrum of the solvent (THF)-cast film without any surface treatment is shown in Figure 7 (curve 1). The point of major interest in this spectrum is the intensity of the peak at 289 eV due to the COO carbon atom, which reflects the number density of the carboxyl groups in the vicinity of the surface. It can be seen from Figure 7 that the peak at 289 eV is very small, which indicates that the amount of carboxyl groups on the surface is negligible. This can be explained on the basis of the principle of minimization of interfacial free energy, which prevents the carboxyl groups from migrating to the surface while the polymer film is being cast from the THF solvent.

Figure 7 (curve 2) also shows the XPS spectrum of the solvent-cast film treated with sodium hydroxide solution (50 mL of  $5.0 \times 10^{-5}$  N NaOH solution; in 10% excess over the stoichiometric amount required to neutralize the carboxyl groups in the film) for 72 h at 20°C. It can be seen from this figure that the intensity of the COO carbon peak at 289 eV has increased remarkably in contrast to the untreated solvent-cast film. Also shown in Figure 7 (curve 3) is the XPS spectrum for the film cast from the core/shell (15/56/30 Sty/*n*-BA/MAA) latex film. This figure clearly illustrates that there has been a substantial migration of the carboxyl groups towards the surface on treating with sodium hydroxide solution. It can be seen that approximately 60–70% of the carboxyl groups have been able to migrate to the surface when comparing the intensity of the carbon peak at 289 eV for the core/shell latex film and the alkali-treated solvent-cast film. However, it should be mentioned that the peak widths of the spectra of the core/shell latex film and the solvent-cast film were very different, as evident from Figure 7. The core/shell latex film exhibits a large tail due to excessive localized charging at the surface due to the large amount of functional groups, which was the major reason for not attempting to quantify the migration of carboxyl groups in the case of the solvent-cast film as compared to the core/shell latex film.

Figure 8 compares the XPS spectra of the solvent (THF)-cast film treated with NaOH solution (50 mL

of  $5.0 \times 10^{-5}$  N NaOH solution; in 10% excess over the stoichiometric amount required to neutralize the carboxyl groups in the film) for 72 h at two different temperatures, 20°C and 70°C. The copolymer of composition 14/56/30 (wt) styrene/*n*-butyl acrylate/methacrylic acid has a glass transition temperature of approximately 60°C. It was expected that by treating the solvent-cast film with NaOH solution at a temperature higher than the glass transition temperature of the copolymer, that a greater mobility would be imparted to the polymer chains and, hence, a greater migration of the carboxyl groups towards the surface could be induced. It can be inferred from Figure 8 that this, indeed, has occurred.

One complicating factor that has been introduced by treating the solvent-cast film in the presence of alkali at elevated temperatures is the hydrolysis of *n*-butyl acrylate. It can be noticed in Figure 8 that the surface concentration of carboxyl groups appears somewhat higher than even that found in the original core/shell latex film (see Figure 7). It would be misleading at this point to attribute this entire change to the greater mobility of the polymer chains at higher temperature. Further experiments are required to resolve this issue.

## SUMMARY

It can be concluded from the XPS results that by increasing the methacrylic acid content in the core/shell latex, it has been possible to achieve significantly higher surface and subsurface loading of carboxyl groups in these latexes. The preliminary studies on the solvent (THF)-cast films in this research work have adequately demonstrated that coulombic interactions can be used as a means to enhance the migration of the carboxyl groups towards the surface. XPS has been used successfully as a technique to follow the changes in the surface composition. It was observed that there has been a significant change in the carboxyl content at the surface on treating with sodium hydroxide solution. This change was even higher upon treating the film with an alkali solution at higher temperatures. Quantification of the amount of change affected by different treatments has not been attempted because the peaks widths were very different in each case due to different amounts of localized charging.

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