Direct Verification of the Core−Shell Structure of Shell Cross-Linked Micelles in the Solid State Using X-ray Photoelectron Spectroscopy

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X-ray photoelectron spectroscopy (XPS) is used to probe the nanostructure of shell cross-linked micelles in the solid state. A novel ABC triblock copolymer was synthesized via atom transfer radical polymerization (ATRP) comprising quaternized nitrogen atoms in the relatively hydrophilic "A" block, cross-linkable hydroxy groups in the middle "B" block, and neutral nitrogen atoms in the relatively hydrophobic "C" block. Two types of micelles were prepared: conventional micelles with the C block in the core in aqueous media and inverted micelles with the A block in the core in nonaqueous media. Efficient shell cross-linking of both types of micelles was achieved using divinyl sulfone (DVS), which reacts with the hydroxy groups in the central B block at room temperature. Although the XPS sampling depth of 2−10 nm is comparable to the dimensions of the micelle layers, and despite the probability of some micelle deformation in the absence of solvent, analysis of the high-resolution N 1s spectra provided the first direct evidence for the expected core−shell nature of SCL micelles in the solid state.

Introduction

In principle, shell cross-linked (SCL) micelles combine the properties of micelles, microgels, nanoparticles, and dendrimers, and various applications such as targeted drug delivery, sequestration of metabolites, and entrapment of environmental pollutants have been suggested.[1,2] Recently we have demonstrated[3] that ABC triblock copolymers offer significant advantages over AB diblock copolymers, since the former allow shell cross-linking to be carried out in concentrated solution with negligible intermicellar fusion. Other notable advances include the synthesis of "hollow" nanoparticles from SCL micelles,[4,5] SCL micelles with tunable hydrophilic/hydrophobic micelle cores for triggered release,[6,7] a one-pot solventless synthesis of SCL micelles at high solids starting from monomers,[8] and the development of atom transfer radical polymerization (ATRP) for the facile synthesis of the block copolymer precursors without protecting group chemistry.[8,9] In addition, a wide range of techniques has been applied to the characterization of SCL micelles. For example, laser light scattering[1,3−8] and analytical ultracentrifugation[10] studies report micelle size distributions and micelle aggregation numbers, transmission electron microscopy[3−8] and atomic force microscopy (AFM)[11] provide insight regarding nanomorphology, aqueous electrophoresis measurements indicate the surface charge and mobility, UV[4,9c] and FT-IR spectroscopy[12] have been used to monitor the extent of cross-linking, and ^{1}H NMR spectroscopy studies[3,6−8] generally support the core−shell nanostructures expected in solution on the basis of chemical intuition. However, most of these analytical methods are "wet" techniques; relatively little work has been devoted to the characterization of dried SCL micelles. In fact, as far as we are aware, there is currently no experimental evidence to indicate that the core−shell nanomorphology that is generally assumed for SCL micelles actually persists in the solid state. Micellar self-assembly is driven by solution thermodynamics: in a selective solvent the blocks have differing solubilities. Thus, in the absence of any solvent it is pertinent to ask to what extent, if any, the original SCL micelle nanostructure is retained. In this context it is noteworthy that conventional, non-cross-linked micelles can adopt flattened, nonspherical structures when adsorbed at charged interfaces, even in the presence of solvent.[13] Furthermore, AFM studies indicate that substantial deformation of SCL micelles can occur in some cases, even at apparently high degrees of shell cross-linking.[2,14] Hence, in the present study we have utilized a proven surface-specific spectro-

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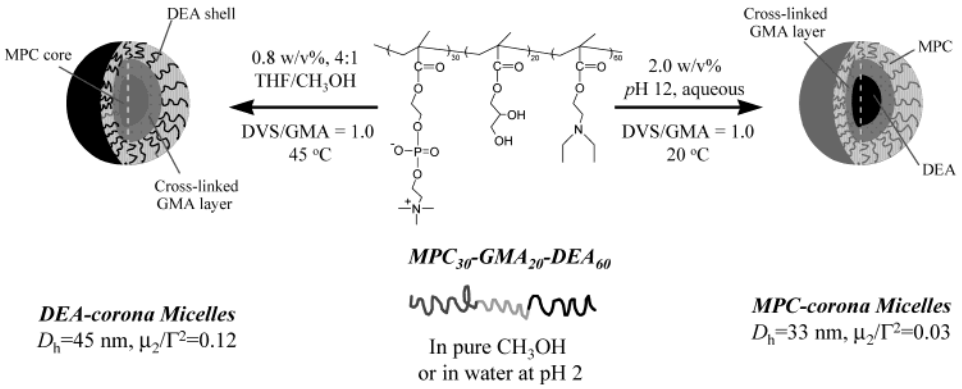

Figure 1. Schematic representation of the two types of shell cross-linked (SCL) micelles formed by the MPC_{30}−GMA_{20}−DEA_{60} triblock copolymer. MPC−corona SCL micelles are formed in aqueous solution, whereas DEA−corona SCL micelles are formed in 4:1 THF/methanol solution.

scopic technique, X-ray photoelectron spectroscopy (XPS), to probe the nanostructures of SCL micelles in the solid state.

Over the past decade or so, XPS has been successfully used to characterize the surface compositions of a wide range of latexes,[15,16] polymer-stabilized particles,[17,18] and colloidal nanocomposites.[19,20] Depending on the experimental setup and the elements present, this technique typically has a sampling depth of 2−10 nm.[21] Thus, XPS reports detailed information on near-surface elemental compositions, indicates the location and role played by polymeric steric stabilizers, and can also provide strong evidence for core−shell particle morphologies. However, literature reports on the use of XPS to characterize conventional block copolymer micelles are very rare.[22] As far as we are aware, this is the first time that XPS has been employed to examine SCL micelles.

Herein we have examined the nanomorphology of a new ABC triblock copolymer that is reasonably well suited to XPS analysis. This copolymer comprised 2-methacryloyloxy phosphorylcholine (MPC), glycerol monomethacrylate (GMA), and 2-(diethylamino)ethyl methacrylate (DEA) (see Figure 1). Three forms of this MPC−GMA−DEA triblock were prepared for XPS characterization: (i) the linear, non-cross-linked precursor; (ii) MPC−corona SCL micelles prepared in aqueous solution; (iii) DEA−corona SCL micelles prepared in nonaqueous media.

Experimental Section

Synthesis and Characterization of the MPC_{30}−GMA_{20}−DEA_{60} Triblock Copolymer. We have recently published accounts of the polymerization of MPC and GMA monomers via ATRP in protic solvents.[23,24] The MPC−GMA−DEA triblock copolymer used in the present study was prepared in a one-pot synthesis in methanol via sequential monomer addition using ATRP, with the MPC monomer being polymerized first. Full details of this synthesis will be reported elsewhere in due course. Aqueous GPC analysis (Viscotek G2500PW_{XL} and G5000PW_{XL} columns, poly(2-vinylpyridine) calibration standards, refractive index detector, and an eluent comprising 0.5 M acetic acid and 0.3 M Na_2SO_4 at pH 2) indicated unimodal molecular weight distributions and the expected shift to higher molecular weight at each stage of the triblock copolymer synthesis by sequential monomer addition. However, the final polydispersity (M_w/M_n) of the triblock was 1.50, which is relatively high for a copolymer prepared by ATRP chemistry. Recently we have obtained good evidence that there is a column retention problem under the low pH conditions required to dissolve the DEA block for the aqueous GPC protocol. For example, the MPC homopolymer precursor, which has a polydispersity of 1.2 when analyzed by aqueous GPC at neutral pH using alternative GPC columns, has an apparent polydispersity of 1.5 at pH 2 using the Viscotek GPC columns employed for the analysis of the triblock copolymer in the present study. Thus, we believe that the polydispersity of 1.50 cited above for the final triblock copolymer is probably an overestimate of its true polydispersity. It is emphasized that the apparently broad molecular weight distribution of the triblock copolymer did not prevent the formation of well-defined micelles in aqueous solution. The triblock composition was determined by ^{1}H NMR spectroscopy (spectra were recorded on 1.0 w/v % copolymer solutions in either D_2O or d_8-2-propanol using a Bruker Avance DPX 300 MHz spectrometer): the degrees of polymerization of MPC, GMA, and DEA block were 30, 20, and 60, respectively. Relatively low degrees of polymerization were targeted because of constraints imposed by the ATRP chemistry.

Preparation of Shell Cross-Linked Micelles. The shell cross-linking chemistry involved cross-linking of the hydroxy groups on the central GMA block using divinyl sulfone (DVS).[25−27]

(a) In Aqueous Media for the Preparation of MPC−Corona SCL Micelles. The MPC_{30}-GMA_{20}−DEA_{60} triblock copolymer was molecularly dissolved in water at pH 2 at 2 w/v %, and the solution pH was adjusted to pH 12 so as to induce micelle formation. Shell cross-linking was achieved using DVS (at a DVS/GMA molar ratio of 1.0) at pH 12 and stirring this solution for 2−3 h at room temperature. After shell cross-linking, the solution pH was adjusted to pH 8−9 to minimize hydrolysis side reactions. For the XPS measurements, a portion of this aqueous solution was freeze-dried to obtain a solid white power. Sulfur microanalyses were also carried out on these SCL micelles, both before and after purification by dialysis.

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(b) In Nonaqueous Media for the Preparation of DEA−Corona SCL Micelles. The MPC_{30}−GMA_{20}−DEA_{60} triblock copolymer was first dissolved in methanol (2.5 w/v % solution), and then THF was slowly added to obtain a 4:1 THF/methanol mixture. The solution temperature was increased to 45 °C. After addition of a small amount of 1.0 M NaOH in methanol, DVS (at a DVS/GMA molar ratio of 1.0) was added and the stirred solution was allowed to react overnight at 45 °C. A portion of this SCL micellar solution was dried under vacuum prior to XPS analysis.

Dynamic light scattering (DLS) studies were performed using a Brookhaven Instruments Corp. BI-200SM goniometer equipped with a BI-9000AT digital correlator using a solid-state laser (125 mW, $\lambda = 532$ nm) at a fixed scattering angle of 90°. The intensity-average hydrodynamic diameters ($\langle D_h \rangle$) and polydispersities (μ_2/Γ^2) of the micelles were obtained by cumulants analysis of the experimental correlation function.

Transmission electron microscopy (TEM) images were recorded using a Hitachi 7100 microscope. Samples were prepared by dipping a Formvar-coated copper grid into an aqueous solution of SCL micellar or gold colloids, followed by air-drying at ambient temperature.

X-ray Photoelectron Spectroscopy Studies. The XPS analysis was performed using a Thermo VG Scientific Sigma Probe spectrometer at the University of Surrey, U.K. A twin Mg Kα source ($E = 1253.6$ eV) with a spot size of 500 μm operating at a power of 200 W was used: the pass energy was set at 100 eV for the survey spectra and at 20 eV for the high-resolution spectra of all elements of interest (C 1s, O 1s, N 1s, S 2p, P 2p, etc.). Data processing was performed using Avantage 1.46 software supplied by the manufacturer. Quantitative surface compositions were calculated using the integrated peak areas of the high-resolution spectra, after background subtraction (Shirley baseline), and employing sensitivity factors that were corrected for the spectrometer transmission function. For the peak fitting of the high-resolution spectra, the parameters associated with each peak were the binding energies at the peak maxima, the full widths at half-maximum (fwhm), the areas, and the Gaussian-to-Lorentzian ratios. Sample charging effects of the order of 3 eV were observed, and charge referencing was accomplished by setting the CC/CH component at 285.0 eV.

Results and Discussion

Dilute solutions of both types of SCL micelles were characterized in terms of their particle size distributions and supramolecular nanostructures using DLS and ^{1}H NMR spectroscopy, respectively. In addition, TEM studies were undertaken. The DLS data are indicated within Figure 1: the MPC−corona SCL micelles had a $\langle D_h \rangle$ of 33 nm ($\mu_2/\Gamma^2 = 0.03$), and the DEA−corona SCL micelles had a $\langle D_h \rangle$ of 45 nm ($\mu_2/\Gamma^2 = 0.12$). Figure 2 summarizes the results obtained from the ^{1}H NMR studies. The MPC_{30}−GMA_{20}−DEA_{60} triblock composition was calculated from the NMR spectrum obtained in d_4-methanol by comparing the integrated relative peak intensities at δ 3.0, δ 3.4−3.6, and δ 2.4−2.7 due to the MPC, GMA, and DEA residues, respectively. For the MPC−corona SCL micelles prepared in D_2O at pH 12, the NMR signals due to the DEA chains are invisible, since this block is hydrophobic and hence forms the nonsolvated micelle cores. Conversely, the signals due to the MPC residues are not detected for the DEA−corona SCL micelles; instead, the NMR spectrum is dominated by the signals due to the DEA residues, as expected.

Transmission electron microscopy studies (see Figure 3) confirmed that both types of SCL micelles had spherical morphologies. The DEA−corona SCL micelles were somewhat more polydisperse than the MPC−corona SCL micelles. Allowing for polydispersity and solvation effects, the mean particle diameters estimated on the basis of the TEM studies were in reasonable agreement with those obtained by DLS.

An Mg Kα X-ray source was selected in preference to the widely used Al Kα ($E = 1486.6$ eV) source. Since the former source is less energetic, the XPS analysis is a little more surface-sensitive. This is particularly important in the present study because the thickness of the micelle corona in the solid state is expected to be similar to the XPS sampling depth of analysis (ca. 2−10 nm). Given the poor intraelemental resolution that is inherent to XPS, we have always attempted to use a "unique elemental marker" strategy wherever possible, since this eliminates the uncertainties usually introduced by curve-fitting procedures.[16,18,19] Unfortunately, this is not possible in the present study. In principle, phosphorus can act as a convenient elemental marker for the MPC block. In practice, this approach is flawed (see below), because of the well-documented depletion of the polar MPC residues from the near-surface of films.[28] Similarly, both the MPC and the DEA blocks contain nitrogen, so this element is not a unique marker. Thus, we were forced to rely on curve-fitting analysis of the high-resolution N 1s spectra

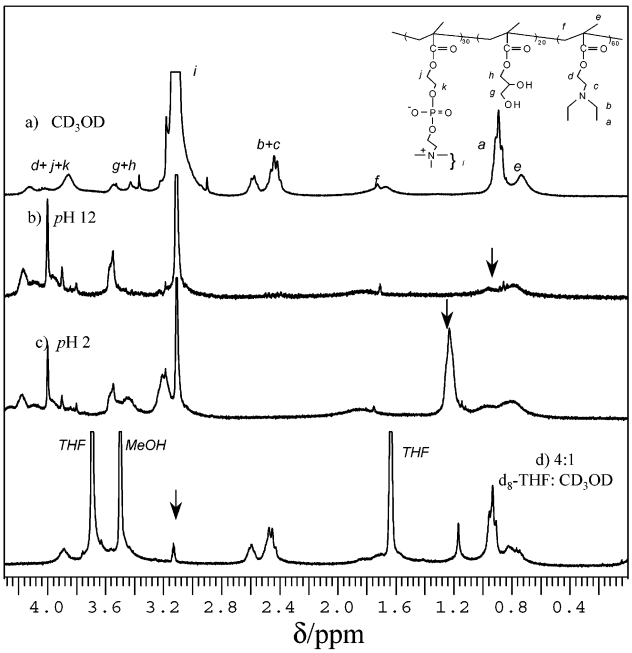

Figure 2. ^{1}H NMR spectra obtained for the MPC_{30}−GMA_{20}−DEA_{60} triblock copolymer: (a) linear, non-cross-linked precursor in CD_3OD; (b) MPC−corona SCL micelles in aqueous media at pH 12 (note the disappearance of the signals assigned to the DEA block); (c) MPC−corona SCL micelles in aqueous media at pH 2 (note the reappearance of the signals assigned to the DEA block); (d) DEA−corona SCL micelles in nonaqueous media (4:1 d_8-THF/CD_3OD by volume); note the disappearance of the nonsolvated MPC signals in this mixed solvent system.

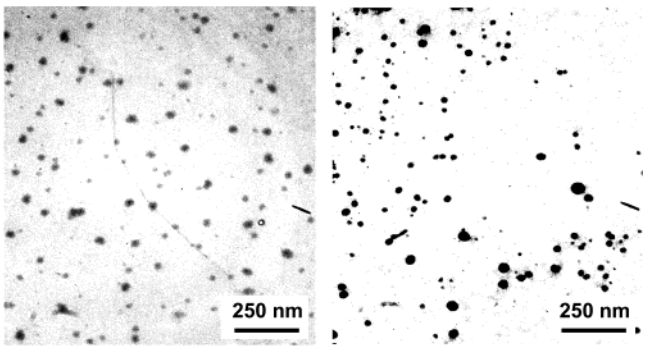

Figure 3. Typical transmission electron micrographs of (a) MPC−corona SCL micelles prepared in aqueous media and (b) DEA−corona SCL micelles prepared in nonaqueous media.

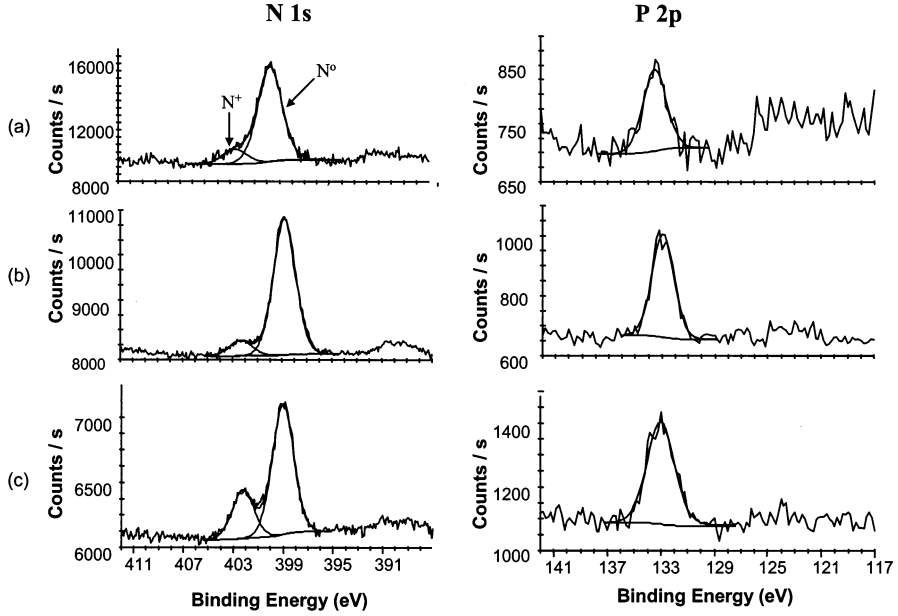

Figure 4. High-resolution N 1s and P 2p peak-fitted X-ray photoelectron spectra for (a) DEA−corona shell cross-linked micelles prepared in nonaqueous media, (b) the non-cross-linked, linear triblock copolymer precursor, and (c) MPC−corona shell cross-linked micelles prepared in aqueous media. Note the relative increase in intensity from parts a to c for the N^+ component, which is diagnostic of the MPC residues.

in order to quantify the relative proportions of cationic nitrogen (N^+) due to the quaternized MPC residues and neutral nitrogen (N^0) due to the DEA residues. However, one bonus is that sulfur is a unique elemental marker for the DVS reagent used to cross-link the GMA residues in the central block.[25−27]

MPC and DEA homopolymers were examined as reference materials in preliminary experiments. These initial studies assisted in the correct assignment of binding energies for the N^+ and N^0 species. For the relatively hydrophobic DEA homopolymer, only C, N, and O were detected, in approximately the expected proportions. For the MPC homopolymer, it was found that the P/N^+ atomic ratio obtained from XPS analysis was approximately 0.96. Bearing in mind the associated experimental errors, this is in good agreement with the theoretical value of unity. However, this sample had a carbon-rich surface composition, which suggested that the polar MPC residues were partially depleted from the surface, presumably being replaced by the more hydrophobic methacrylate backbone. A similar observation was reported by Davies and co-workers.[28] This group studied MPC-based statistical copolymers by XPS and found that the hydrophobic lauryl methacrylate comonomer preferentially migrated to the surface at the expense of the more polar MPC residues.

Figure 4 shows the three curve-fitted N 1s envelopes obtained for the linear $MPC_{30}−GMA_{20}−DEA_{60}$ triblock copolymer and the two SCL micelles synthesized using this copolymer. The major component of the N 1s signal at approximately 399 eV is due to the N^0 species, which is characteristic of the DEA residues. The minor N^+ component located at higher binding energy (around 402 eV) is diagnostic of the quaternized MPC residues. Qualitatively, it is apparent that the proportion of N^+ is highest for the MPC-corona SCL micelles and lowest for the inverted DEA−corona SCL micelles, with the non-cross-linked linear copolymer having an intermediate N^+ content. This trend is also consistent with the signal-to-noise ratios observed in the P 2p spectra: the weakest P signal is obtained for the DEA−corona SCL micelles, as expected. These observations support the existence of the SCL micelle nanostructures that are predicted on the basis of chemical intuition. However, XPS analysis also reveals some unexpected features. Prior to the XPS studies it was anticipated that no P signal (or N^+ signal) would be observed for the DEA−corona SCL micelles and, conversely, no N^0 signal would be detected for the MPC−corona SCL micelles. However, this is not the case. We believe that this discrepancy mainly occurs because the XPS sampling depth is comparable to the dimensions of the coronal layers of the SCL micelles in the absence of solvent. Thus, even with the more surface-specific Mg Kα X-ray source,[21] we were able to detect the P signal originating from the cores of the SCL micelles. Furthermore, even at the relatively high target degrees of cross-linking employed in the present study, we cannot exclude the possibility of some deformation of the SCL micelles occurring in the solid state (absence of solvent). In this regard, we note that Wooley and co-workers have observed[2] significant deformation for SCL micelles with low T_g cores in the dry state using AFM. If such deformation occurred in the present study, it would inevitably complicate the XPS analysis.

Table 1 summarizes the XPS data obtained for the $MPC_{30}−GMA_{20}−DEA_{60}$ triblock copolymer. In its linear, non-cross-linked form, this copolymer should have zero sulfur content, a theoretical P/N^{tot} atomic ratio of 0.33 (where $N^{tot} = N^0 + N^+$), and a N^+/N^0 atomic ratio of 0.50. In reality, its surface sulfur content is zero, the experimental P/N^{tot} atomic ratio is 0.06, and the N^+/N^0 ratio is 0.15. These data indicate that the polar MPC residues are depleted from the polymer−vacuum interface; that is, the surface thermodynamics ensure that the XPS composition of this copolymer is dominated by the hydrophobic DEA residues. This hypothesis is consistent with our earlier observations with the MPC homopolymer (see above) and also the findings of Davies and co-workers.[28]

Turning to the MPC−corona SCL micelles, we find that curve-fitting analysis of the spectrum shown in Figure 4

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Table 1. Summary of the X-ray Photoelectron Spectroscopy Data Obtained on the Linear and Two SCL Micelle Forms of the $MPC_{30}-GMA_{20}-DEA_{60}$ Triblock Copolymer[a]

XPS sample	atom % C	O	N	P	S	P/N^{tot} expected	P/N^{tot} meas	N^+/N^0 expected	N^+/N^0 meas
$MPC_{30}-GMA_{20}-DEA_{60}$ triblock copolymer	72.0	21.6	6.1	0.37		~0.33	0.06	~0.50	0.15
MPC−corona SCL micelles	67.6	25.5	3.2	0.73	3.0	~1	0.23	~∞	0.37
DEA−corona SCL micelles	73.2	20.6	4.4	0.28	0.8	~0	0.06	~0	0.10

[a] N^+ is the fraction of quaternized nitrogen atoms due to the MPC residues, N^0 is the fraction of neutral nitrogen atoms due to the DEA residues, and N^{tot} is the total number of nitrogen atoms, all in atom %.

leads to an experimental N^+/N^0 atomic ratio of 0.37, whereas the theoretical ratio should be infinity (see Table 1). However, the latter ratio assumes that the XPS sampling depth is no greater than the dimensions of the MPC coronal layer. Since the N 1s spectrum is dominated by the N^0 signal due to the DEA residues, it is clear that this assumption is not valid. Similarly, the experimental P/N^{tot} atomic ratio is actually 0.23, as compared to the theoretical P/N^{tot} atomic ratio of 1.00. Again, this indicates that the DEA residues (which on the basis of ^1H NMR studies must be located in the nonsolvated micelle cores in the presence of water at neutral pH) are unexpectedly detected by XPS. In view of this, we cannot exclude the possibility that some partial internal rearrangement and/or deformation of the SCL micelles occurs in the solid state, as the mobile low-T_g DEA block tries to migrate toward the interface in order to displace the polar MPC block and hence minimize the surface free energy of the system. Nevertheless, if the XPS data for the MPC−corona SCL micelles are compared to those obtained for the non-cross-linked, linear triblock copolymer, it is obvious that there are significant differences and the surface concentration of the MPC residues is much higher in the SCL micelle system, as expected. Presumably shell cross-linking inhibits the mobility of both the MPC and the DEA blocks, which in turn minimizes the degree of interfacial migration/segregation relative to that observed for the non-cross-linked copolymer. It is also noteworthy that sulfur atoms originating from the DVS cross-linker are detected by XPS, which confirms that successful cross-linking of the GMA residues has occurred, as anticipated.[25−27,29]

Finally, the DEA−corona SCL micelles were examined by XPS. In terms of potential applications, this "inverted" structure is of little interest, because its synthesis requires the use of organic solvents, rather than aqueous solution. Nevertheless, in the context of the present study, there is the opportunity to assess the ability of XPS to differentiate between the MPC−corona and the DEA−corona SCL micelles. First, XPS analysis confirmed the presence of sulfur, which indicated that the DVS-based shell cross-linking chemistry had been successful in nonaqueous media. Ideally, XPS should not detect the MPC residues, since these were expected to be located in the micelle cores; hence, the theoretical P/N^{tot} and N^+/N^0 atomic ratios should both be zero. In practice, the P/N^{tot} value is 0.06 and the N^+/N^0 ratio is 0.10, which are quite similar to the values of 0.06 and 0.15 observed for the non-cross-linked linear triblock copolymer. In retrospect this is perfectly understandable, since the latter sample has a DEA-rich surface composition (see above) similar to that expected for the DEA−corona SCL micelles.

In summary, we have used XPS to examine the surface compositions of two types of SCL micelles prepared from the same MPC−GMA−DEA triblock copolymer. Unfortunately, the XPS sampling depth was comparable to the SCL micelle dimensions and the more hydrophobic DEA block showed a marked propensity to migrate to the interface; both these problems hindered interpretation of the XPS data. Notwithstanding these difficulties, our XPS study of the MPC−corona SCL micelles provides the first direct spectroscopic evidence for the expected nanostructured nature of these fascinating materials in the solid state.

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