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A New Class of Surfactants with Multinuclear, Inorganic Head Groups

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Abstract: The main ability of amphiphilic molecules is to alter the energy of interfaces. They aid in the formation of various materials characterized by a high surface to volume ratio. Furthermore, amphiphiles tend to self-organize into structures of higher complexity. In the current study anionic surfactants containing a purely inorganic multinuclear head group of the polytungstate type R-$[PW_{11}O_{39}]^{3-}$ were synthesized. Alkyl chains of different length were attached to the head group via siloxy bridges. Furthermore, the counterions could be varied. Ultimately, a heteropolyacid surfactant (H^+ as the counterion) could be prepared. The self-assembly behavior of the polyoxometalate surfactants into micelles and even lyotropic phases was studied. For instance, the formation of a phase with *P*6/*mm* symmetry containing hexagonally packed cylinders has been observed. Finally, it was possible to extend the functionality of classical amphiphiles. The polyoxometalate amphiphiles have been used for the emulsification of and, at the same time, as the initiator for the cationic polymerization of styrene. As a result, interesting organic–inorganic hybrid polymer latexes with surfaces containing heteropolyacid entities were prepared.

Introduction

The properties and applications of amphiphiles are widespread. Amphiphilic molecules have proven to be of extraordinary value, because they bear the potential to bridge from the molecular scale to the nanoscale. Two entities characterized by different solvent compatibilities are linked together in one molecular species. The most important examples of amphiphiles are surfactants. They contain an ionic and water-soluble head group attached to a hydrophobic alkyl tail. This antagonism joined on the molecular level is responsible for the characteristic behavior of surfactants in contact with solvents, which are specifically interacting with only one of the mentioned molecular parts.[1,2] The classical case is water. The tendency of surfactants to minimize the water–alkyl and to maximize the water–head group interfaces is responsible for the well-documented self-assembly processes leading to micelles, lyotropic phases, and emulsions, depending on the concentration and the presence of additives.[3] Further parameters induce finer differences between individual amphiphiles. The molecular structure of the surfactant controls the shape and size of the resulting aggregates. The volume of the tail V_{tail} in relation to the product of the projected head group area A_{head} and the tail length L_{tail} enter the packing parameter P_S,[4,5] which defines a measure for the shape of the surfactant. Surfactants with P_S close to 1 (cylindrical shape) tend to form self-assembled structures with small curvatures. If on the other hand P_S is significantly different from 1 (cone shape), aggregates with strong curvature, for instance, micelles, are prepared.

Consequently, there have been major efforts in the synthesis of organic surfactants with systematic variations regarding the length, the number, and the chemical nature of the tail and also regarding the head group. Good examples are the so-called bolaform surfactants containing two or more head groups in one molecule.[6] Less attention was devoted to the fact that also the charge and the charge density of the head group will have a balanced effect on the molecular self-assembly processes. It is worth noting that the head groups of most known cationic surfactants are still ammonium groups.[7] For anionic surfactants one has to mention sulfonates (as in sodium dodecyl sulfate, SDS) and phosphonates in phospholipids.

It is an important task to prepare surfactants with alternative head groups. For instance, Landfester et al. have reported an interesting case regarding an amphiphile containing a sulfonium cation as the hydrophilic entity.[8] Furthermore, there are numerous arguments why it is very interesting to equip head groups with metal centers, in particular elements from the d block of the periodic table. Some examples for metal-containing amphiphiles exist already in the emerging field of metallomesogens.[9,10] However, one of the encountered problems is that, due to the low stability of the M–C bond in protic solvents, it is difficult to attach the hydrophobic chain directly to the metal. Either metals were introduced as counterions to the head group or the

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head group itself contained a multidentate ligand capable of binding to certain metal cations (Werner complexes). An interesting perspective of metal-containing surfactants was demonstrated by Matyaszewski et al.[11,12] The authors describe atom transfer radical polymerization (ATRP) catalyzed with Cu^{I} coordinated by tridentate ligands modified with a long alkyl chain. Some papers discuss the possibility that interesting nanostructured materials can be directly prepared from the self-assembled metal-containing amphiphile structures. Gin et al. describe the preparation of Pd nanoparticles via a liquid crystalline phase containing a cationic Pd complex.[13] Our group has reported the first example of an organometallic amphiphile with a $Zn^{II}-CH_3$ head group and a poly(ethylene glycol) tail.[14] An interesting self-assembly process ranging over several dimensions has been observed, and nanostructured zinc oxide materials could be prepared directly from the self-organized phase.

The next level of complexity is envisioned for surfactants containing a multiply charged, redox-active, multinuclear head group. A class of compounds which fulfill the mentioned requirements are the polyoxometalates (POMs).[15,16] One of the first known polyoxometalates is the so-called Keggin ion, isolated by Berzelius in 1826.[17−19] Four groups of edge-shared "MoO_6" octahedra are linked together by one central phosphate, resulting in the polyoxometalate cluster $[PMo_{12}O_{40}]^{3-}$ with an icosahedral structure. A topologically identical compound is also known for tungsten instead of molybdenum. However, the Keggin ion is only a relatively simple member of a large class of compounds with complex and large structures. Probably the most amazing examples have been reported by Müller et al., such as the giant polyoxometalate wheels (e.g., $[Mo_{154}(NO)_{14}O_{434}(OH)_{14}(H_2O)_{70}]^{28-}$)[20−22] or the keplerates (e.g., $[Mo_{132}O_{372}(COO)_{30}(H_2O)_{72}]^{42-}$).[23] An interesting review article about polyoxometalate-based molecular materials was published by Coronado et al. in 1998.[24] Since then, interesting self-organization phenomena have been described by Kurth et al., who reacted anionic polyoxometalate clusters with cationic surfactants.[25−27] Our group has described the formation of a liquid crystalline phase of a giant polyoxomolybdate wheel attached to cationic double-tailed surfactants.[28] However, it is not absolutely correct to speak about surfactants in the mentioned cases, as the hydrophilic part (the charged POM) and the hydrophobic part (the alkyl chain of the surfactants) are not part of one molecule and, in addition, the POM surfactant aggregates do not have dipolar character. One further step toward surfactants with POM head groups was undertaken by Cronin et al.[29,30] First, they prepared the so-called Mn−Anderson anions containing two tris(hydroxymethyl)amino methane groups. Then, they attached long alkyl chains via amide bonds. The resulting compound is also not an ideal dipolar surfactant because the long alkyl chains are located at each side of the platelike POM cluster.[29,30] Nevertheless, Cronin et al. have described very interesting self-assembly processes such as the formation of vesicles. Antonelli et al. have published a stimulating paper about the formation of toroidal mesoporous molybdenum oxide.[31] A binuclear Mo−alkoxide complex modified by a long-chain amine becomes amphiphilic and self-assembles into an unusual structure in course of the hydrolysis of the alkoxide groups. The latter examples show that whenever an amphiphile with a multinuclear transition-metal-containing head group has been described, unusual and complex self-organization processes have been observed.

A new, unusual surfactant with a POM group related to the Keggin ion is described in the current paper (see Scheme 1). Its self-organization behavior has been investigated depending on various parameters like length of the alkyl-chain and also surfactant counterions. Finally, we describe the synthesis of an unprecedented nanostructured polyoxometalate -polymer latex hybrid materials.

Results and Discussion

Synthesis of a New Class of Surfactants with Polyoxometalate Head Groups. The synthesis of the POM surfactants is described in the Supporting Information and also depicted in Scheme 1. A lacunary W−Keggin ion was used as a starting point. In lacunary polyoxometalate species at least one W=O group has been cleaved.[32] A small pocket with four oxygen atoms at the periphery forms. Lacunary Keggin ions have therefore been used as interesting ligands with unusual properties.[33] Thouvenot, Proust, et al. have shown that it is possible to insert short-chain organosilicate species and other interesting compounds into the pocket of the lacunary Keggin ion.[34−36] We have used the latter approach, and $[PW_{11}O_{39}](K)_7$ was reacted with the long chain organo-alkoxysilane $CH_3(CH_2CH_2)_{n-2}CH_2Si(OCH_2CH_3)_3 \equiv C_nSi(OCH_2CH_3)_3$ ($n = 8, 12, 18$) under acidic conditions (see Scheme 1) in the presence of ammonium ions ($[NR_4]^+$ with R

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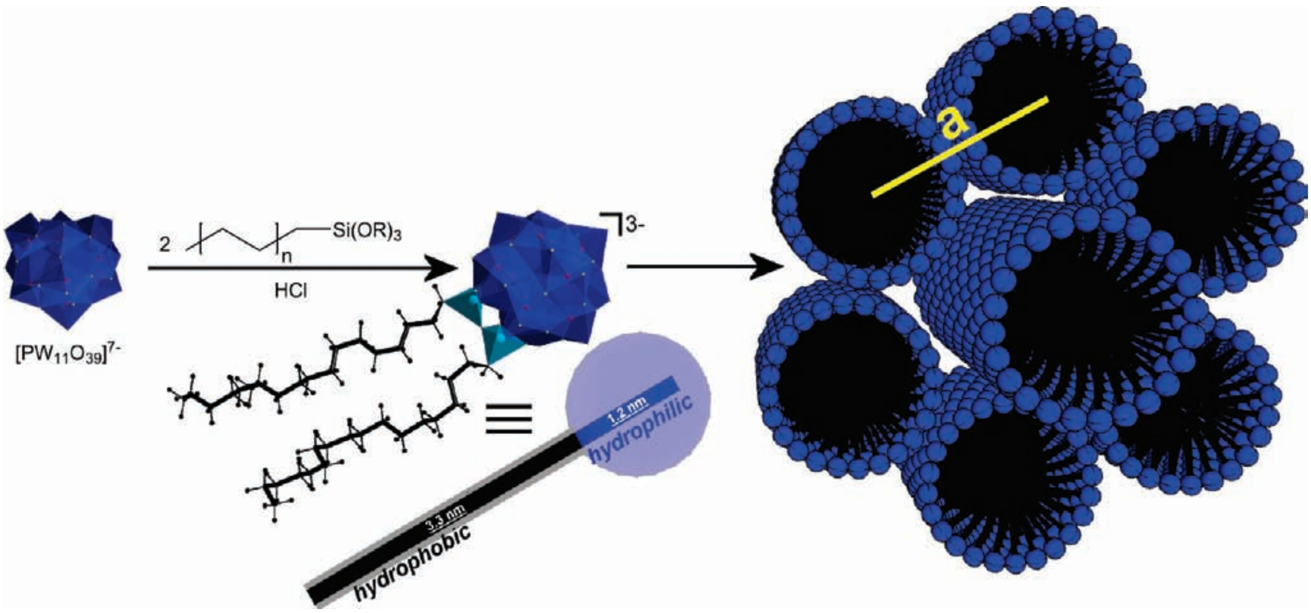
Scheme 1. Illustration for the Synthesis of New POM Surfactants[a]



[a] A lacunary polyoxometalate species is modified with two alkylsiloxy groups. Depending on the tail length and counterions, different lyotropic phases form in contact with water such as the shown assembly of cylinders in a hexagonal fashion in the case of $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$.

= Me, Et, Bu). The resulting colorless precipitates are the desired products $[PW_{11}O_{39}(SiC_n)_2](NR_4)_3$. The production of $[PW_{11}O_{39}(SiC_n)_2](NEt_4)_3$ (discussed as a representative example) is difficult to confirm, because the presence of the long alkyl chains prohibits us from growing single crystals which can be used for X-ray diffraction analysis. The resulting compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FT-Raman, and FT-IR spectroscopy and elemental analysis (see also the Supporting Information, SI-1). In the ^{1}H NMR spectrum signals of the tetraethylammonium cation and of the alkyl chain of the silane are visible. The quartet at 3.21 ppm and the triplet at 1.17 ppm represent the methylene and methyl protons of the tetraethylammonium group. The other signals belong to the alkyl chain. The intensity ratio of alkyl chain and cation protons is in agreement with theory. The purity of the product was additionally proven by ^{31}P and ^{29}Si NMR. In both spectra only one signal exists. Furthermore, there is a small shift to higher field in the ^{31}P NMR spectrum. This is a hint of the modification of the POM cluster. This modification of the cluster can also be monitored by IR and Raman spectroscopy. Each type of POM cluster exhibits its typical IR and Raman spectrum. In addition to the typical vibrations of alkyl groups, there are many signals between 1200 and 650 cm^{-1} belonging to vibrations of the POM cluster. It is possible to assign each of the vibrations to a specific group (see SI-1). The most important signals of the Raman spectrum are located at 997 and 983 cm^{-1}. These peaks represent the symmetric vibrations of the terminal W=O bonds. The mentioned vibrations are characteristic for all kinds of POMs and are very sensitive to any modification of the cluster. Although the mentioned analytical methods give a good indication for the formation of the desired compound, ultimately they are not decisive. Therefore, electron spray ionization mass spectra (ESI-MS) were acquired. Several intense signals characterized by a complex isotope pattern could be recorded (see SI-1). It is possible to assign all of the signals. The signal with the highest intensity is centered at m/z 991.8. The distance of the single peaks in the isotope pattern is 0.33, which means that the charge of the compound causing the mentioned signal is ±3. The expected pattern for the ion $[PW_{11}O_{39}(SiC_8)_2]^{3-}$ was simulated. The comparison to the measured data is clear proof that the desired POM surfactant could be successfully prepared (see Figure 1).

The counterions of the as-prepared POM surfactants are the relatively bulky and partially hydrophobic tetraalkylammonium cations. The solubility of the $[PW_{11}O_{39}(SiC_n)_2](NR_4)_3$ compounds in water as well as in apolar solvents is thus very limited. Furthermore, because the organic cations are located near the anionic head group, it can be expected that the amphiphilic character of the entire system is reduced. It is worth noting that, for classic anionic surfactants, alkali-metal ions (Na$^+$, K$^+$) are used as counterions. However, the related desired POM surfactant compounds $[PW_{11}O_{39}(SiC_n)_2](M)_3$ with M = Na$^+$, K$^+$ cannot be obtained directly via the exchange of the organic ammonium cations during the synthesis. Instead, the cation exchange was successful by postpreparative ion-exchange chromatography (see the Supporting Information). Not only $[PW_{11}O_{39}(SiC_n)_2](Na)_3$ but also the novel heteropoly acid surfactant $[PW_{11}O_{39}(SiC_n)_2](H)_3$ could be obtained. The latter compound is particularly interesting, since heteropoly acids are well-known heterogeneous and homogeneous catalysts.[37−40] The successful ion exchange process has been proven by ^{1}H NMR spectroscopy (see SI-2 in the Supporting Information). The signals corresponding to the organic ammonium cation vanish completely. For $[PW_{11}O_{39}(SiC_n)_2](H)_3$ as the product, a new signal corresponding to H_3O^+ appears at δ 5.46 ppm. Furthermore, it is important to confirm that the described procedure has no effect on the integrity of the "$PW_{11}O_{39}$" head group. The characteristic spectroscopic fingerprint corresponding to "$PW_{11}O_{39}$" in FT-Raman and ^{31}P NMR data has remained unchanged before and after ion exchange (see Figure 1b,c). However, the solubility of the POM surfactants in water has

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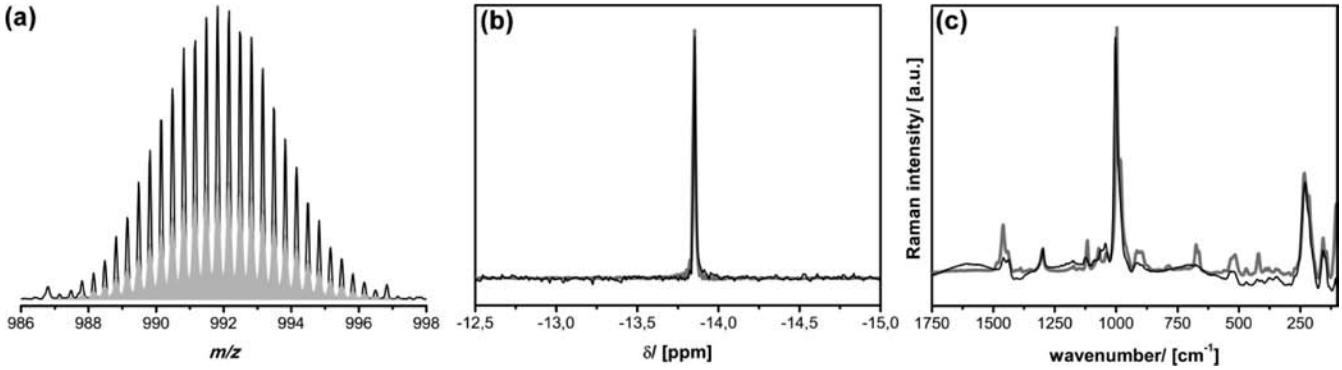

Figure 1. (a) Characteristic signal in the ESI-MS spectrum of the POM surfactant (black) and its assignment due to the simulation of the ion $[PW_{11}O_{39}(SiC_8)_2]^{3-}$ (gray). The entire spectrum is shown in SI-1 in the Supporting Information. (b) ^{31}P NMR and (c) FT-Raman spectra of $[PW_{11}O_{39}(SiC_8)_2](NEt_4)_3$ (gray) and $[PW_{11}O_{39}(SiC_8)_2](Na)_3$ (black).

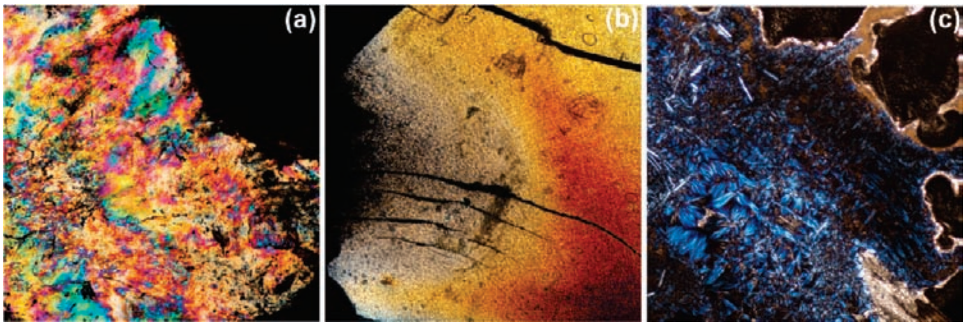

Figure 2. Polarization microscopy images of $[PW_{11}O_{39}(SiC_{12})_2](Na)_3$ (a), $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$ (b), and $[PW_{11}O_{39}(SiC_{16})_2](NBu_4)_3$ (c).

increased significantly as a result of the cation exchange. It can be summarized that a set of novel POM surfactants are available, characterized by a systematic variation in tail length and also counterions.

Self-Assembly Behavior of $[PW_{11}O_{39}(SiC_n)_2]^{3-}$ Surfactants. A convincing indication that the described compounds have amphiphilic character comes from polarization microscopy images taken from the as-prepared materials containing a certain amount of water. The photographic images shown in Figure 2 are typical for liquid crystalline materials.[41] The observed birefringence of the materials with waxlike consistence is often accompanied by the appearance of bright colors. Because the textures of the liquid crystals are different for $[PW_{11}O_{39}(SiC_{12})_2](Na)_3$ (Figure 2a), $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$ (Figure 2b), and $[PW_{11}O_{39}(SiC_{16})_2](NBu_4)_3$ (Figure 2c), it can be concluded that both the length of the alkyl chain and the nature of the positively charged counterions are influencing the structure of the liquid crystals. Differential scanning calorimetry data support the conclusions drawn on the basis of the microscopy data. For instance, a reversible phase transition has been observed for $[PW_{11}O_{39}(SiC_{16})_2](NEt_4)_3$ at $T = 124$ °C (see SI-1). However, while polarization microscopy is a very powerful technique for thermotropic liquid crystals,[41] it is much less informative regarding structure determination in the case of lyotropic phases as are present here.

Therefore, the liquid crystals were also investigated by small-angle X-ray scattering (SAXS). The SAXS pattern of $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$ shown in Figure 3a is characterized by three reflexes at $q = 1.56$, 2.70, and 3.11 nm^{-1}. A fourth, weak signal is present at $q = 2.22$ nm^{-1}. A satisfactory simulation of the data could be achieved assuming a phase containing hexagonally packed cylinders (space group $P6/mm$) characterized by a core−shell structure; see also Scheme 1. The simulations of the SAXS patterns were performed using the program SCATTER by Förster et al.[42,43] The extension of the length of the hydrophobic chain leads to a change in the lattice constant $a(C_{16}) = 4.62$ nm to $a(C_{18}) = 5.37$ nm (see Figure 3b). The described findings are nicely supported by transmission electron microscopy (TEM). In Figure 4a one sees the structure of the $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$ liquid crystal at a position perpendicular to the main axis of the cylinders (see Scheme 1). The value for the distance between two cylinders (∼4.8 nm) fits well to the lattice constant $a_{SAXS}(C_{16})$, and the thickness of the walls (∼1.5 nm) can be correlated to the extension of the $[PW_{11}O_{39}]$ head group (see Scheme 1). TEM images in which a variety of orientations of the liquid-crystalline structure can be seen, for instance the side view of the cylinders, is shown in SI-3 in the Supporting Information. It is worth noting that also in the wide-angle X-ray scattering (WAXS) region (5−40° 2θ) several broad reflexes have been observed (see SI-4 in the Supporting Information). Interestingly, the position of those reflexes does not vary with the surfactant tail length. A Pawley fit of the data using the program TOPAS[44] of the system ($P6/mm$) results in $c = c(C_{16}) = c(C_{18}) = 1.1$ nm for the orthogonal lattice parameter. Therefore, the latter data are also consistent with the packing of the surfactant head groups (∼1.2 nm diameter) in the POM-containing domain of the liquid crystal (see Scheme 1). For the surfactant with a shorter tail (C_{12}) not all reflexes

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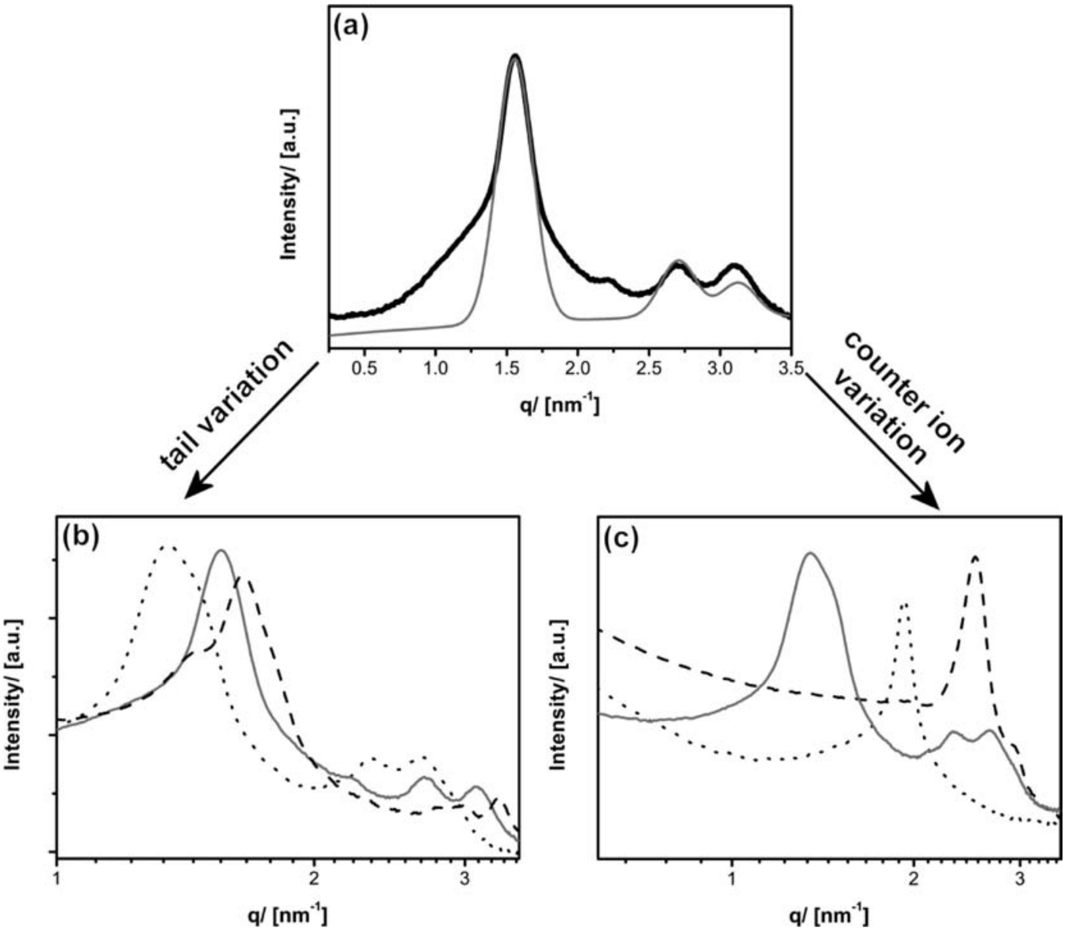

Figure 3. (a) Experimental (black; background corrected) and simulation SAXS data (gray) of $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$. (b) SAXS data of $[PW_{11}O_{39}(SiC_{18})_2](Na)_3$ (dotted line), $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$ (solid line), and $[PW_{11}O_{39}(SiC_{12})_2](Na)_3$ (dashed line). (c) SAXS data of $[PW_{11}O_{39}(SiC_{18})_2](H)_3$ (dashed line), $[PW_{11}O_{39}(SiC_{18})_2](Na)_3$ (solid line), and $[PW_{11}O_{39}(SiC_{18})_2](NEt_4)_3$ (dotted line).

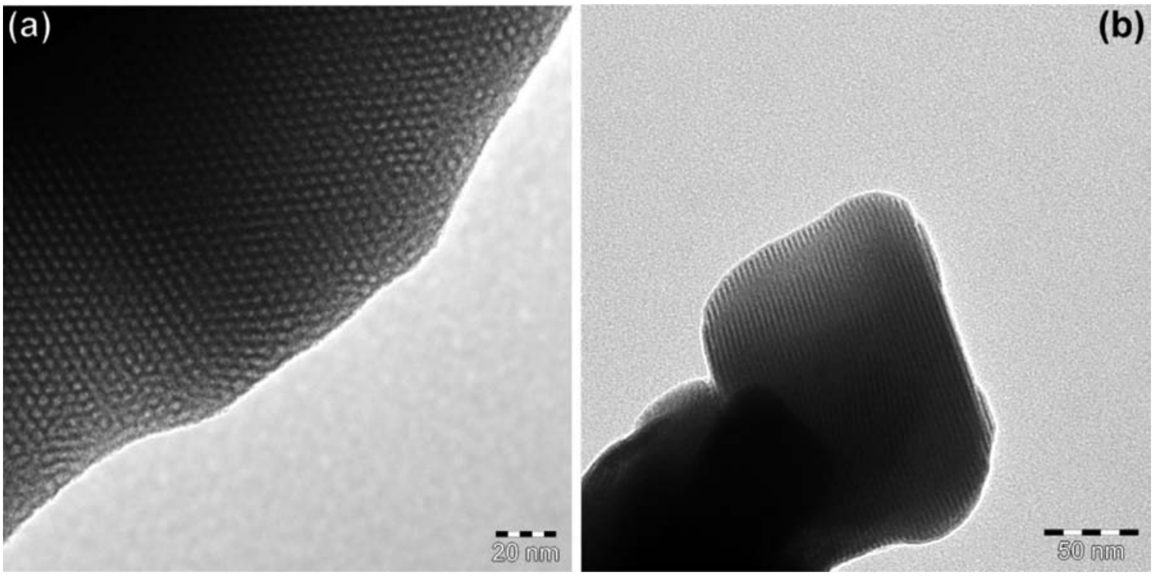

Figure 4. TEM micrographs of the liquid crystalline phases resulting from $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$ with *P*6/*mm* (a; for images taken at lower magnification, see SI-4 in the Supporting Information) and from $[PW_{11}O_{39}(SiC_{18})_2](H)_3$ with a lamellar structure (b).

can be assigned to the space group *P*6/*mm* (a = 4.4 nm) but additional signals are present at q = 1.46 and 2.98 nm^{-1}. The latter result indicates that a different structure is present as well. The best fit can be achieved assuming a hexagonal close packing (*P*6/*mmc*; a = 4.98 nm) of spherical micelles.

Interestingly, the exchange of the counterions while maintaining the tail length leads to marked differences regarding the structure of the liquid crystalline phases (see Figure 3c). In the SAXS pattern of $[PW_{11}O_{39}(SiC_{16})_2](H)_3$ (d_{001} = 2.5 nm) and also for all POM surfactants with organic ammonium cations

(d_{001}([$PW_{11}O_{39}(SiC_{16})_2$]($NEt_4)_3$) = 3.3 nm) as counteranions, only one diffraction signal can be observed. Such a pattern is typical for lamellar structures. The latter assumption could be verified by WAXS for which also the higher order diffraction signals have been identified (see SI-5 in the Supporting Information). The small interlamellar distance points to a significant interdigitation of the hydrophilic chains in those structures. Interestingly, for all materials with lamellar structures one observes a large number of additional sharp reflexes in WAXS. This indicates a crystalline structure of each sheet in which the single POM head groups are aligned (see SI-5). The lamellar structures have also been observed in TEM measurements (Figure 4b).

Micellization and Emulgation with [$PW_{11}O_{39}(SiC_n)_2$]$^{3-}$ Surfactants. The formation of a liquid crystalline phase is only one of the interesting self-organization features of amphiphilic molecules. Therefore, aqueous solutions of the POM surfactants at low concentrations were studied next. Objects with a hydrodynamic diameter D_h of ~4.3 nm can be observed in dynamic light scattering measurements (DLS; Figure 5a) of an aqueous solution of [$PW_{11}O_{39}(SiC_{16})_2$]($Na)_3$. The mentioned value fits well to the diameter expected for a micellar aggregate constructed from POM surfactants (see also Scheme 1). The corresponding experiments with [$PW_{11}O_{39}(SiC_{12})_2$]($Na)_3$ and [$PW_{11}O_{39}(SiC_{18})_2$]($Na)_3$ show that the size of the micelles scales with the length of the alkyl chain (Figure 5a). Assuming a linear correlation, the dependency is $\Delta D_h = 0.32$ nm per CH_2 group in the alkyl chain, which is in good agreement with findings reported for classical surfactants.[45−47] Additional information could be obtained from SAXS measurements (Figure 5c). The SAXS pattern is characteristic for the shape factor of spherical objects with relatively narrow size dispersity. An adequate compliance between the experimental data and a simulated scattering pattern could be achieved for spherical aggregates containing a homogeneous core with a radius of 3.6 nm and a shell of 1.8 nm. It should be noted that a minor amount of larger aggregates with the diameter $D_h = 10-20$ nm can also be seen in DLS. Therefore, also cryo transmission electron microscopy images were acquired (see Figure 5b). A large number of structures with an approximate radius of 10−15 nm were found. For a certain number of objects it even seems as if a core−shell structure becomes apparent. The latter observation would also fit to a POM surfactant aggregate, because the electron density of the hydrophilic polyoxotungstate shell possesses electron density significantly higher than that of the organic core.

The final feature that is explored for the new POM surfactants is their ability as emulsifying agents. Cyclohexane/water emulsions were prepared by sonication. When there was no amphiphile present, phase separation took place very quickly. However, when the POM surfactant [$PW_{11}O_{39}(SiC_{16})_2$]($H)_3$ is used, emulsions could be prepared which are stable for more than 12 h (see the photographic image shown in SI-6 in the Supporting Information). Motivated by this good result, the next step was that analogous emulsions styrene in water emulsions were prepared (see the Supporting Information). The emulsion was stirred for 3 h at 50 °C. A white powder was obtained after removal of the solvent. The analysis of the powder showed that it contained the POM surfactant and polystyrene. It could be redispersed in polar solvents such as water and methanol. DLS measurements indicate that a large amount of particles with a hydrodynamic diameter D_h between 200 and 400 nm are present (Figure 6a). However, the polydispersity is quite high. The findings from DLS are supported by SEM measurements, shown in Figure 6b. A large number of spherical objects with diameters in the size range 300−350 nm can be seen. Further information could be gathered by TEM measurements. Spherical objects with the same size have been observed. However, each of the particles are terminated by a dark rim. This indicates that the electron density of the material located on the rim is much higher than

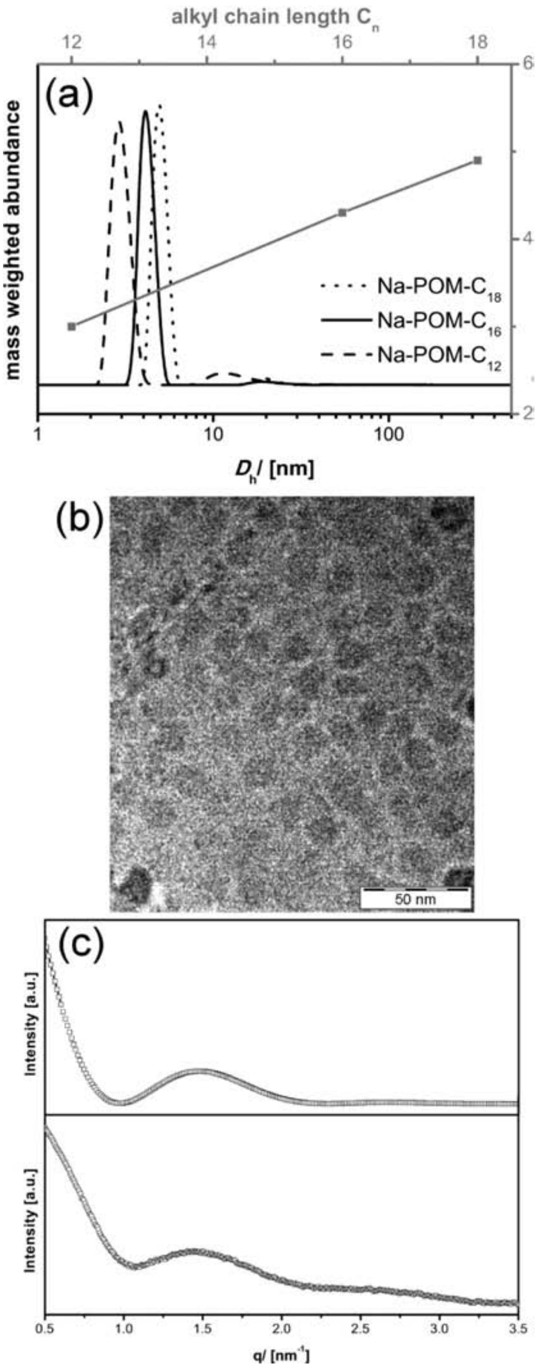

Figure 5. (a) Size distribution functions from DLS data for three POM surfactants with different alkyl chain lengths C_n (black) and their influence on the aggregate size (gray). (b) Cryo-TEM images. (c) Experimental SAXS data of a micellar solution of [$PW_{11}O_{39}(SiC_{18})_2$]($Na)_3$ (spherical symbols for data points) and the simulated pattern (square symbols).

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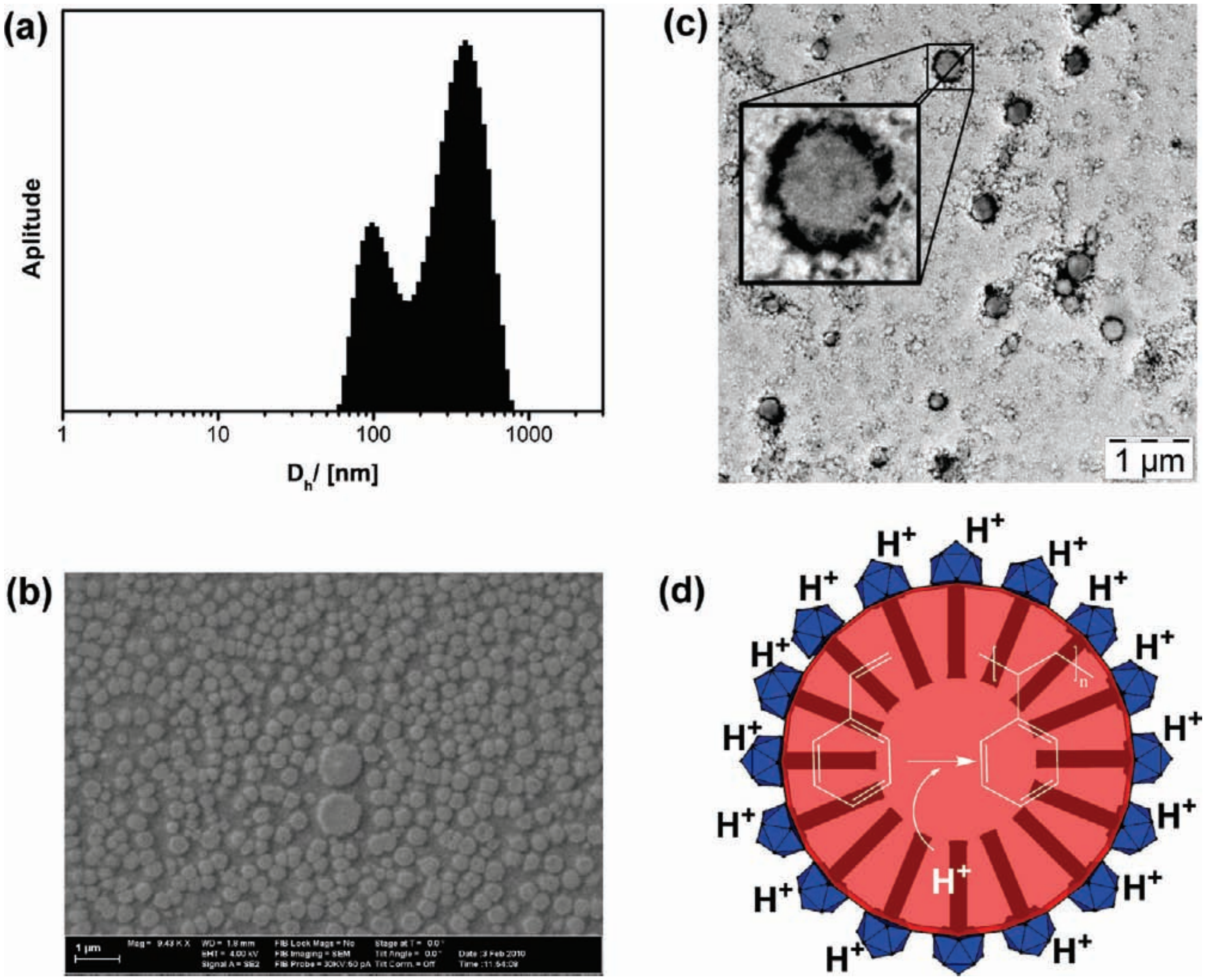

Figure 6. DLS (a), SEM (b), and TEM measurements (c) of the prepared polystyrene−POM surfactant particles. (d) Schematic image demonstrating the two functions of the POM surfactant: as an emulsifying agent and as a source of the protons for the cationic polymerization of the styrene (shown in red).

in the bulk of the particle. The latter finding can be rationalized if one assumes that the POM surfactant with the "PW_{11}" head group is located on the surface of the polymer particle (see Figure 6d).

Conclusion

The results presented in the current study can be summarized as follows. New anionic surfactants with the multinuclear polyoxometalate "PW_{11}" head groups have been introduced. A range of surfactants with systematic variations in tail length or counterions have been provided. The POM surfactants exhibit interesting self-assembly behavior. The formation of liquid crystalline phases or micelles in solution has been observed.

The POM surfactants have also been utilized as emulsification agents. However, the latter experiments point to a new and more general perspective in materials science. The POM surfactants fulfill two functions at once. They act as amphiphiles, and the heteropolyacid head group is catalytically active at the same time. For proof of principle the cationic polymerization of styrene has been described (see Figure 6d). Finally, interesting organic−inorganic hybrid materials, polystyrene particles with surfaces covered by POM surfactants, have been described.

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Supporting Information Available: Text giving experimental details and figures giving additional analytical data for the POM surfactants (SI-1), cation exchange studied by ^{1}H NMR spectroscopy (SI-2), additional TEM for $[PW_{11}O_{39}(SiC_{16})_2](Na)_3$ (SI-3), wide-angle X-ray diffraction of the liquid crystals with *P*6/*mm* phase (SI-4), SAXS and WAXS of the liquid crystals formed with $[PW_{11}O_{39}(SiC_{16})_2](H)_3$ (SI-5), and photographic images of a cyclohexane/water mixture after ultrasonification (SI-6). This material is available free of charge via the Internet at http://pubs.acs.org.

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