Ordered Hydrophobic Organosilicates Templated by Block Copolymers

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Hydrophobic organosilicates with controlled morphologies at the nanometer length scale have many potential applications in microelectronics and photonics. Here we report the use of block copolymers of poly(butadiene-*b*-ethylene oxide) (PB-*b*-PEO) as templates to create 10−20-nm periodic hexagonal arrays of cylinders in hydrophobic organosilicates. The self-assembly process of the block copolymers is monitored and studied by solid-state NMR, transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). It is found that the microstructure and phase behavior of the nanocomposites are very sensitive to the polymer−matrix interface and the intrinsic properties of the block copolymers. When methyltriethoxysilane (MTES) is solely used as sol precursor to swell polymer domains, a disordered structure is always obtained, presumably because MTES changes its nature from hydrophilic to increasingly hydrophobic during curing, and block copolymers are repelled from the matrix. A hydrophilic silicate precursor, (3-glycidyoxypropyl)-trimethoxysilane (GPTS), is introduced as an amphiphilic organosilicate precursor and to preserve the polymer−silicate interface. A layered core-shell structure is formed with PEO and GPTS located at the interface, while PEO and GPTS are microphase separated. Understanding of the templating mechanism may provide a new route for nonlithographic nanopatterning and incorporating functionalities for photonic applications.

Introduction

Organic−inorganic hybrid nanocomposites, which combine properties from both organic and inorganic materials, have many potential applications, such as separation membranes, and in the fields of catalysis, automobile, microelectronics, optics, and biology.[1−5] Compared to soft polymeric materials, highly cross-linked silicates are more chemically and mechanically robust as a matrix. The addition of organic species in the silicates makes them elastic and miscible with organic guest molecules, and the composite can be synthesized easily through sol−gel chemistry. Material properties can be further modified through introduction of functional groups in both templates and organosilicates. Functional groups, such as epoxy, amines, and acrylates, in the silicates make the film hydrophilic, whereas the presence of methyl, phenyl, or trifluoromethyl groups makes the cured silicates hydrophobic. The hydrophobic organosilicates have attracted great interest in microelectronics and photonics because of the minimal moisture absorption and improved chemical stability of the final devices. With the continuing miniaturization of microelectronic and photonic devices, it becomes increasingly important to design complex structures whose properties can be confined at nanometer length scale. The challenge is to make highly ordered materials with the functionality required for device applications. While highly ordered silica materials have been prepared, materials with the requisite methyl, phenyl or trifluoromethyl functionalities have yet to be reported.

By tailoring the guest−host interaction and using self-assembly as a tool, ordered inorganic silicates have been obtained using small surfactant molecules[6] or block copolymers[7] as templates. Similarly, periodic 2D and 3D mesophases in organosilicates has been created by evaporation-induced self-assembly through dip-coating.[8,9] The process is fast and simple, but is limited to thin film fabrication and the mesostructure is typically less than 10 nm. An alternative approach is to selectively swell one domain in the microphase separated

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block copolymers by sol−gel.[10] Film up to 1 mm thick is obtained and the domain size ranging from several to 100 nm can be tuned by polymer molecular weight. However, creation of hydrophobic periodic organosilicates through this approach remains as a challenge, and few of these materials have been addressed at the molecular level to understand the self-assembly process in the hydrophobic system. For example, little is known regarding how the characteristics of block copolymers (morphology and order−disorder transition temperature), the nature of organosilicates before and after curing, the links and interaction between block copolymers and organosilicates at the interface, and the accessibility of organosilicates to polymer domains may govern the formation of periodic structures in hydrophobic organsilicates.

Here we report the use of block copolymers of poly(butadiene-*b*-ethylene oxide) (PB-*b*-PEO) as templates to create 10−20-nm periodic hexagonal arrays of cylinders in hydrophobic methyl silsequioxane (MSQ) from methyltriethoxysilane (MTES) precursors. The self-assembly process of the block copolymers is monitored and studied by solid-state proton NMR, transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). When MTES is solely used as sol to swell polymer domains, a disordered structure is always obtained because the silicates become increasingly hydrophobic during curing and block copolymers are repelled from the matrix. To control the nature at the polymer−silicate interface, we introduce a hydrophilic organosilicate precursor, (3-glycidyoxypropyl)-trimethoxysilane (GPTS), which remains hydrophilic during the curing, as a co-sol. Then we tune the sol−gel chemistry between MTES and GPTS so that they prefer cross-condensation at the initial stage to form an amphiphilic organosilicate precursor. The role of GPTS in our system is different from that in previous work by Wiesner and co-workers,[10] who also used block copolymers to template the mixed organosilicates of GPTS and aluminum *sec*-butoxide. The hydrophilic GPTS was the major sol component in ref 10 and was chosen because of its appealing physical properties, such as high abrasion resistance. It had good compatibility with block copolymers themselves and the use of aluminum *sec*-butoxide further introduced hydrogen bonding between GPTS and PEO blocks, resulting in intimate mixing between sol−gel and block copolymer templates. In this paper, our goal is to understand how to self-organize periodic structures in hydrophobic organosilicates, which itself is not compatible with the block copolymer templates. The introduction of GPTS and formation of amphiphilic organosilicate precursors are critical to controlling the nature of the polymer−sol interface and forming an ordered nanostructure. Macroscopic phase separation is avoided, and the self-assembly is not perturbed in the subsequent heat treatment. A layered “core−shell” structure is proposed in the system we studied as a mechanism to minimize the interfacial energy where PEO and GPTS are located at the interface. Without ring opening of the epoxy in GPTS, the very different chain dynamics revealed by solid-state proton NMR suggest that PEO and GPTS are microphase separated. Finally, the orientation of ordered structures is studied by both TEM and SAXS. Induced by solvent evaporation, the long axes of the cylinders are aligned along the film plane.

The ability to form ordered nanostructures in hydrophobic organosilicates broadens the applications of organic−inorganic hybrid materials to many promising fields. The concept of using amphiphilic organosilicate provides flexibility to incorporate novel functionalities in the matrix for advanced materials.

Experimental Section

Material Preparation. The film was prepared in a way similar to that which was described in the literature.[10] A 0.2-g portion of PB-*b*-PEO (from Polymer Source; $\overline{Mn}$ of PB and PEO block is 5000 and 10 000, respectively) was dissolved in a 1:1 mixture of chloroform ($CHCl_3$) and tetrahydrofuran (THF) to form a 5 wt % clear solution. The sol was prepared by mixing (3-glycidyoxypropyl)-trimethoxysilane (GPTS) and methyltriethoxysilane (MTES) in different molar ratios at 0 °C. First, 15% of the stoichiometric amount of water required for the complete hydrolysis was added. The water contained HCl in a molar ratio (relative to sol) of 1.1×10^{-2}:1. After 15 min of stirring, the temperature was raised to room temperature. Fifteen min later, the residual water with HCl was added, followed by stirring for 1 h. The mixture was then added into the block copolymer solution and stirring was continued for 2 h. The mixture was transferred to a Petri dish and maintained at 65−70 °C for 1 h to evaporate solvents, and was then cured at 130 °C in a vacuum for 1 h to lock block copolymers in organosilicates. The final film had thickness of 0.1−1 mm. Samples with different PB-*b*-PEO/sol molar ratios were also prepared in a similar manner.

Characterization. The thermal transition temperatures were monitored by a Perkin-Elmer differential scanning calorimeter DSC 7. The morphologies of nanocomposites were observed by a JEOL-2000FX transmission electron microscope (TEM) equipped with a 14-bit charge-coupled device array detector. The acceleration voltage was 200 KV. Samples were crushed to obtain small fragments with thickness about 50−100 nm and then dispensed on carbon-coated copper grid. Some samples were subsequently stained by RuO_4 (2 wt %) for 15 min or by OsO_4 (4 wt %) for 30 min. Samples were also embedded in epoxy for microtoming both along the film plane and along the film thickness. The microtomed samples were examined in TEM using 120 kV to minimize the charging problem. Solid-state proton NMR experiments were performed at 500 MHz using a Tecmag NMR spectrometer with a 4 mm magic-angle spinning probe and spinning speed regulation at 4 kHz. The proton pulse widths were 3.5 ms and a delay time of 40 ms was used to measure the chain dynamics and for the spin diffusion experiments. Solid-state carbon NMR spectra were 1 ms. X-ray scattering (SAXS) diffraction patterns were collected at MHATT-CAT Sector 7 beamlines at the Advanced Photon Source. Samples 100−200 μm thick s were loaded in glass capillaries (2 mm diam) for measurement. The diffraction patterns were obtained by illuminating the sample with a 0.15−0.5-mm-diam incident beam of 10 keV X-rays and imaging the scattered photons with a liquid-nitrogen-cooled charge-coupled device camera at a distance of 75 cm from the sample. A 500-μm Pb wire was used as beamstop.

Results and Discussion

Characteristics of Block Copolymers. Amphiphilic block copolymers are sequences of blocks with controlled molecular weights and distribution and covalently linked together at the interface. When the dissimilarity between each block is sufficiently large, which is determined by the Flory−Huggins interaction parameter (χ) and overall degree of polymerization (N), block copoly-

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mers microphase-separate into an ordered structure.[11] Depending on the volume fraction (*f*) between the blocks, a variety of morphologies can be formed, and the domain size can be tuned on the order of several to 100 nm by synthesizing blocks with different molecular weights. This makes it appealing to use block copolymers as direct agents to form ordered mesostructures in organosilicates. However, a block copolymer with high order–disorder transition temperature (ODT) will be preferred as a template to maintain ordered structures during the subsequent heat treatment in sol–gel process. Poly(ethylene oxide) (PEO) is known to be soluble in water and alcohol, and block copolymers containing PEO blocks have been extensively studied as nonionic surfactants to direct the self-organization of sol–gel.[3,7,10] Block copolymers of PB-*b*-PEO were chosen in our system as templates to study the mechanism of self-organization in hydrophobic organosilicates. The low glass transition temperature of PB block provides high chain mobility to rapidly self-organize during solvent evaporation and before the structure is fixed at a higher temperature, due to the curing of organosilicates. Second, the relatively high ODT of this block copolymer makes it possible to maintain the ordered structures in these heat treatments. Small-angle X-ray scattering (SAXS) experiments showed that the PB-*b*-PEO had PB chains packed in hexagonal arrays in the PEO matrix when heated above 60 °C. In contrast, F88 (from BASF), a triblock copolymer of poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) with $\overline{Mn}$ of 12 000 and 80 wt % PEO, became isotropic at this temperature and the organosilicates templated by F88 were always found disordered.

Precursors of Organosilicates. Methyl silsequioxane (MSQ) is a hydrophobic organosilicate because of the presence of CH_3 group. Its sol–gel precursor, methyltriethoxysilane (MTES), however, is hydrophilic, and is used here as a model compound to investigate the self-assembly process in hydrophobic organosilcates directed by block copolymers. Disordered spherical structures are observed by TEM in the cured composites of PB-*b*-PEO and MTES at different molar ratios. We believe that disordering occurs during the curing process when MTES changes its nature at the polymer–sol interface. Initially, the MTES sol is hydrophilic and thus it prefers to stay close to the PEO domains. When the polycondensation of silanol groups in MTES proceeds during curing, the film becomes increasingly hydrophobic. Therefore, the PEO blocks will be repelled from the methyl silsequioxane, which now prefers to stay close to the PB domains. This change at interface perturbs the self-organization process, resulting in disordered spherical structures. To control the chemistry at interface, (3-glycidyoxypropyl)-trimethoxysilane (GPTS) with epoxy groups is introduced as a hydrophilic organosilicate, which does not change its nature during curing and has been used to anchor the PEO blocks.[10] Depending on the reaction rates between alkoxysilane moieties, self- or cross-condensation between MTES and GPTS would occur.[12] Here, cross-condensation will be preferred so that amphiphilic organosilicates with hydrophobic CH_3 head and hydrophilic epoxy tail can be formed to maintain the polymer–sol interaction through the curing process (Scheme 1). Previously, Prabakar et al. found that the cross-condensation products were formed in all alkyltriethoxysilane/tetraethoxysilane (RTES/TEOS, R = methyl, ethyl, phenyl) systems in the early stages of the reaction.[13] Although we do not have direct evidence of cross-condensation in our system, we believe cross-condensation has happened because disordered structures are obtained if we hydrolyze and self-condense MTES first before the addition of GPTS, or if the addition of GPTS is less than 30 mol % of the total sol. When more than 30 mol % of GPTS is added into MTES, the interface is preserved and a hexagonal lattice (diameter of each cylinder ca. 13 nm) is observed by TEM (Figure 1) provided that the mixing molar ration between PEO and silicates (MTES– GPTS) ranges from $^{2}/_{1}$ to $^{1}/_{2}$ and they are cured at 130 °C. Samples that are heated at 70 °C for solvent evaporation also show ordered structures before the curing of the organosilicates. This is consistent with the assumption that cross-condensation is favored to form an amphiphilic organosilicates precursor, which is critical to the formation of ordered mesostructures. Currently, the kinetics of hydrolysis and condensation is under study by ^{29}Si NMR. When the molar ratio between PEO and sol is increased to $^{1}/_{3}$, disordered “wormlike” micelles are formed. In the following discussion, ordered structures are prepared by mixing PEO blocks with sol (50:50 MTES/GPTS) in a molar ratio of $^{1}/_{2}$ and cured at 130 °C.

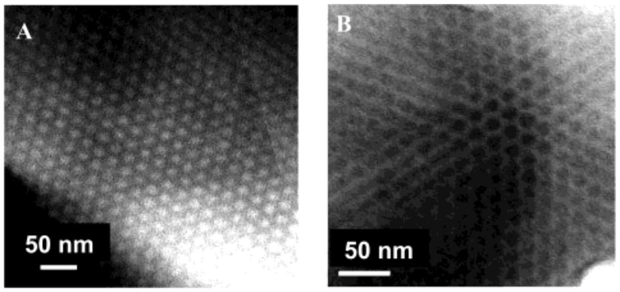
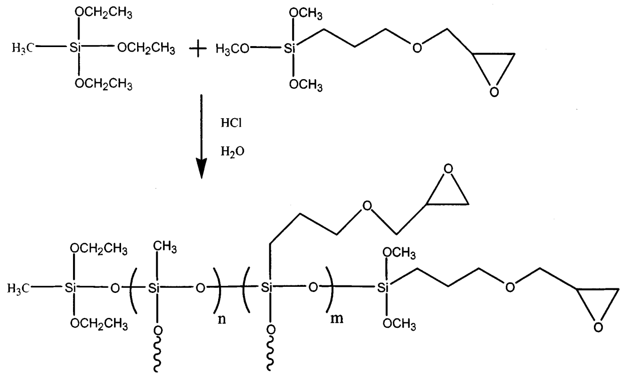


Figure 1. Transmission electron micrographs (TEM) of the nanocomposites from samples (A) as prepared, and (B) stained by OsO_4. The scale bar is 50 nm.

Scheme 1. Structure of the Amphiphilic Organosilicate Precursors



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Phase Model. As seen in Figure 1A, the block copolymers appear brighter as the inner phase in an as-prepared sample due to their smaller mass than that of silicates. When the sample is stained by OsO_4, which preferentially stains double bonds in poly(butadiene), the minor phase becomes darker than the matrix (Figure 1B). We note that the size is slightly smaller than that in Figure 1A, indicating that a core−shell structure is formed in the nanocomposites with a PB interior. Thus, GPTS and PEO must be located at the polymer−silicate interface to minimize the interfacial energy. However, the interaction between PEO and GPTS at the molecular level remains to be answered, whether PEO and GPTS are microphase separated or interpenetrated. Depending on the specific interaction between PEO block and the matrix, two kinds of phase models have been proposed. In the system of aluminosilicated/poly(isoprene-*b*-ethylene oxide), a “two-phase” model was suggested that PEO notably penetrated in aluminosilicates.[14] In the system of epoxy thermosets/poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide), the PEO block was rejected from the thermoset network during curing, resulting in a “three-phase” structure.[15] Here, if the PEO is completely dissolved in the organosilicates, the mobility of polymer chains is greatly reduced. This strong interaction between polymers and silicates will be preferred in certain photonic applications, such as nonlinear optical (NLO) materials, where high chemical and thermal stability of dye molecules in the silicates is important to device shelf life.[16] On the other hand, the intimate mixing makes it difficult to remove the polymer templates afterward to generate nanoporous structures. In the latter case, a sharp interface between the PEO block and organosilicates will be advantageous.

Previously we have used 2D exchange NMR to identify the polymer near the methyl silsesquioxane (MSQ) interface in composites for ultralow dielectric constant applications.[17] However, the results are ambiguous when incorporating GPTS in the matrix because some of the GPTS peaks overlap with the ethylene oxide peaks (Figure 2). This spectrum was gathered with 4 kHz magic angle spinning (MAS) and did not show a well-resolved peak for the methyl protons of MSQ. The strongest cross-peak is between the butadiene peaks at 5.5 and 2.1 ppm. A weak cross-peak can be observed between the butadiene peaks and the ethylene oxide peak at 3.6 ppm. Another weak peak between the GPTS peak at 2.7 ppm and the ethylene oxide peak at 3.6 ppm is also observed. This could arise either from magnetization exchange between the GPTS and the ethylene oxide or from magnetization exchange between GPTS protons.

Proton spin diffusion is a useful tool to map out the close proximity of neighboring polymer domains. By taking advantage of the difference in chain dynamics for the matrix and the polymer, we used the Goldman−Shen experiment[18] to probe the structure of the polymers at the interface. We monitored proton spin diffusion in the composite by measuring the intensities of the PB, PEO, and GPTS peaks as a function of the spin diffusion delay time τ_m in solid-state proton NMR. Figure 3 shows a plot of the decay as a function of the delay time for the ethylene oxide peak at 3.6 ppm, the butadiene peak at 5.5 ppm, and the GPTS peak at 2.7 ppm. The ethylene oxide peak shows the largest effect, and it decays by 40% as the spin diffusion delay time increases. The butadiene peak shows the smallest effect and decreases by only 10% over the delay time. The GPTS peak first decays quickly to 80% of the equilibrium value and then increases at longer delay times. This is mostly consistent with a core−shell “three-phase” structure with PB wrapped inside (Figure 4). Because the PB is surrounded by PEO, which is shielded from the MTES by a layer of GPTS, it loses magnetization much more slowly. GPTS is nearest the rigid

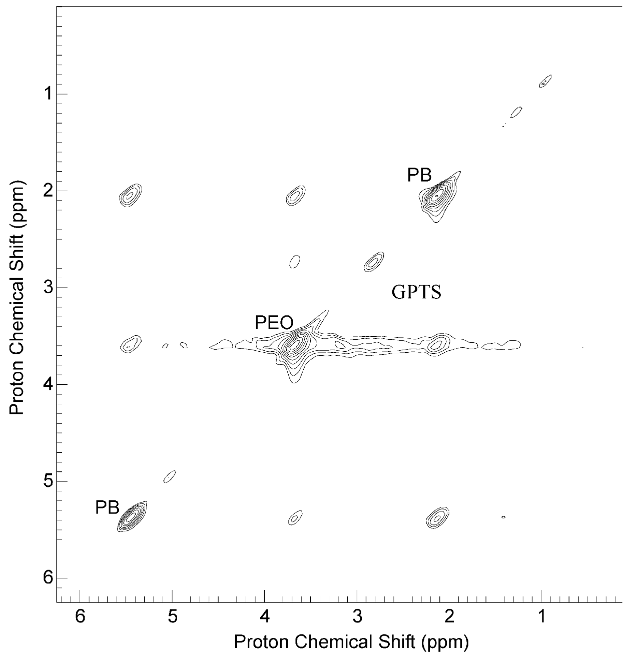

Figure 2. 2D exchange NMR of the nanocomposite. The sample was prepared from a 1:2 ratio of block copolymer to silicates (GPTS/MTES = 50:50).

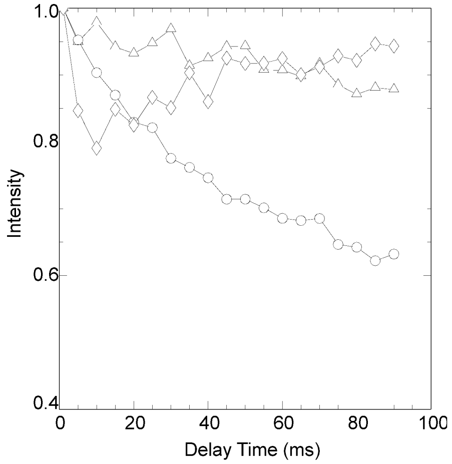

Figure 3. Spin diffusion in the nanocomposite. The sample was prepared from a 1:2 ratio of block copolymer to silicates (GPTS/MTES = 50:50): (○) ethylene oxide peak at 3.6 ppm, (△) butadiene peak at 5.5 ppm, and (◇) GPTS peak at 2.7 ppm.

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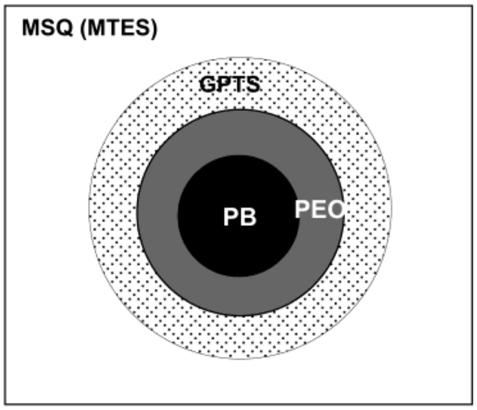

Figure 4. Schematic structure of the phase behavior of PB-*b*-PEO/organosilicate nanocomposite.

MTES, magnetization is quickly exchanged between the MTES and the GPTS, which accounts for the rapid decrease in GPTS intensity at short delay times. After the GPTS intensity is partially diminished, it increases because of magnetization exchange with the PEO block, while PEO steadily loses magnetization to the GPTS interface.

This core−shell "three-phase" model is further supported by DSC results. A small yet distinct melting point at 61 °C is clearly present, which suggests that the PEO is expelled from the organosilicates for crystallization. Similar results have been observed by Bates and coworkers in their "three-phase" system.[15]

Role of Aluminum *sec*-Butoxide [$Al(OBu^s)_3$]. To further understand whether we can chemically modify the polymer−silicates interface and possibly form a "two-phase" structure, we study the role of aluminum *sec*-butoxide [$Al(OBu^s)_3$]. $Al(OBu^s)_3$ has been used as a catalyst for epoxy ring opening reaction in GPTS and formation of ordered aluminosilicates.[10,19] The ring-opening products, oligo(ethylene oxide) derivatives, allow deep penetration of aluminosilicates into PEO blocks, resulting in intimate mixing. In ^{13}C cross-polarization magic angle spinning (CP MAS) NMR, we observed two peaks at 42 and 49 ppm from the epoxy ring in the composites without addition of $Al(OBu^s)_3$, suggesting that the epoxy ring is intact in the hydrolysis conditions in our experiment (Figure 5). When 2 mol % $Al(OBu^s)_3$ was introduced, the two sharp epoxy peaks disappeared, resulting in several broad peaks in the range of 53−80 ppm from the ring opening reactions. We anticipate that addition of $Al(OBu^s)_3$ to the sol may form a "2-phase" model as shown in the literature.[10] Instead, we found that the timing of adding $Al(OBu^s)_3$ was important in our system. If we open the epoxy ring and hydrolyze GPTS before addition of MTES, disordered structures are always obtained, irrespective to the molar ratio between PEO and sol. This suggests that the self-condensation of GPTS may be dominant and the interface between block copolymers and silicates may not be homogeneous, and that PEO blocks are randomly swelled by GPTS or MTES. When the condensation proceeds further and MTES becomes hydrophobic, PEO are expelled from methyl silisequioxane domain, resulting in disordered structures. If GPTS and MTES are first mixed, hydrolyzed, and cross-condensed, the addition of $Al(OBu^s)_3$ does not interfere with the nature of the interface. However, poorer contrast between polymers and silicates in unstained samples seen in the TEM image suggests that PEO may dissolve into GPTS. Again, it shows that the formation of an amphiphilic organosilicate precursor is critical in the initial stage.

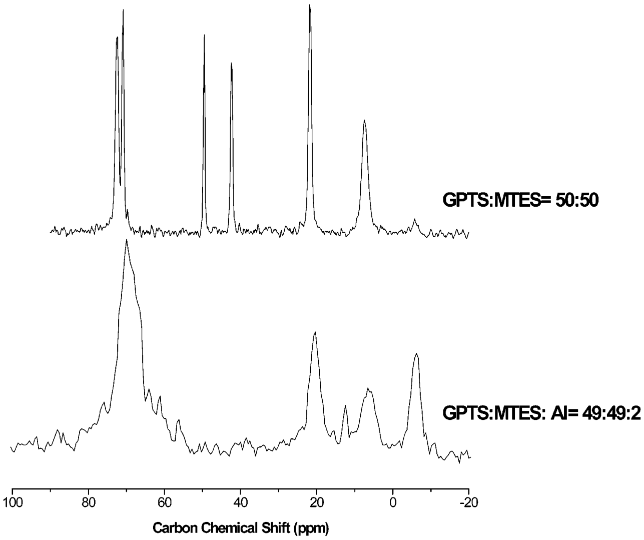

Figure 5. ^{13}C CP MAS NMR spectra of the composites with and without addition of $Al(OBu^s)_3$ to the sol.

Orientation of the Cylinders. Finally, we studied the orientation of cylinders in these thick films, which is induced by solvent casting. Films were microtomed from different directions, along the film plane vs along the film thickness. For samples microtomed along the film plane, a lamellar structure was observed by TEM and only rings of scattering were observed in SAXS with the incident beam along the surface normal of the cast film (Figure 6A). The isotropic pattern from SAXS suggests that the lamellae are parallel to the film surface. In comparison, a well-defined hexagonal lattice was found in TEM for samples microtomed along the film thickness. The diffraction pattern obtained from SAXS sampled a much larger area than that in TEM, and consisted of sharp crystalline reflections with distorted hexagonal symmetry (Figure 6B). Because the size of ordered region is small compared to the X-ray extinction distance that is typically in micron size, the distortion may be a diffraction artifact due to the nonperfect sample orientation with respect to the incident X-ray beam. Results from both TEM and SAXS imply that the large-scale orientation of the film is dominated by the solvent-casting process, which macroscopically induced the alignment of the long axes of the cylinders lying in the plane of the sample.

Conclusions

Hydrophobic organosilicates with periodic nanostructures have been formed using block copolymers of poly(butadiene-*b*-ethylene oxide) (PB-*b*-PEO) as templates. We find that the self-organization and phase behaviors of the nanocomposites are very sensitive to parameters such as the morphology and order−disorder transition temperature of block copolymers, the nature of organosilicates before and after curing, the links and interaction between block copolymers and organosilicates at

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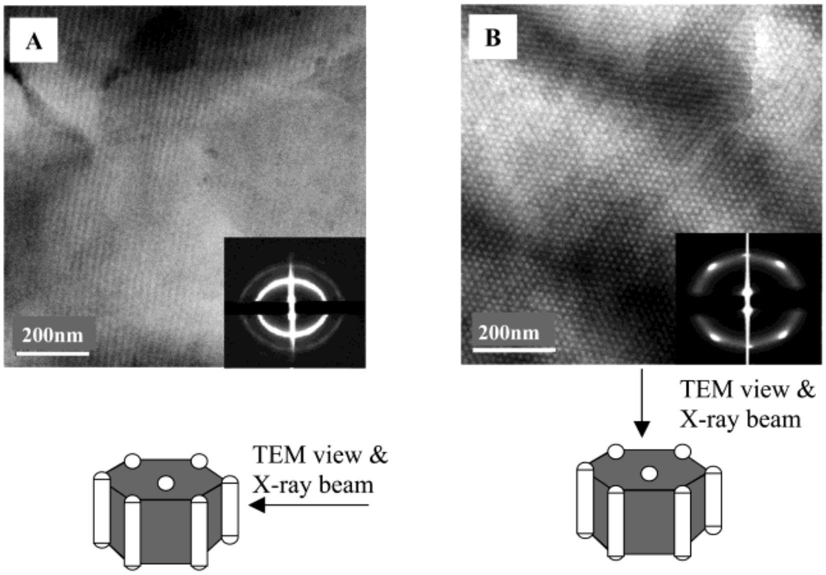

Figure 6. TEM images from nanocomposites microtomed from different directions. Inset: two-dimensional SAXS pattern obtained with the incident radiation directed to the same direction as the TEM view. The bright spots are crystalline reflections from the ordered structure. The white vertical streak and dark horizontal band are the image artifact and the Pb-wire beamstop, respectively.

the interface, and the accessibility of organosilicates to polymer domains. A hydrophilic organosilicate precursor, (3-glycidyoxypropyl)-trimethoxysilane (GPTS), is introduced in methyl silsequioxane to form an amphiphilic organosilicate precursor at initial stage and preserve the polymer−silicate interface during curing. To minimize the interfacial energy, PEO block and GPTS stay at the interface. With detailed study of the templating mechanism, we have created ordered nanostructures in hydrophobic organosilicates, which will broaden the applications of organic−inorganic hybrid materials to many promising fields. The concept of using amphiphilic organosilicate provides flexibility to incorporate novel functionalities in the matrix for advanced materials.

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