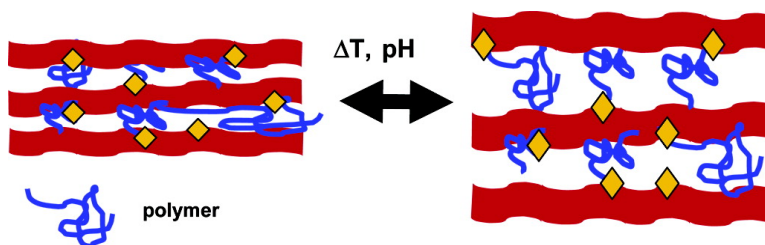Communication

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Self-Assembly of an Environmentally Responsive Polymer/Silica Nanocomposite

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As we have learned from natural materials such as seashells, layered hard (inorganic)/soft (organic) materials may be simultaneously hard and tough and strong. However, it has proven difficult to organize and react inorganic and organic precursors efficiently and controllably on the nanoscale. Recently, we demonstrated that evaporation-induced self-assembly (EISA) can organize hydrophilic, inorganic and hydrophobic, organic precursors into ordered layered nanostructures.[1] Starting with a solution of oligosilicic acid, surfactant, alkyl methacrylate monomers, cross-linkers, and initiators in an ethanol/water solvent, preferential ethanol evaporation induces the formation of micelles and the partitioning of the organic constituents into the hydrophobic interiors, while organizing oligosilicic acid species around the hydrophilic micellar exteriors.[2] Continued evaporation results in the self-assembly of hybrid (silica−surfactant−organic) mesophases, simultaneously positioning the inorganic and organic precursors into the desired nanolaminated form. Here, we extend this approach to form films with environmentally responsive nanostructures.

Polymers such as poly(methacrylates) and poly(*N*-isopropylacrylamide) (PNIPAM) show a pronounced response toward changes in pH and temperature, respectively.[3] In water, PNIPAM exhibits a phase transition at the lower critical solution temperature (LCST) of approximately 32 °C.[3] This temperature can be controlled through random copolymerization of NIPAM with methacrylic acid.[4] Below the LCST, the hydrogel incorporates water and swells, whereas water release at higher temperatures causes shrinkage. The (de)swelling of these films upon change of pH or temperature is of interest for controlled release of molecules or for membranes with switchable permeabilities.

PNIPAM and random NIPAM/acrylate copolymers are normally prepared by solution polymerization resulting in mechanically fragile bulk gels.[3,4] Thermoresponsive poly(acrylamides) were incorporated into lamellar clay-nanocomposites, but the thermoresponsive behavior was maintained only with low clay loadings or was less pronounced as compared to that of the bulk polymer.[5,6] Liang et al. incorporated larger amounts of PNIPAM into montmorillonite, but the mesostructure was almost lost upon swelling/deswelling.[7] Here, we report the incorporation of PNIPAM or its copolymers with dodecyl methacrylate (DM) into mesoscopically ordered nanocomposite thin films with silica contents of up to 80%.

Nanocomposite films were prepared by evaporation-induced self-assembly followed by polymerization and washing as depicted in Scheme 1. EISA begins with a homogeneous solution of silicic acid,[1] monomers (NIPAM and/or dodecyl methacrylate), surfactant (cetyltrimethylammonium bromide, CTAB), coupling agent (trimethoxy(7-octen-1-yl)silane, 7-OTS, featuring an alkoxysilane headgroup and a polymerizable double bond), and thermal initiator, 1,1′-azobis(1-cyclohexanecarbonitrile) (ACHN). Initiators such as per-

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Scheme 1. Preparation of Environmentally Responsive Nanocomposite Thin Films*a*
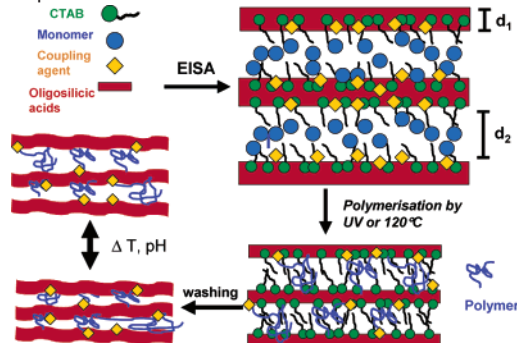
a For clarity, the initiator is omitted.

sulfates were incompatible with the procedure. The molar ratio of reactants was 1 TEOS:22 EtOH:5 H_2O:0.004 HCl:0.21 CTAB:0.16 7-OTS:0.32 DM:(0−0.14) NIPAM:0.02 initiator. Solutions were sonicated and filtered prior to dip-coating (in dry N_2) on silicon substrates. Solvent evaporation (during dip- or spin-coating or aerosol processing) drives the self-assembly of a lamellar mesostructure composed of hundreds of alternating layers of silicic acid and organic species (monomers, coupling agents, initiators, and surfactants). A heat treatment (120 °C for 3 h in N_2) is then employed to initiate the free-radical polymerization of the confined monomers and promote the condensation of the silica framework. Finally, the films are washed successively in ethanol and acetone to remove the surfactant and any unreacted monomers. As compared to ref 1, the procedure was modified to incorporate NIPAM and to develop its thermal responsiveness.

Solid-state ^{13}C NMR was used to determine the extents of organic polymerization and interfacial bonding. Figure 1 shows MAS solid-state ^{13}C NMR spectra of films containing PNIPAM, before (A) and after polymerization (B). The double-bond conversion was calculated using the integral intensity of the CTAB/7-OTS hydrocarbon chain peaks between 0 and 40 ppm (HC) as an internal standard. About 15−25% of the double bonds of 7-OTS are converted, while the decrease of the isopropyl signal **7** suggests partial sublimation (about 30%) of NIPAM. The shift in the carbonyl peak **6** upon polymerization indicates that approximately 80% of the remaining NIPAM is polymerized; DM shows a comparable reactivity.[1] A differentiation between PNIPAM and PDM in the random copolymers (see Supporting Information) is inhibited by the overlap in their ^{13}C spectra and by signal broadening.[8] Therefore, the exact copolymer composition in the films is unknown. Nevertheless, NMR and TGA results prove that NIPAM and DM are polymerized and that random copolymers are formed, further indicated by ^{13}C NMR on bulk samples. Without 7-OTS, the polymers are washed out, suggesting that it serves to link the polymers to silica. The final polymer content is about 20 wt %. ^{13}C NMR data for a washed sample are shown in the Supporting Information.
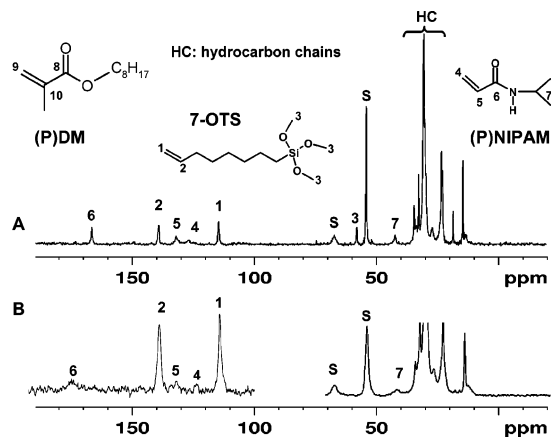
Figure 1. ^{13}C solid-state MAS NMR of films prepared with NIPAM, before (A) and after heat treatment applied for polymerization (B, magnified). Carbon atoms next to the ammonium group of CTAB cause the signals S.
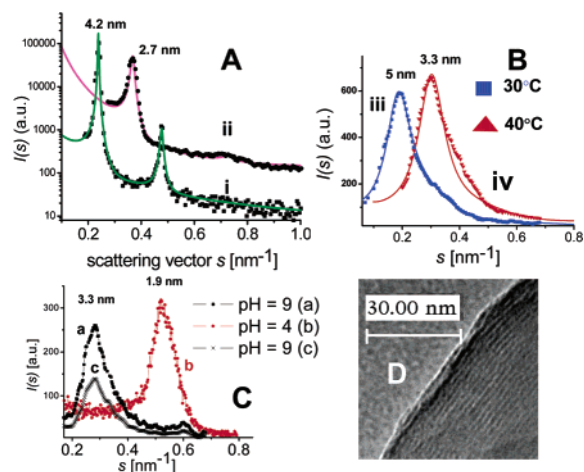

Figure 2. SAXS data of a film prepared with NIPAM and DM before (A,i) and after (A,ii) heat treatment, and in water at 30 °C (B,iii) and 40 °C (B,iv). Solid lines: fit based on ref 9. (C) pH sensitivity of PDM films. Curve c is scaled down by a factor of 2 for better visualization. (D) TEM micrograph of the nanocomposite film corresponding to Figure 2A,ii.

The mesostructure and the environmental responsiveness were studied by small-angle X-ray scattering (SAXS). Figure 2A shows SAXS data, measured in symmetric reflection, of a film prepared with NIPAM and DM, prior to (i) and after (ii) heat treatment for polymerization ($s = 2 \sin \theta/\lambda$, 2θ = scattering angle, $\lambda = 0.1542$ nm). The thicknesses of films i and ii are ca. 500 and 300 nm, respectively. Curve i contains two pronounced interference maxima, representing the (001) and (002) reflections of a lamellar mesostructure with a d spacing of $d_{001} = 4.2$ nm. Heat treatment results in a shift of the (001) reflection (ii), corresponding to a decrease in d_{001} to 2.7 nm. The average thicknesses d_1 and d_2 of the organic/inorganic layer constituting the lamellar mesostructure as well as their variances σ_1 and σ_2 were evaluated using a recently reported approach.[9] Assuming that the lamellae are oriented parallel to the substrate (as confirmed by 2D SAXS) for (i), we obtain $d_1 = 1.25$ nm and $d_2 = 2.94$ nm ($\sigma_1 = 0.15$ nm, $\sigma_2 = 0.3$ nm), which can be related to the silica and the organic layer, respectively, based on TGA. The values for (ii) ($d_1 = 0.7$ nm, $d_2 = 2$ nm, $\sigma_1 = 0.1$ nm, $\sigma_2 = 0.2$ nm) indicate that the heat treatment causes shrinkage of both the siliceous layers (loss of water, siloxane condensation) and the organic layers (polymerization and solvent evaporation), without significant loss in order. Figure 2D shows a TEM micrograph, corresponding to the sample in Figure 1B and Figure 2,ii, confirming an average d-spacing of ca. 3 nm for the heat treated (polymerized) sample. To study the thermoresponsive behavior, the washed film

was immersed in water at temperatures above and below the LCST. In water, a pronounced interference maximum is observed (Figure 2B), indicating the presence of the mesostructure but also a loss in perfection. Temperature change induces a significant shift of the lamellar d spacing from $d = 3.3$ nm (40 °C) to $d = 5$ nm (30 °C). Because a considerable increase in d only occurred below ca. 30 $\pm$ 3 °C, this swelling/deswelling must be attributed to the phase transition of the confined NIPAM/DM copolymers. The shape similarity of the reflections in Figure 2,iii and iv suggests a homogeneous swelling of the organic layer in the lamellar nanocomposite. The swelling/deswelling process is reversible and takes ca. 5 h, which is comparable to that of bulk systems.[3,4,7] While pure PNIPAM shows a LCST at 32 °C, the thermoresponse spans a wider temperature range, 31 $\pm$ 4 °C, for our films and for other PNIPAM nanocomposites possibly due to a wider molecular weight distribution.[7] Heating and cooling over a larger temperature range, for example, between 10 and 50 °C, rather than 30−40 °C, increased the magnitude of the swelling/deswelling response. Because of the substantial width of the SAXS reflections, the structural parameters obtained from (2,iii) and (2,iv) have a lower precision. We obtain $d_1 \approx 1$ nm, $d_2 \approx 3.7$ nm (2,iii) and $d_1 \approx 1$ nm, $d_2 \approx 2$ nm (2,iv). It is noteworthy that the parameters show that only the polymer phase (d_2) swells, while the rigid silica phase (d_1) does not change in thickness. Nanocomposite films containing PDM were studied with respect to their pH sensitivity (Figure 2C). Poly(methacrylates) are hydrogels showing pronounced changes in chain conformation upon (de)protonation of the carboxyl groups. Starting with pH = 9 (Figure 2c, curve a, $d = 3.3$ nm), the SAXS patterns show a significant peak shift upon exposure of the film to pH = 4 for 5 h (Figure 2c, curve b, $d = 1.9$ nm), probably due to partial deesterification. Changing the pH back to 9 reestablishes the original SAXS profile (Figure 2c, curve c). As for NIPAM nanocomposites, d_2 changes, while d_1 remains almost unchanged, and the swelling/deswelling was reversible over several cycles. We note that these films, prepared without NIPAM, do not show (de)swelling upon temperature change, confirming that the thermoresponse described above is attributable to PNIPAM.

To the best of our knowledge, these films represent the first example of an ordered environmentally responsive composite nanostructure. Future work will address details of the polymerization, for example, the copolymer composition and molecular weight, and the influence of swelling/deswelling on permeability and release.

Supporting Information Available: SAXS, NMR/TGA data(PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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