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. This temperature can be controlled through random copolymerization of PNIPAM with methacrylic acid.4 Below the LCST, the hydrogel incorporates water and swells, whereas water release at higher temperatures causes shrinkage. The degree of 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, 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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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 \( \bar{d} = 3.3 \) nm (40 °C) to \( \bar{d} = 5 \) nm (30 °C). Because a considerable increase in \( \bar{d} \) only occurred below ca. 30 ± 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.\(^4\,5\,6\) While pure PNPIM shows a LCST at 32 °C, the thermoresponsiveness spans a wider temperature range, 31 ± 4 °C, for our films and for other PNPIM 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 \( \text{pH} = 9 \) (Figure 2c, curve a, \( d = 3.3 \) nm), the SAXS patterns show a significant peak shift upon exposure of the film to \( \text{pH} = 4 \) for 5 h (Figure 2c, curve b, \( d = 1.9 \) nm), probably due to partial deestherification. 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 thermoresponsive behavior described above is attributable to PNPIM.

To the best of our knowledge, these films represent the first example of an ordered environmentally responsive composite nanomaterial. 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.

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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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