Supporting Information

Facile formulation of high density well-ordered nanoparticle-copolymer nanocomposites

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Experimental methods

Small-angle X-ray scattering (SAXS) profiles were acquired in transmission on a Nanostar-U instrument (Bruker AXS) with a copper anode source, Goebel mirrors and a HiSTAR 2-D detector giving access to scattering vector q values from 0.1 to 2 nm^{-1}. The resulting 2-D images were found to be isotropic, and the data were azimuthaly averaged to yield scattering curves of the intensity corrected from experimental background versus $q = (4\pi/\lambda) \sin \theta$, where λ = 0.154 nm is the wavelength of the Cu Kα radiation and θ is half the scattering angle. The SAXS intensities I(q) present peaks corresponding to the lattice structure factor $S(q)$, and allow extraction of the interdomain spacing *d*.

Freeze-fracture replica preparation (FF) was performed by first pressing a drop of the sample between the two copper planchettes of a sandwich holder, then freezing it by quickly plunging the holder into liquid propane at the temperature of liquid nitrogen. The freezing step must be fast in order to vitrify the sample and avoid structure disruption due to crystallization. Frozen samples were then fractured by mechanical separation of the two planchettes at a temperature of -150°C and a pressure of the order of 10^{-6} mBar in a BAF 300 Balzers apparatus. The freshly fractured surface was shadowed by the deposition of platinum at an angle of 45° and the replica was reinforced by carbon deposition at an angle of 90°. The copper planchettes were then dissolved in chromerge (a mixture of sulfuric acid, chromic acid and water). The detached replicas were rinsed once with hydrofluoric acid, then several times with basic water and then left in tetrahydrofurane for 4 days before being rinsed again in water. This long process was proven necessary to remove properly the silica particles and the copolymer. The replicas were finally collected on 200μm-mesh copper grids and dried before TEM imaging.

Transmission electron microscopy (TEM) was performed with a JEOL 1200 EX TEM at 100 kV. Solid samples were prepared as unstained films, embedded in epoxy cured at 50 °C. Sections (70-100 nm) were obtained at room temperature with an Ultracut E ultramicrotome (Reichert-Jung) and were examined as such.

Materials

The PS-b-PAA copolymer was synthesized as described before[1] using the MADIX controlled radical polymerization technique[2]. In short, a precursor poly(styrene)-block-poly(ethyl acrylate) was synthesized in the presence of a xanthate control agent, in aqueous emulsion with a concentration of polymer latexes close to 30% (w/w) at the end of the synthesis. The ethyl acrylate units were hydrolyzed to sodium acrylate with two molar equivalents of NaOH in water at 95°C. The copolymers were finally purified as poly(styrene)-b-poly(acrylic acid) and freeze-dried. The composition and molecular mass of the copolymers were determined by size exclusion chromatography (SEC) and nuclear magnetic resonance (H1 NMR). The poly(styrene) block has a mass of Mn=7890 g/mol, and the poly(acrylic acid) block a mass of Mn=6952 g/mol.

Colloidal silica (LUDOX LS-30) was purchased from Aldrich and was cleaned by dialysis against milli-Q water using cellulose Spectra/pore membranes of MWCO 6-8000 g.mol^{-1}. The particles bear negative charges on their surface, which ensures their colloidal stability. The counter-ions are Na$^+$. Analysis of the SAXS data in terms of a sphere form factor allowed to determine a Gaussian size distribution of mean radius R_0=7.7 nm and width σ=1.2 nm.

Cerium oxide (CeO2) nanocrystals, dispersed in water and stabilized by a layer of citrate, were kindly provided by Rhodia. They were cleaned by dialysis, following the same procedure as the silica(see above). Analysis of the SAXS

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data in terms of a sphere form factor allowed to determine a Gaussian size distribution of mean radius R_0=3.5 nm and width σ=0.6 nm.

Structural analyses of the pure copolymer system

Morphologies of the melt phases – Solid films 0.2-0.4 mm thick were cast over a few days from 15 wt % solutions in THF in poly(tetrafluoroethylene) molds and then dried overnight under vacuum at room temperature to remove traces of THF. These films were studied by both transmission electron microscopy and small-angle X-ray scattering. The SAXS pattern shows up to six Bragg peaks, evidencing a high degree of long-range order (results not shown).

Swelling with water –The solid films described before were grounded as a coarse powder and dispersed in water at fixed weight fraction w and with an addition of sodium hydroxide so as to reach the desired value of pH. Different pH values were investigated between 4 and 8.2. Due to the osmotic effect of the counter-ions associated with the ionization of the brush chain segments[3], the increase of pH induces an increase of the lamellar period and of the (water + PAA) layer thickness. When the pH is varied from 4 to 8.2, the lamellar period varies from 53 to 94 nm, and the (water + PAA) layer thickness varies from 31 to 71 nm, as measured by SAXS (results shown on Figure 1).

Analysis of the amount of ceria nanoparticles introduced in the lamellar phase

Calibration SAXS curves – The SAXS signals I(q) of dispersions of ceria nanoparticles at 0.5, 1, 2 and 3 vol.% were acquired and normalized by the thickness and transmission of the samples. The values of the scattered intensity at q=0.7 nm^{-1} and q=1 nm^{-1} were both found proportional to the nanoparticle volume fraction, showing that the signal is fully dominated by the form factor of the nanocrystals.

Nanocomposites analysis – Swollen PS-b-PAA lamellar phases at pH values of 4.9, 6.0, 7.8 and 8.2 were left for one week in equilibrium with excess dispersions of ceria nanocrystals at the same pH (adjusted with addition of NaOH). The SAXS signals I(q) of the lamellar phases were then acquired and normalized. They were found to be dominated by the form factor of the nanocrystals. The values of the scattered intensity at q=0.7 nm^{-1} and q=1 nm^{-1} were used, in comparison with the calibration curves, to extract the concentration of nanoparticles within the lamellar phase.
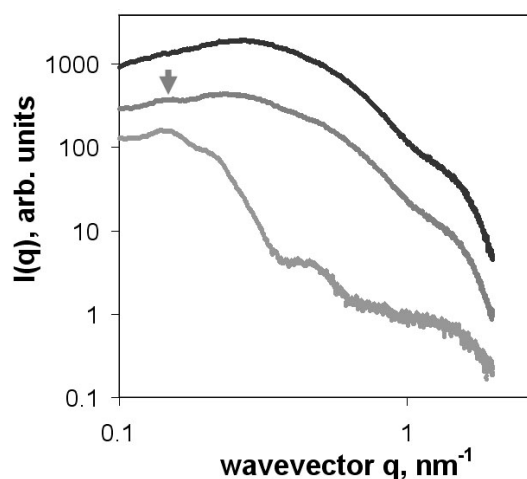

Figure S1. SAXS scattered intensity curves I(q) of the swollen lamellar phase dispersed in water at pH 6 (bottom curve), of the swollen lamellar phase mixed with a dispersion of ceria nanocrystals at pH 6 (middle curve) and of a dispersion of ceria nanocrystals at pH 6 and 2 vol.% (upper curve). The curves are vertically shifted for clarity. The two uppermost curves are dominated by the form factor signal of the nanocrystals, except at very small q, where a small bump corresponding to the lamellar structure factor is visible in the mixed system curve (noted by an arrow). Quantitative analysis of the middle curve allows to extract the particle volume fraction in the lamellar phase (here 1.7%).

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[3] Bendejacq, D.; Ponsinet V.; Joanicot, M. *Eur. Phys. J.* E, **2004**, *13*, 3