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‘Cross-linking of Cationic Block Copolymer Micelles by Silica Deposition’

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Experimental

Materials.

2-(Dimethylamino)ethyl methacrylate (DMA) and 2-(diisopropylamino)ethyl methacrylate) (DPA) were purchased from Aldrich and Scientific Polymer Products (USA), respectively. Tetramethyl orthosilicate (TMOS), methyl iodide (MeI), 1,2-bis-(2-iodoethoxy)ethane (BIEE), $HAuCl_4$, $NaBH_4$, NaOH, HCl, NaCl, methanol and ethanol were all purchased from Aldrich and were used as received. De-ionized water was used in all experiments.

1. Preparation of the PDMA-PDPA diblock copolymer, micelles and SCL micelles

The $PDPA_{23}$-$PDMA_{68}$ diblock copolymer was synthesized by sequential monomer addition (DMA polymerized first) in anhydrous THF using group transfer polymerization, as described previously.[13] Gel permeation chromatography analysis indicated an M_n of 18,000 and an M_w/M_n of 1.08 using a series of near-monodisperse poly(methyl methacrylate) calibration standards. The mean degrees of polymerization of the PDPA and PDMA blocks were estimated to be 23 and 68, respectively, using ^{1}H NMR spectroscopy. Partial quaternization of the PDMA block (targeting a degree of quaternization of either 30 %, 50 % or 100 %) using MeI was conducted in THF for 24 h, as described in our previous publication.[13c]

Noncross-linked micelles of the $PDPA_{23}$-$PDMA_{68}$ diblock copolymer (degree of quaternization = 0 %) were prepared by molecular dissolution at pH 2, followed by adjusting the solution pH to pH 7.2 using NaOH. Dynamic light scattering (DLS) studies at 25^{o}C indicated an intensity-average micelle diameter of 37 nm for a 0.25 wt. % copolymer micelle solution at pH 7.2.

Noncross-linked micelles prepared using either 50 % or 100 % quaternized $PDPA_{23}$-$PDMA_{68}$ diblock copolymers were also prepared by pH adjustment, as described above. DLS studies conducted at pH 7.2 indicated intensity-average diameters of 29 nm and 26 nm for 0.25 wt. % aqueous solutions of 50 % and 100 % quaternized copolymer micelles, respectively.

Shell cross-linking of the coronal PDMA chains was achieved by adding a bifunctional quaternizing agent, BIEE (0.15 moles per DMA residue for a target degree of cross-linking of 30 %) to a 0.25 % $PDPA_{23}$-$PDMA_{68}$ copolymer micelle solution at pH 7.2.[14] Shell cross-linking was carried out at 25°C for at least 72 h. After shell cross-linking, DLS studies indicated an intensity-average diameter of 32 nm, and TEM studies suggested a number-average diameter of 26 nm for the dried SCL micelles (data not shown). On adjusting the aqueous SCL micelle solution to pH 2, DLS studies indicated an intensity-average diameter of 45 nm due to swelling of the SCL micelles. This experiment also confirmed successful shell cross-linking, since the noncross-linked micelles simply dissociated at low pH to form a molecular solution. This is because the PDPA chains are highly protonated, and hence no longer hydrophobic, at low pH. In addition, SCL micelles prepared using the 50 % quaternized copolymer had an intensity-average diameter of 37 nm at pH 7.2 as indicated by DLS.

2. Synthesis of the hybrid copolymer-silica particles

The following protocol is typical. TMOS (1.0 mL) was added to 2.0 mL of a 0.25 wt.% aqueous solution of $PDPA_{23}$-$PDMA_{68}$ diblock copolymer micelles (intensity-average micelle diameter = 29 nm at pH 7.2, as indicated by DLS) in which the PDMA chains had been 50 % quaternized using methyl iodide. TMOS hydrolysis within this initially heterogeneous aqueous copolymer micelle solution was allowed to continue at 20°C for 20 min. with continuous stirring. Similar syntheses were conducted using either an unquaternized or 100 % quaternized $PDPA_{23}$-$PDMA_{68}$ diblock copolymer, using shell cross-linked micelles prepared using BIEE, for varying amounts of TMOS, for longer reaction times (40 min and 8 h) and using methanol co-solvent (see later for further details). In each case, purified copolymer-silica particles were obtained by diluting with ethanol, followed by three centrifugation/redispersion cycles at 16,000 rpm for 5 min. Redispersal of the sedimented copolymer-silica particles was achieved with the aid of an ultrasonic bath.

3. Characterization of the block copolymer, micelles and hybrid copolymer-silica particles

Gel permeation chromatography (GPC)

The GPC set-up comprised a Perkin-Elmer LC pump and a refractive index detector. The GPC columns were either Mixed 'D' or Mixed 'E' (Polymer Labs, UK) and calibration was carried out using a series of near-monodisperse poly(methyl methacrylate) standards ranging from 680 to 53,000 g mol^{-1}. The eluent was HPLC grade THF stabilized with BHT and the flow rate was 1.0 ml min^{-1}.

^{1}H NMR spectroscopy

The block composition and degrees of quaternization of the tertiary amine methacrylate diblock copolymer were assessed in $CDCl_3$ and D_2O, respectively using an AC-P 300 MHz NMR instrument. The block composition was assessed by comparing the integrated dimethylamino signal of the DMA residues at 2.3 ppm with the methine signal due to the DPA residues at 3.0 ppm. Degrees of quaternization were calculated by comparing the integrated dimethylamino signal of the DMA residues at 2.3 ppm with that of the trimethylammonium signal at 3.3 ppm. The degree of protonation of the core chains within the hybrid copolymer-silica particles was assessed using DCl/D_2O and $NaOD/D_2O$ mixtures, respectively.

Thermogravimetry

A Perkin-Elmer Pyris 1 instrument was used at a heating rate of 20^{o}C per min. Dried samples were heated in air to 800°C and the observed mass loss was attributed to the quantitative pyrolysis of the copolymer, with the remaining incombustible residues assumed to be pure silica (SiO_2).

Dynamic Light Scattering

Measurements were made at 20^{o}C using a Brookhaven Instruments Corp. BI-200SM goniometer equipped with a BI-9000AT digital correlator using a solid-state laser (125 mW, λ = 532 nm) at a fixed scattering angle of 90^o. Intensity-average particle diameters (D_z) and polydispersities were calculated by cumulants analysis of the experimental correlation function using the Stokes-Einstein equation for dilute, non-interacting monodisperse spheres.

FT-IR spectroscopy

FT-IR spectra were recorded in KBr disks using a Nicolet Magna 550 instrument. The average number of scans per spectrum was 128 and the spectral resolution was 4 cm^{-1}.

Transmission electron microscopy

TEM studies were conducted using a Philips CM 100 instrument operating at 100 kV. Dilute dispersions of the hybrid copolymer-silica particles were allowed to dry onto a carbon-coated copper grid under ambient conditions prior to examination.

Aqueous electrophoresis

Measurements were performed in 1 mM NaCl solution using a Malvern Zetasizer NanoZS instrument. The solution pH was adjusted by the addition of HCl or NaOH.

Small-angle x-ray scattering studies

Small-angle x-ray scattering (SAXS) measurements were carried out at room temperature using a Bruker AXS NanoStar laboratory instrument equipped with a two-dimensional (2D) position-sensitive gas detector (Hi-Star, Siemens AXS). The primary x-ray flux was collimated using cross-coupled Gobel mirrors and a three-pinhole collimator providing a CuK_α radiation beam with a full width at half maximum of about 0.4 mm at the sample position. Data were acquired using a sample-detector distance of 1.045 m over the wave vector range: 0.01 $Å^{-1} < q < 0.2$ $Å^{-1}$ ($q = 4\pi \sin\theta / \lambda$, where θ is half the scattering angle and λ is the wavelength of the x-ray radiation); a silver behenate standard was used to calibrate the camera. A liquid cell comprised of two mica windows (each of 25 μm thickness) separated by a polytetrafluoroethylene spacer of 1 mm thickness was used as a sample holder. 2D SAXS patterns were reduced to one-dimensional profiles by a standard procedure using Bruker software supplied with the instrument. The SAXS profiles shown in Figure 7 were subjected to both incident beam intensity (the instrument was modified with a semi-transparent beam stop in order to measure this parameter) and also background corrections. Distance distribution functions [$p(r)$, see Figure 8 were calculated indirectly by a regularization technique using the GNOM computer program.[15,16] A smearing effect caused by the width of the x-ray beam was corrected using a profile of the direct x-ray beam. The $p(r)$ curves were further examined to determine structural parameters of the core-shell particles. *Dyefe*, an open source computer program developed by D. I. Nerukh and co-workers,[17,18] was used to fit the distance distribution functions using an analytical expression developed for core-shell structures by Glatter.[19]

The two $p(r)$ curves were fitted using the core-shell model (see solid lines in Figure 8 assuming a normal distribution for the overall particle radius. Parameters used for this core-shell model were R_c = 45 Å, R_s = 101 Å, σ = 20% and R_c = 64 Å, R_s = 144 Å, σ = 15 % for the hybrid copolymer-silica particles synthesized from 50 % quaternized shell cross-linked and 50 % quaternized noncross-linked micelles, respectively. In both cases, the electron density parameters (ξ) were taken to be ξ_c = 0.363 electrons/Å^3, ξ_s = 0.510 electrons/Å^3 and ξ_m = 0.334 electrons/Å^3. It was further assumed that the silica component of these hybrid particles was non-porous, that the particle cores comprised solely PDPA chains, that the shells comprised both PDMA chains and the silica shell and that the mass ratio of PDPA:PDMA:silica was 5:11:84, as determined by both thermogravimetric analysis and the known block composition from ^{1}H NMR spectroscopy. Furthermore, the mass densities ρ of the PDPA, PDMA and silica were taken to be 1.01, 1.10 and 1.80 g cm^{-3}, respectively and the respective chemical formulae used for these components were $C_{12}H_{23}O_2N$ (PDPA), $C_8H_{15}O_2N$ (PDMA) and SiO_2. The equation $\rho = \xi M / z / N_A$, where M and z represent the molecular weight and the number of electrons per molecular unit respectively and N_A is Avogadro's number, was used to convert mass densities into electron densities.[20]

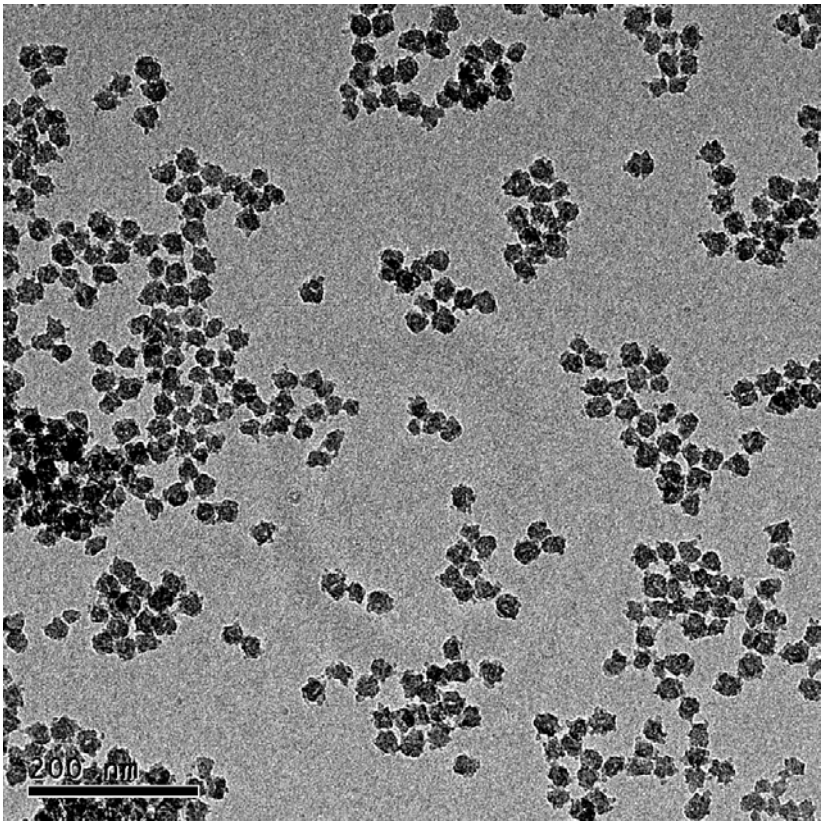

Figure S1. Transmission electron micrograph of hybrid copolymer-silica particles obtained from micelle templates prepared using the quaternized $PDPA_{23}$-$PDMA_{68}$ copolymer (100 % quaternization of the PDMA chains). The synthesis conditions were the same as those used for templating micelles prepared with the 50 % quaternized copolymer. In this case there is little or no evidence for a well-defined core-shell morphology: silicification seems to occur throughout the micelle interior.

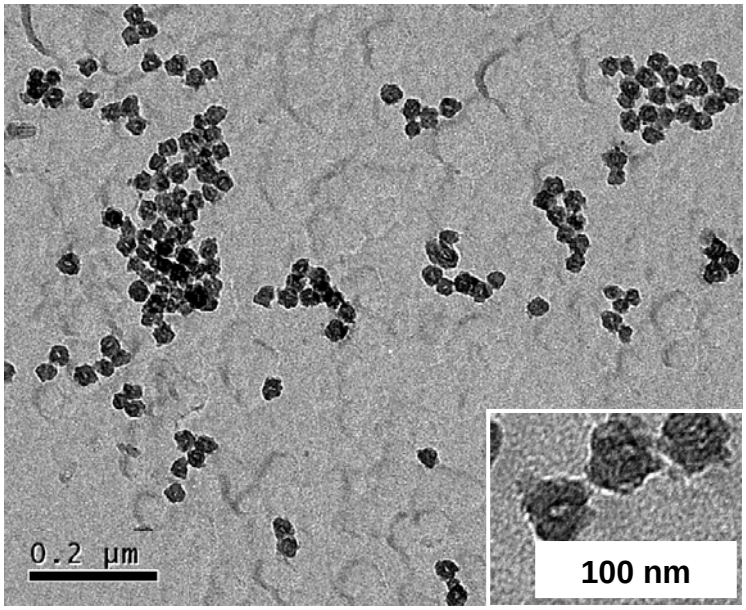

Figure S2. Transmission electron micrograph of hybrid copolymer-silica particles (the same particles as shown in Figure 2B, formed by 50 % quaternized $PDPA_{23}$-$PDMA_{68}$ micelles) after redispersion in acidic solution at pH 2 with the aid of an ultrasonic bath.

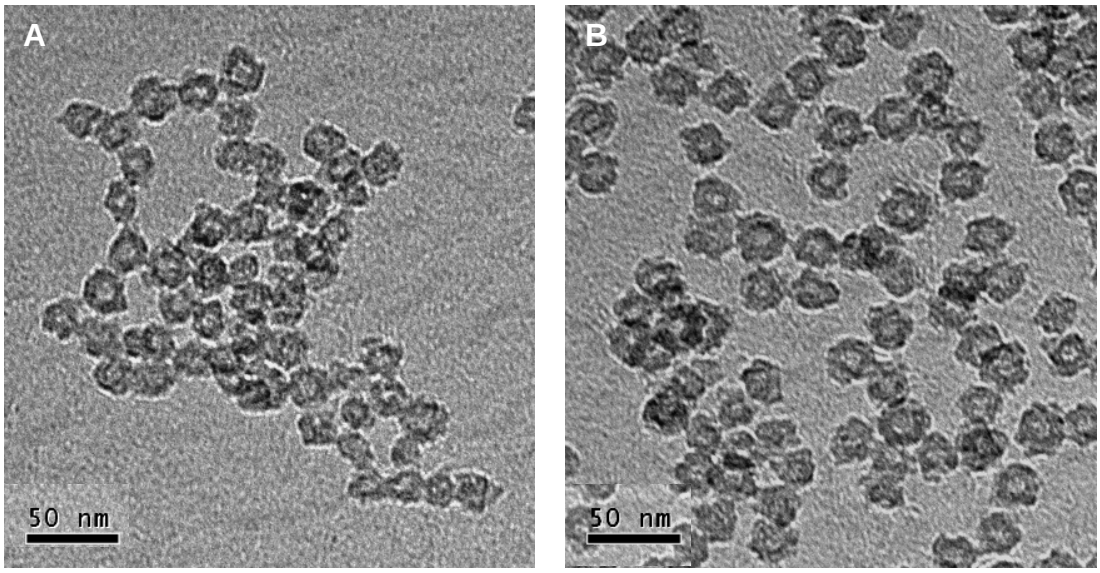

Figure S3. TEM images obtained for hybrid copolymer-silica particles using SCL micelles (50 % mean target degree of crosslinking by BIEE) as templates and a reduced excess of TMOS: (A) prepared by stirring a mixture of 2.0 mL of a 0.25 wt. % copolymer micelle solution with 58 mg TMOS for 20 min; (B) prepared by stirring a mixture of 2.0 mL of a 0.25 wt. % copolymer micelle solution with 116 mg TMOS for 20 min.

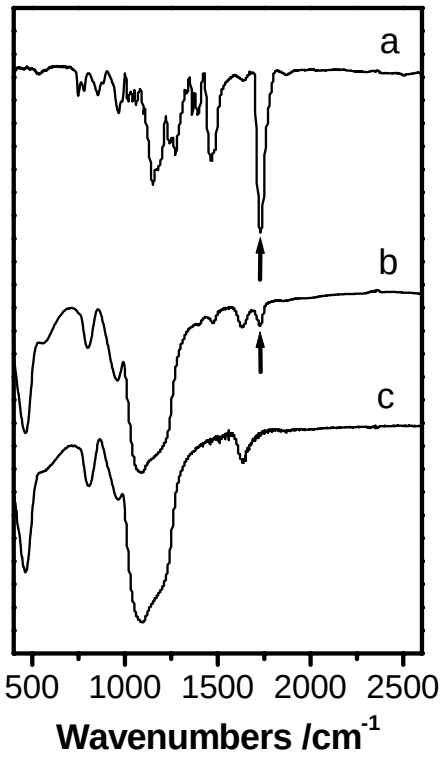

Figure S4. FT-IR spectra recorded for: (a) the $PDPA_{23}$-$PDMA_{68}$ diblock copolymer precursor; (b) hybrid copolymer-silica particles obtained after silica deposition onto shell cross-linked micelles obtained from the $PDPA_{23}$-$PDMA_{68}$ diblock copolymer (target degree of cross-linking = 30 % using BIEE) under the stated conditions (see Figure 3A); (c) hybrid copolymer-silica particles obtained after pyrolysis of the copolymer by calcination at 800°C. The FT-IR spectrum of the hybrid copolymer-silica particles contains IR bands that are characteristic of both the silica network (1080 cm^{-1}, multiplet corresponding to Si-O stretching; 950 cm^{-1}, Si-OH vibration mode; 800 cm^{-1}, Si-O-Si bending; 470 cm^{-1}, Si-O bending) and also the copolymer (the carbonyl ester stretch at 1730 cm^{-1}). This latter carbonyl band disappears after calcination of the copolymer, as expected.

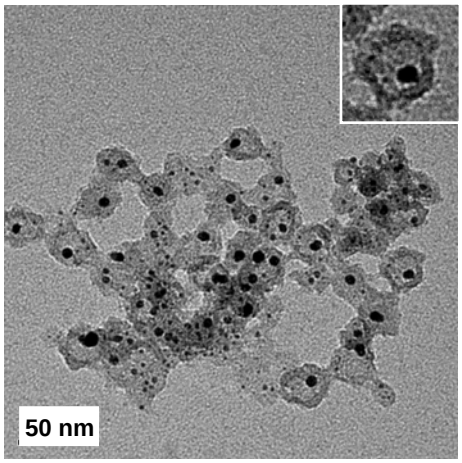

Figure S5. Transmission electron micrograph of hydrid copolymer-silica particles obtained by protonating the PDPA chains within the cores of the silica-coated micelles using $HAuCl_4$, followed by in situ reduction using $NaBH_4$. This experiment confirms that the PDPA chains remain located within the micelle cores after silica deposition, as expected.