About the synthesis of HCN-like poly(methyl methacrylate)/polystyrene/silica colloidal molecules

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Experimental section

Materials
Styrene (99% from Acros) was purified by passing over a column of basic aluminum oxide. Methyl methacrylate (MMA, 99% from Acros), methacryloxy propyl dimethyl methoxysilane (MPDMS, 92% from ABCR), sodium dodecyl sulfate (SDS, 99% from Aldrich), Synperonic® NP30 (NP30, from Fluka), divinyl benzene (DVB, 80% from Aldrich), sodium persulfate (NaPS, 98% from Acros) and 2,2'-azobis(N,N'-dimethylene isobutryramidine) dihydrochloride (ADIBA, Wako chemicals Gmbh) were used without further purification. All chemical structures are shown in the Supporting Information (Scheme S1). Commercial silica particles (Klebosol®, 30R50, AZ Materials) was centrifuged at 15 000 rpm for 15 min in order to remove the small particles (diameter ≤ 50 nm) which were also present. After this separation step, the number average diameter \( D_n \) determined by TEM was 80 nm \( (D_w/D_n = 1.02) \). Water was deionized before use (Purelab Classic UV, Elga LabWater).

Synthesis of dimeric PS/silica seeds

MPDMS was added to the silica suspension (10 g.L\(^{-1}\)) containing NP30 at 743 mg.L\(^{-1}\) and SDS at 7.5 mg.L\(^{-1}\), i.e. NP30/SDS = 99/1 wt./wt., such as the nominal MPDMS surface density at the silica surface was 0.1 function.nanom\(^{-2}\). The mixture was stirred at room temperature overnight. Then styrene and possibly DVB (used in various weight ratios with a total concentration of 25 g.L\(^{-1}\)) were added. The mixture was introduced in a 250 mL glass thermostated reactor fitted with a condenser and purged with nitrogen under stirring (275 rpm) then heated to 70°C. SPS (0.5 wt.% relative to the monomers) dissolved in 1 mL of deionized water was added to start the emulsion polymerisation. Samples were cooled down after 30 min (monomer to polymer conversion: ~25 %) to stop the polymerisation. The residual monomers were eliminated by evaporation under vacuum.

Seeded-growth emulsion polymerisation of MMA in the presence of MPDMS

NP30 (2.97 g.L\(^{-1}\)), SDS (30 mg.L\(^{-1}\)) and MPDMS were added to a suspension of the dimeric PS/silica seeds (16.3 g.L\(^{-1}\)). The mixture was stirred at room temperature overnight. MMA was then added and the resulting suspension introduced in a 250 mL glass thermostated reactor fitted with a condenser and purged with nitrogen under stirring (275 rpm), and finally heated to 70°C. NaPS (0.5 wt. % relative to monomer) dissolved in 1 mL of deionized water was added to start the polymerisation. Elapsed time between additions of MMA and NaPS was 1 h.

Seeded-growth emulsion polymerisation of MMA initiated by ADIBA
The synthesis of the biphasic silica/PS particles was similar to the one depicted above using MPDMS. Silica was first modified with MPDMS, and no DVB was used with styrene for the synthesis of the PS nodule. In addition, the polymerization was carried out for 180 min (instead of 30 min) to reach a higher final monomer to polymer conversion (90%). ADIBA was added to the suspension of silica/PS particles ([silica]_{final} = 9.6 \text{ g.L}^{-1}). Adsorption of the bicationic initiator was performed at room temperature under inert atmosphere and constant stirring. In order to preserve the colloidal stability of the biphasic particles suspension, the initiator concentration was fixed to 0.05 \text{ g.L}^{-1} and the pH was increased to 9.8 by adding a given volume of a NaOH 0.1 mol.L$^{-1}$ standard solution. The suspension was introduced in a 250-mL glass thermostated reactor fitted with a condenser and purged with nitrogen under stirring (320 rpm) at room temperature. Then, degassed MMA (25 \text{ g.L}^{-1}) and a degassed solution of surfactants in deionized water (NP30 1.71 \text{ g.L}^{-1}; SDS 35 \text{ mg.L}^{-1}, \textit{i.e.} NP30/SDS = 98/2 \text{ wt./wt.}) were added at once before increasing the temperature at 60°C to start the polymerisation.

**Characterization**

Monomer consumption was followed by gravimetric analysis. The morphology of the particles was characterized by transmission electron microscopy (TEM) using a Philips CM120 microscope operating at 80 kV (Centre Technologique des Microstructures (CTµ), Claude Bernard University, Villeurbanne, France). Specimens were prepared as follows: samples, as directly collected from the reactor, were diluted in deionized water and one drop of the diluted suspension was deposited on a 200 mesh copper grid coated with a carbon/formvar membrane. The number- and mass-average particle diameter ($D_n$ and $D_w$, respectively) as well as the particle diameter dispersity ($D_w/D_n$) were determined using AnalySIS software (Soft Imaging System).
**Supplementary figures**
(in the order in which they are called from the main text)

![Chemical structures](image)

**Scheme S1.** Chemical structures of the main chemicals used in this study.
**Figure S1.** TEM images of dimeric PS/silica particles synthesized in the presence of a) 0 wt.% of DVB (monomer to polymer conversion = 25%) b) 4 wt.% of DVB (monomer to polymer conversion = 20%) and c) 15 wt.% of DVB (monomer to polymer conversion = 28%). [Silica] = 10 g.L⁻¹; [MPDMS] = 0.5 function.nm⁻²; [Styr + DVB] = 25 g.L⁻¹.

**Figure S2.** TEM images of triphasic clusters synthesized by MMA emulsion polymerisation from dimeric PS/silica seeds whose PS nodule was made from a) pure styrene (MMA-to-PMMA conversion = 57%), b) 4 wt.% of DVB (MMA-to-PMMA conversion = 58%) and c) 15 wt.% of DVB (MMA-to-PMMA conversion = 57%). [dimeric PS/silica seed] = 15 g.L⁻¹; [MMA] = 100 g.L⁻¹.