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Towards a one-step method for preparing silica/polymer heterodimers and dimpled polymer particles

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ABSTRACT

Silica/PS and silica/PMMA heterodimers were obtained in very good yields using 80 nm silica particles first functionalized with a polymerizable alkoxysilane and then used as seeds for the emulsion polymerization of either styrene or methyl methacrylate. Aiming at a one-pot and scalable process, a commercial silica sol was used and the grafting reaction of silica with the functional silane was directly performed in the mixture of surfactants subsequently used for the polymerization. The effect of silica content, nature and concentration of the surfactant, of the reactive alkoxysilane or of the monomer, on the formation of the silica/PS heterodimers was investigated. Either dumbbell- or snowman-like dimers were obtained depending on monomer conversion. The typical morphological yield reached 60% with respect to all morphologies. The synthesis of silica/PMMA dumbbell-like dimers was also successful. In addition to TEM and DLS, the emerging technique of charge detection mass spectrometry (CD-MS) was used to provide the mass distribution and the sample composition in terms of morphologies. Finally, this system also proved to be efficient for the synthesis of dimpled polymer particles.

1. Introduction

In recent years many efforts have been devoted to the synthesis of colloidal clusters of spherical particles for both fundamental studies and preparation of new materials [1–4]. In particular, anisotropic clusters constituted of both organic and inorganic particles have been the topic of many studies and different processes both physicochemical and chemical have been developed and a vast range of morphologies obtained [5–19]. A few years ago we reported a one-pot seeded-growth emulsion polymerization process allowing the nucleation and growth of a controlled number of polystyrene (PS) latex nodules onto the surface of silica seed particles [20]. To promote the affinity between both phases, the surface of the silica seed was previously treated by an alkoxysilane bearing a polymerizable group. The idea was to promote the capture of the growing chains initiated in water by copolymerizable species located at the surface of the silica seed, and thus favour the nucleation/growth of the polymer nodules onto the seed. According to this strategy various morphologies have been observed such as dumbbell- or snowman-like dimers [21], and multipod-like clusters [20,22]. Various parameters such as the concentration and nature of the compatibilizing agent, the nature and concentration of the surfactant, the size and concentration of the silica seed or the grafting density of the silane molecules proved to strongly impact the final morphology.

To date, the synthesis of heterodimers (either snowman- or dumbbell-like) has been limited to low monomer conversions and the influence of the experimental conditions on the control of the morphology has not been studied in details. Aiming at a scalable and robust process allowing the formation of a large quantity of dissymmetrical particles in one step, the original process [21] has been modified and improved in many ways. Within this work, a

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commercial silica sol was used instead of home-made silica seeds. In place of common hydroalcoholic protocols, the grafting reaction was performed directly in water in the presence of the surfactants subsequently used for the emulsion polymerization, providing the opportunity to skip time-consuming steps of separation/redispersion of the silica in water. To improve both the polymerization kinetics and the colloidal features of the polymer nodules (stability and dispersity), an anionic surfactant was added to the non-ionic one used in the initial recipe. Using this new protocol, the effect of various experimental parameters (silica content, nature and concentration of the surfactants, alkoxysilane and monomer) on the formation of silica/PS dimers was investigated. The formation of silica/poly(methyl methacrylate) (PMMA) dimers is also reported for the first time using alkoxysilane-modified seeds. The final silica/polymer dimers were characterized by using conventional transmission electron microscopy (TEM) and dynamic light scattering (DLS) techniques. A very innovative aspect of this work is that the emerging technique of charge detection mass spectrometry (CD-MS) [23] was used as a complementary tool for the characterization of the silica/polymer dimers [24] to clear any doubt about the sample composition in terms of cluster morphology. Finally, this system also revealed to be an efficient strategy for the synthesis of dimpled polymer particles.

2. Experimental

2.1. Materials

Styrene (Sty, 99% from Acros) was purified by passing over a column of basic aluminum oxide. Methyl methacrylate (MMA, 99% from Acros), sodium dodecyl sulfate (SDS, 99% from Aldrich), Synperonic® NP30 (NP30, from Fluka), sodium persulfate (NaPS, 98% from Acros), methacryloxy methyl triethoxysilane (MMS) and methacryloxy propyl dimethyl methoxysilane (MPDMS, 92% from ABCR) were used without further purification. Commercial silica particles (Klebosol 30R50, AZ Electronic Materials, 32 wt%) were first centrifugated at 15 000 rpm for 15 min to remove the very small particles (diameter $\leq$50 nm) present in the sample. The number- and mass average particle diameter (D_n and D_w, respectively) as well as the particle-diameter dispersity (D_w/D_n) of the silica seeds after centrifugation were determined from TEM observations ($D_{n,Silica}$ = 80 nm, D_w/D_n = 1.02). Water was deionized before use (Purelab Classic UV, Elga LabWater). All chemical structures are shown in the Supporting Information (Scheme S1).

2.2. Surface modification of the silica seed

The surface of the silica seeds was treated by grafting MMS or MPDMS directly in water. The silane (0.1 function nm^{-2}) was added to the silica suspension containing NP30 and/or SDS and the mixture (pH = 8.5) was stirred at room temperature overnight.

2.3. Emulsion polymerization

Styrene or MMA was added to the silane-modified silica suspension. The mixture was introduced in a 250 mL glass thermostated reactor fitted with a condenser and purged with nitrogen under stirring (275 rpm) for 30 min. It was then heated to 70 °C and NaPS (0.5 wt.% relative to the monomers) dissolved in 1 mL of deionized water was added to start the emulsion polymerization. The regular withdrawal of samples allowed us to follow the monomer conversion with time by gravimetric analysis. The various polymerizations performed for this study are presented in Table 1.

2.4. Formation of dimpled PS particles

A polymerization experiment was carried out following a D8-type recipe (run D11, see Table 1), stopped after 35 min (corresponding to 34% styrene conversion). The sample was then gently stirred for one week under nitrogen bubbling.

2.5. Analytical techniques

The latexes (diluted solution deposited on a carbon/formvar-coated copper grid and allowed to evaporate) were observed by transmission electron microscopy (TEM) with a Philips CM120 microscope operating at an accelerating voltage of 80 kV (Centre Technologique des Microstructures (CTμ), plate-forme de l'Université Claude Bernard Lyon 1, Villeurbanne, France). In order to provide a more reliable analysis of particle size and morphology, some selected samples of silica/PS dimers and all silica/PMMA samples were observed in their natural hydrated environment using cryogenic TEM (cryo-TEM). Thin liquid films of the suspensions were deposited onto 300 Mesh holey carbon films (AgarScientific, UK) and quench-frozen in liquid ethane using a cryo-plunge workstation (made at LPS Orsay). The specimens were then mounted on a precooled Gatan 626 specimen holder, transferred in the microscope and observed as described previously (at an accelerating voltage of 120 kV). 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).

The number ratio of polymer (PMMA or PS) latex particles to silica particles, N_{Latex}/N_{Silica}, was determined through statistical analysis of the TEM images. Silica and polymer particles show significantly different contrast and can be thus unambiguously identified on the micrographs. However, the procedure for PS was different from that used for PMMA. For the silica/PS dimers, the average diameter of the PS nodules, $D_{n,PS}$, was determined by TEM and the ratio N_{Latex}/N_{Silica} calculated using equation (1):

$$N_{Latex}/N_{Silica} = \left(\frac{C_{PS}}{C_{Silica}}\right) \times \left(\frac{d_{Silica}}{d_{PS}}\right) \times \left(\frac{D_{n,Silica}}{D_{n,PS}}\right)^3 \quad (1)$$

with C_{Silica} and C_{PS} (g L^{-1}) the silica and PS concentrations, respectively, d_{Silica} and d_{PS} (g cm^{-3}) the silica and PS densities (2.0 and 1.05, respectively), and $D_{n,Silica}$ and $D_{n,PS}$ (nm) the diameters of the silica and PS particles determined by TEM, respectively. For the silica/PMMA dimers, due to the likely swelling of PMMA particles by residual MMA, the N_{Latex}/N_{Silica} ratio was directly determined from the cryo-TEM images by manually counting the number of latex particles and the number of silica particles in the cryo-TEM images, and making the ratio. The morphological yield was calculated with respect to the total number of morphologies present in the sample (i.e. organic/inorganic particles, free polymer particles and free silica seeds).

Charge detection mass spectrometry (CD-MS) experiments were performed on a custom-built charge detection-mass spectrometer coupled with an electrospray source (ESI). This instrument was described in details in previous works [25]. CD-MS simultaneously and independently measures m/z and z (m is the molar mass and z the number of charges) for individual ions. Highly charged ions, produced by ESI, pass one at a time through a small metal flight tube attached to a charge-sensitive preamplifier that captures their image current. Once frequency-filtered, amplified and shaped, the primary image current signal is characterized by a