

Synthesis of fluorescent monodisperse non-spherical dumbbell-like model colloids†

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Received 5th August 2012, Accepted 5th September 2012

DOI: 10.1039/c2jm35229j

We describe a facile and flexible approach for synthesizing uniform non-spherical micron sized PMMA (poly(methyl methacrylate)) colloids with well-controlled protrusions. When homogeneously cross-linked PMMA spheres were used as seeds in a swelling process using again a methyl methacrylate monomer, they were found to transform into non-spherical particles with a single or multiple protrusions mainly depending on the cross-link density of the seeds. Alternatively, if core-shell PMMA spheres bearing a highly cross-linked shell around an uncross-linked 'soft' core were employed as seed particles, they always developed just a single protrusion. Precise control over the anisotropy of the particles was achieved by varying the amount and composition of the swelling mixture as well as the concentration of the stabilizer. Subsequently, the phase separation was enhanced and protrusions could be readily polymerized through temperature elevation of the system, yielding PMMA 'snowman'-like or dumbbell-like colloids. Furthermore, these particles could be labeled with fluorescent dyes either before or after the polymerization, and transferred into apolar, refractive index and density matching liquids (cyclohexyl bromide (CHB) and/or decalin), enabling their use in quantitative confocal fluorescence microscopy studies in concentrated systems. Some examples of the use of these particles as a model system for real space analysis are given. These examples include the formation of plastic crystals, a special form of a colloidal crystal where the particles are positionally ordered but orientationally disordered. Additionally, the non-spherical particles could be organized into semi-flexibly bonded colloidal chains aided by an electric field in a polar solvent (formamide). Such chains of anisotropic particles are interesting as polymer analogs and for the preparation of new materials.

Introduction

Anisotropic colloidal particles and their self-assembly have been studied for a long time in the field of colloid science, see *e.g.* the review in ref. 1. However, the number of papers compared to those on spherical colloids has stayed relatively low until recently. As is apparent from some recent review papers^{1–6} more complex colloids⁷ made specifically with further self-assembly in mind are becoming a main stream topic. This is not only because it is realized that the extra degrees of freedom of anisotropic particles give rise to interesting new ways to tune materials' properties, such as in liquid crystal phases or photonic crystals, but also because new phenomena can be probed in model studies, such as the role of particle rotations in crystallization and the glass transition.

So many synthesis procedures have been developed for anisotropic inorganic,^{8,9} organic particles^{10–12} or mixed inorganic-organic particles^{13–15} that we can only give here some typical examples that focus on methods that also take spheres as a starting material. In this paper we present a study on making anisotropic particles starting from spherical polymer particles through a method that is already several decades old and relies on swelling polymer seed particles with a monomer and relying on the fact that for certain conditions a subsequent polymerization can result in anisotropic polymer particles. On swelling cross-linked seed particles with a monomer and by a subsequent heating step elastic stress build-up causes the excess monomer to phase separate in the form of a protrusion which can be polymerized. For instance, Sheu *et al.*¹⁶ demonstrated this method to produce several micrometer sized polystyrene (PS) particles with the shape of two interpenetrating spheres (now often called 'snowman' particles or for equal sized sphere sections, dumbbells). Of much more interest in recent times is the extension of this method by Mock *et al.*^{17,18} to anisotropic particles of sub-micrometer size by the addition of a grafted hydrophilic layer on the surface of the seed particles to modify the surface tension and thus the wetting of the PS seed particles.

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† Electronic supplementary information (ESI) available: Electric field; semi-flexible strings made of nonspherical particles. See DOI: 10.1039/c2jm35229j

In addition, this method was also extended to hetero-phase dumbbell particles by using different monomers in the swelling stage.^{13,19} However, almost all the seed species were cross-linked PS particles. Developing new classes of seed particles and growing the size of the protrusions on the seed particles larger than the seeds (in other words, inverted snowman shaped), are challenges, in this paper we focus on the material of the seeds and the protrusions being poly(methyl methacrylate) (PMMA).

Sterically stabilized PMMA particles have received great attention in recent years in many model studies as both the refractive index and the mass density of such particles can be matched readily with organic solvent mixtures.^{20–23} Furthermore, the solvent mixtures and polymeric stabilizers can be used to tune the particle interactions from very soft to nearly hard and with external electric fields of high enough frequency (MHz range) a dipolar interaction can be superimposed on top of the hard or long-ranged repulsions as well.^{24–26} In addition, these kinds of particles have also been shown to allow for the creation of systems with oppositely charged interactions that can form equilibrium structures like binary crystals.^{27,28} Also, anisotropic colloids have been made using a stretching method starting from spherical particles.¹² However, as far as we know, snowman or dumbbell shaped colloids of PMMA made using the above mentioned monomer swelling and second polymerization method have not yet been used in model studies on concentrated strongly interacting dispersions. This is probably related to the difficulties that arise in the preparation of uniform, highly cross-linked PMMA colloids as seeds and the subsequent swelling and protrusion formation. We too, experienced such difficulties and often obtained very rough or poly-disperse colloids, or found that the protrusion failed to form at all. Key to a solution is the preparation of seed spheres with an optimal cross-linked architecture. In previous work,²⁹ we succeeded in the production of either lightly or highly cross-linked PMMA seed spheres with a narrow size distribution by feeding the cross-linker slowly to the reaction vessel. By controlling the addition start time, either before or after the nucleation stage has finished, PMMA spheres could be obtained that were cross-linked either homogeneously or only in a shell. The slow cross-linker feed allowed us to obtain particles that were spherical and had a smooth surface up to a cross-link density as high as 10 wt%. With these particles used as seeds it turned out to be possible to produce monodisperse, dumbbell-shaped, all PMMA colloids using the swelling and protrusion method. The typical fabrication processes and some examples of obtained anisotropic particles are shown in Fig. 1. Upon being in contact with methyl methacrylate (MMA), the cross-linked polymer PMMA network first swells by absorbing excess MMA and then expels some of it to form a protrusion (see the second bottom optical microscopy images in Fig. 1). The cross-linked PMMA seeds show similar swelling and protruding behaviors as with PS seeds.^{30,31} This was followed by a heating step in the presence of an initiator that polymerized the swelling monomer and increased the size of the protrusions (see the two bottom right images in Fig. 1). Our technique allows for tuning the shape from a dimeric colloid (snowman or dumbbell) to a colloid with multiple protrusions (rough particles) *via* adjustment of the swelling ratio and the cross-linking structure and density of the seeds, which control the rigidity and swelling capacity of the cross-linked polymer network. Furthermore, we could manipulate the radius ratio of the protrusion to the swollen seed (α , details see

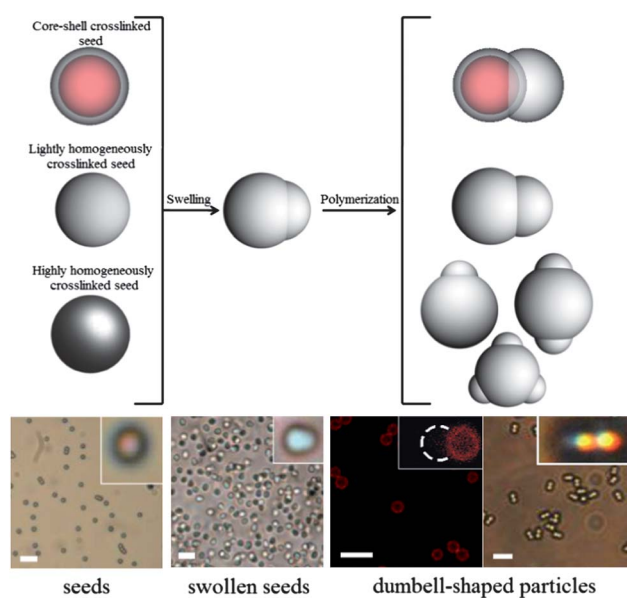


Fig. 1 Schematic diagram showing the formation of the non-spherical homo-phase PMMA particles by the seeded emulsion polymerization technique. The optical and confocal micrographs exemplify the synthesis of non-spherical PMMA particles. The scale bars are 5 μm .

Experimental section), which enables control over the desired dumbbell or snowman shape of the particles. In addition, to make these particles suitable for confocal fluorescence microscopy studies we labeled them with fluorescent dyes and demonstrated the possibility to transfer them into apolar solvents using a surfactant. Some examples of such dispersions and the consequences of our control over the range of the particle repulsions will be shown. Finally, we demonstrate assembly of these particles into semi-flexible chains using a method published by our group recently.^{29,32}

Experimental part

Materials

Methyl methacrylate (MMA, Fluka and Aldrich, chemical grade) was passed over an inhibitor removal column (Aldrich). After the inhibitor had been removed, MMA was stored in a refrigerator at 5 °C and not longer than one month. Azo-bis-isobutyronitrile (AIBN, Janssen Chimica) was re-crystallized in ethanol before use. Ethylene glycol dimethacrylate (EGDMA, Sigma-Aldrich, chemical grade) was used as the cross-linking agent. Polyvinylpyrrolidone (PVP, Sigma) with an average molecular weight of 360 000 g mol^{-1} (K-90) was used as the stabilizer. Hydroquinone (Fluka) was used as the inhibitor. The fluorescent monomers (rhodamine B isothiocyanate)-aminostyrene (RAS) and (7-(diethylamino)-coumarin-3-carboxylic acid *N*-succinimidyl ester)-aminostyrene (CAS) were prepared following the method described in our previous work.²⁹ Sorbitan trioleate (Span 85, Sigma, chemical grade), methanol (Biosolve, chemical grade), formamide (Fluka, chemical grade), decahydronaphthalene (mixture of *cis* + *trans*, decalin, Fluka, $\geq 98\%$), cyclohexyl bromide (CHB, Fluka, chemical grade) and hexane (Biosolve, chemical grade) were used as supplied. Deionized water was used in all experiments.

Procedure for non-spherical particle synthesis

Several series of monodisperse poly(methyl methacrylate) spheres with different cross-linked structures and cross-linked densities were prepared using the previously reported method.²⁹ The core-shell or homogeneously cross-linked structure of our PMMA seed spheres could be controlled by varying the addition start time of a mixture containing a cross-linker; the addition end time was always kept fixed at 3.5 h. The obtained seeds were all monodisperse in size with a smooth surface and their diameters ranged from 770 nm to 1250 nm with polydispersities around 4%. Before carrying out further experiments, the seed spheres were rinsed twice with methanol, three times with a 1 wt% PVP aqueous solution, and finally stored in the 1 wt% PVP aqueous solution at a weight fraction of 0.7% at room temperature no longer than one week. The seed particles needed to be dispersed homogeneously by sonication before further use.

Once the cross-linked seed spheres had been homogeneously dispersed in the 1 wt% of PVP aqueous solution, non-spherical PMMA particles were prepared on the basis of our extension of the seeded emulsion polymerization technique.¹⁶ Typically, 22 g of monomer oil-in-water emulsion (stabilized by 1 wt% PVP, based on total emulsion mass) consisting of 2 g of swelling monomer (MMA) was prepared in the presence of an initiator (AIBN) (1 wt% based on the swelling monomer mass) by homogenizing with a IKA MS2 minishaker at 2500 rpm for 5 min. Then all the monomer emulsion was added slowly to 20 g of seed suspension (0.7 wt%) with a constant stirring. The detailed recipes are summarized in Table 1. All samples were allowed to swell in a 250 ml, three-neck flask equipped with a condenser, and a Teflon-coated magnetic stirring bar with slow stirring (~100 rpm) for around 18 h. Subsequently, nitrogen was bubbled through the reaction system for at least 30 min. Then the polymerization was carried out by temperature elevation to 70 °C. Addition of hydroquinone (0.5 wt% based on the amount of swelling monomer, a water soluble inhibitor) prior to the heating process inhibited secondary nucleation in the water phase at the early stage of the polymerization. The inhibitor (hydroquinone) compelled the polymerization to occur mainly in the protrusion and the swollen seed phase. The reaction was maintained at 70 °C for 8 h before cooling. The obtained particle suspension was washed about 4 times with deionized water by a centrifuge

(Hettich Rotina 46S centrifuge, at 560g for 60 min twice and 30 min twice, respectively), thus separating the desired particles from the secondary nucleation and impurities.

We labeled the particles with a fluorescent dye either during or after polymerization (to which we refer as either pre- or post-labeling). In the pre-labeling process, CAS (0.1 wt% based on swelling monomer) was first dissolved in the swelling monomer in the presence of the initiator. Then the same subsequent steps were followed as just mentioned and fluorescently labeled non-spherical particles were obtained in the end. In the post-labeling process, dried non-spherical (snowman or dumbbell-like) particles (~0.1 g) were first dispersed in a mixture (~5 ml) of acetone-pentanol (1 : 4 by weight) containing 1 mM of RAS by sonication, and then stirred gently overnight in a sealed glass vial (~20 ml in volume) at room temperature. Then the acetone was removed by evaporation at 50 °C for 2 h. The labeled particles were washed two times with pentanol, one time with methanol, and three times with deionized water, respectively, by centrifugation. After drying under a N₂ stream, the fluorescent non-spherical particles were stored in a dark glass vial.

To transfer the particles to an apolar solvent, we modified the transfer approach from Espinosa *et al.*²⁵ A small amount of non-spherical particles (about 0.01 g) was first dispersed in pentanol then sedimented by a Hettich Rotina 46S centrifuge, and the supernatant was removed. Subsequently, they were transferred to hexane (containing 50 mM of the surfactant Span 85) as an apolar intermediate solvent and then further to decalin or CHB containing 50 mM of the surfactant Span 85 as well aided by sonication and centrifugation. After this procedure had been repeated four times, the solvent was considered completely exchanged. For the particle transfer to formamide, the intermediate solvent was skipped, and the surfactant was not necessary. Again the system was washed four times.

Characterization of the non-spherical particles

SEM (scanning electron microscopy) imaging was performed using a field-emission scanning electron microscope (SEM XL FEG30). The samples were prepared by placing a droplet of suspension onto a glass slide and allowing the solvent to evaporate at room temperature. The samples then were sputter-coated with a layer of gold (Au) of 10 nm. The number-averaged re-polymerized

Table 1 Detailed recipe for the synthesis of non-spherical PMMA particles

Batch no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
<i>Seeds system^a</i>																		
Addition start time (h)	0	0	0	0	0	0.33	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total addition time (h)	3.5	3.5	3.5	3.5	3.5	3.1	2	2	2	2	2	2	2	2	2	2	2	2
EGDMA (wt%) ^b	1	2	5	10	2	2	2	1	2	3	4	5	6	2	2	2	2	2
Dye ^c	—	—	—	—	RAS	RAS	RAS	—	—	—	—	—	—	—	—	—	—	—
<i>Swelling monomer dispersion^d</i>																		
Amount of swelling monomer (g)	4	4	4	4	4	4	4	2	2	2	2	2	2	1	4	8	4	4
PVP (wt%) ^e	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.5	1
EGDMA (wt%) ^f	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2

^a Other chemicals: PVP, 3 g; AIBN, 0.025 g; MMA, 2.5 g; solvents, 30.71 g (methanol : water = 8 : 2 in weight). ^b Based on the mass of the PMMA particle. ^c RAS: 0.5 wt% based on the mass of the PMMA particle. ^d Other chemicals: deionized water, 20 g; 1 wt% of PVP, based on the mass of the deionized water; 1 wt% of AIBN based on the mass of the swelling monomer. ^e Based on the total mass of the suspension. ^f Based on the mass of the swelling monomer.

radius (R_s) of the seed spheres and the radius (R_p) of the protrusions of the non-spherical particles and their standard deviations (σ_s , σ_p) were calculated on the basis of using TEM measurement software (iTEM, 5.0). The polydispersities (δ_s of the seed spheres and δ_p of the protrusions) of the colloid systems were defined as

$$\delta_s = \sigma_s/R_s \quad (1)$$

$$\delta_p = \sigma_p/R_p \quad (2)$$

The schematic model of the non-spherical particles is illustrated in Fig. 2, which indicates the geometric relationships between R_s , R_p , and the contact angle (θ) of the protrusion on the re-polymerized seed sphere. The radius ratio (α) of the protrusion and re-polymerized seed sphere was defined as

$$\alpha = R_p/R_s \quad (3)$$

Fluorescence images were obtained using a Nikon confocal scanning laser microscope (CSLM, Nikon C1) with a Leica 63 \times oil confocal immersion lens with a numerical aperture of 1.4. The fluorescent dyes were excited at around 543 nm (RAS) and 408 nm (CAS), and their images were observed at emission wavelengths of around 605 nm (RAS) and 450 nm (CAS), respectively. The fluorescent samples were made using capillaries with a dimension of 0.2 mm \times 2.0 mm (VitroCom, UK) cross-section and a length of 5 cm, the two ends of the capillary were sealed with an epoxy glue. When imaging the phase separation process, we sealed the swollen seed spheres in the same sized glass capillaries which were glued using wax. Optical microscopy was performed with a Leica 63 \times lens and images were recorded with a Nikon (D90) digital camera.

Results and discussion

Homogeneously cross-linked seeds

Initially, a series of homogeneously cross-linked PMMA spheres with cross-link densities of 1%, 2%, 5%, and 10% based on

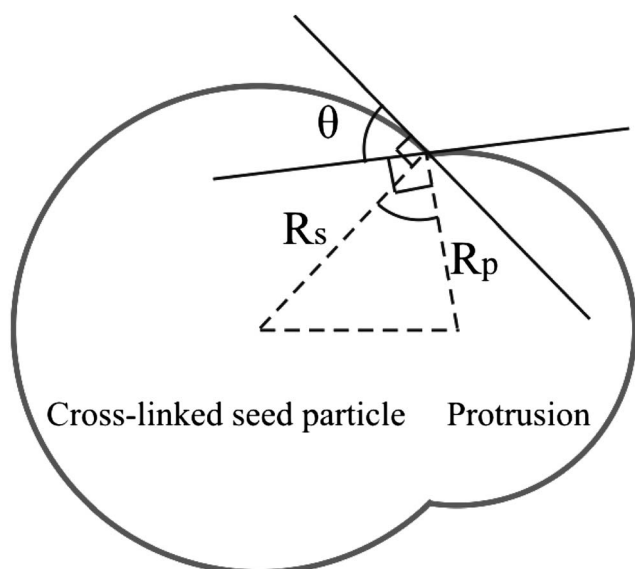


Fig. 2 Schematic model of a non-spherical particle.

monomer mass and with a diameter around one micrometer were used as seeds. The seed particles were dispersed in an aqueous solution stabilized by 1 wt% (based on total emulsion mass) of PVP, these spheres were swelled and subsequently, re-polymerized. The growth of the seed spheres with 1% cross-link density (batch 1 in Table 1) produced a snowman-like structure with a relatively small protrusion, a contact angle of $33^\circ \pm 3^\circ$ and low polydispersity; δ_s and δ_p are 5.6% and 5.8% (see Fig. 3a). The figure illustrates that these non-spherical particles were monodisperse in both size and shape. When the cross-link density of the seed spheres was increased from 1% to 2% (batch 2) and further to 5% (batch 3), the degree of phase separation in the snowman particles increased, as seen from the contact angle that increased from $33^\circ \pm 3^\circ$ to $56^\circ \pm 6^\circ$ and $58^\circ \pm 7^\circ$, respectively (see Fig. 3). On the other hand, the size of the protrusions decreased, corresponding to α decreasing from 0.797 to 0.636. This may be caused by a combination of two factors: one is that the highly cross-linked seeds tend to absorb less swelling monomer, directly resulting in smaller protrusions. The other is that the highly cross-linked network has a higher viscosity, which slows the diffusion of the swelling monomer from the seed to a growing protrusion, leaving the seed larger. These two factors together led to a decreasing α . In addition, and unfortunately, the seed part of the colloids became rather rough (Fig. 3b and c). Increasing the cross-link density of the seeds even further to 10% (batch 4) resulted in the formation of non-spherical particles with multiple protrusions (see Fig. 3d). This is probably caused by the highly cross-linked polymer network of the seeds. Upon heating the system, contraction takes place at the outer shell of the seeds prior to the inner part of the seeds. Strong compressive stress from the inner part of the seeds protruded the swelling monomer at various locations of the surface of the seeds. Although it is not the focus of the present research, it is of interest here to point out that particles with a controllable roughness have been used as a colloidal model system as well (see *e.g.* ref. 33). For instance, it has recently become clear that by controlling particle roughness, the depletion effect, which is a nice way to achieve attractions

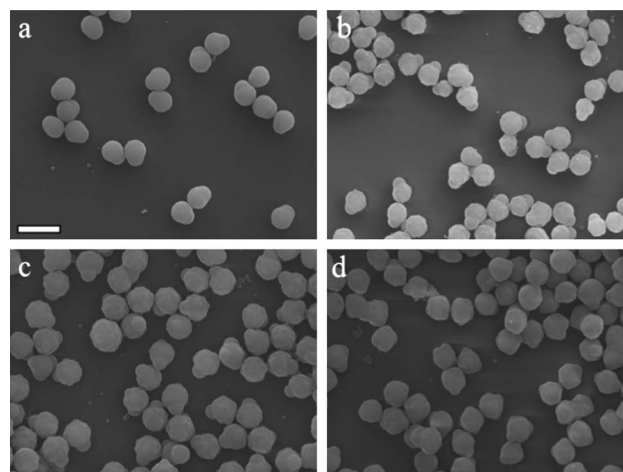


Fig. 3 SEM micrographs of non-spherical PMMA particles made using homogeneously cross-linked PMMA spheres as seeds with different cross-link densities (a) 1%, (b) 2%, (c) 5% and (d) 10%. The scale bar is 2 μ m and the swelling monomer was kept the same amount for all four syntheses (4 g, details see batches 1–4 in Table 1).

between smooth particles, can be effectively switched off if the particles roughness fulfills certain criteria (see *e.g.* ref. 34 and 35).

Core-shell cross-linked seeds

Since our experiments on homogeneously cross-linked PMMA spheres met with only modest success, we decided to try seeds with the cross-linker concentrated in an outer shell. This could combine a higher swelling capacity of the uncross-linked core with a stronger elastic retraction force of the cross-linked shell. Such particles were made by starting the addition of the cross-linker some time after the polymerization of the monomer has started, as shown in our previous work.²⁹ There, we also discovered that the swelling ratio of core-shell cross-linked PMMA spheres was indeed much higher than for homogeneously cross-linked PMMA.²⁹ Therefore, we hypothesized that the core-shell cross-linked seeds might form bigger protrusions. In agreement with our expectations, using a later addition start time, which produced a thinner cross-linked shell, led to a bigger final protrusion (see Fig. 4). Note that the time at which addition was complete was kept constant (3.5 h), as was the total amount of the cross-linker (2 wt% based on monomer mass, other details are listed in Table 1). This resulted in an increasingly thin shell with an increasingly high cross-link density. Fig. 4 shows that the contact angle of the protrusion on the seed increased from $57^\circ \pm 7^\circ$, $66^\circ \pm 5^\circ$ to $70^\circ \pm 3^\circ$ as the time window of cross-linker addition was narrowed (batches 5–7). Additionally, α increased from 0.635, 0.779 to 0.956, implying the growth of the protrusion relative to the seed. It is worth pointing out that there is no significant difference of contact angles between non-spherical particles derived from dyed and un-dyed seeds.

In order to investigate the effect of the cross-link density of the shell on the morphology of the non-spherical particles, a series of core-shell cross-linked PMMA particles were prepared keeping the addition start and end times constant. These were used as seeds to prepare the non-spherical PMMA particles. Results are presented in Fig. 5 (batches 8–13). It is seen that while the size of the protrusion became smaller as the cross-link density was increased, its contact angle became larger. Fig. 5g presents the tendency of the radius ratio (α) as a function of the cross-link density of the core-shell cross-linked shells of the seeds. At first, α decreased with increasing cross-link density of the shells, which can be explained by a reduction of the swelling as the rigidity of the shell is increased. When the density of the polymer network was further increased, the apparently stronger elastic force expelled a large volume of the swelling monomer from the cores

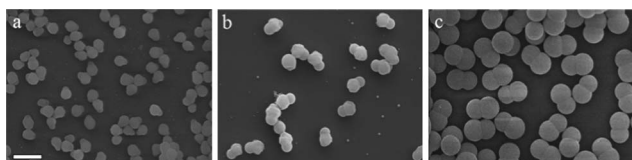


Fig. 4 SEM micrographs of non-spherical PMMA particles made using dye-labeled PMMA spheres with different cross-linking structures as seeds (cross-link density was 2 wt%). The seeds were prepared with different addition start times and total addition times (in all cases the addition was finished after 3.5 h of reaction): (a) 0 h–3.5 h (batch 5 in Table 1); (b) 0.33 h–3.1 h (batch 6) and (c) 1.5 h–2 h (batch 7), the scale bar is 2 μ m.

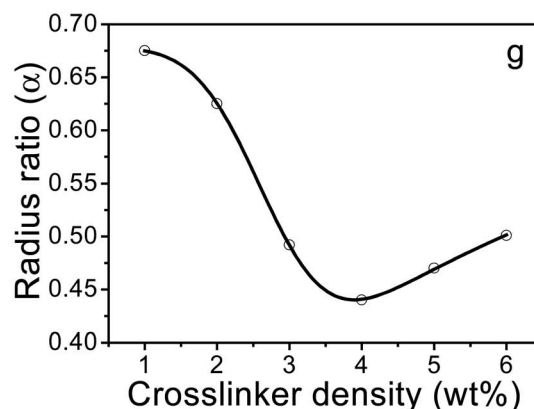
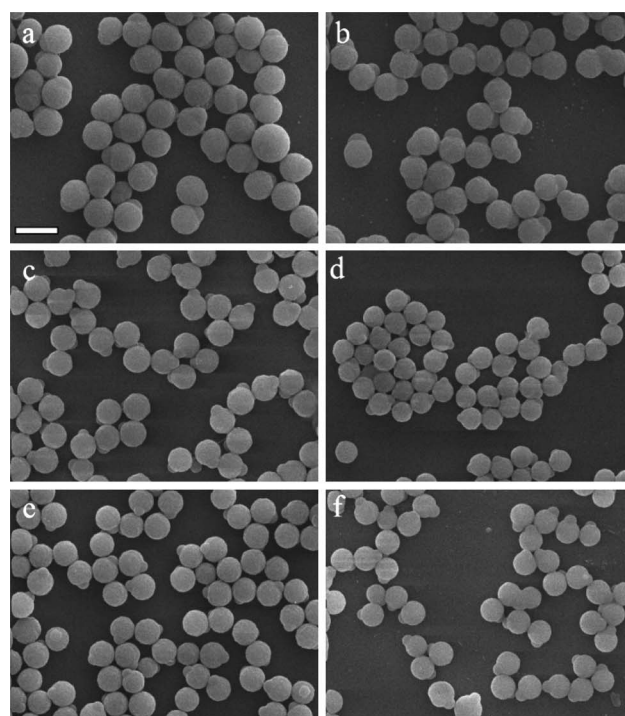


Fig. 5 SEM micrographs of non-spherical PMMA particles made using core-shell cross-linked PMMA spheres as seeds with different cross-link densities (a) 1 wt% (batch 8 in Table 1); (b) 2 wt% (batch 9); (c) 3 wt% (batch 10); (d) 4 wt% (batch 11); (e) 5 wt% (batch 12) and (f) 6 wt% (batch 13), and the corresponding radius ratio (α) on non-spherical particles as a function of the cross-link density of core-shell cross-linked PMMA seeds summarized in (g), in which open circles are experimental values and the solid line is a guide to the eye. The scale bar is 2 μ m.

leading to bigger protrusions relative to the seeds. Note that, the radii of the re-polymerized seeds relative to the original seeds increased as the cross-link densities increased from 4 wt% to 6 wt% (from 1.004 to 1.290 and further to 1.313; this has not been fully understood yet).

Effect of the swelling monomer content

Clearly, the size of the protrusion relative to the seed particle can be controlled through the cross-link density of the shell, but so far only in a relatively narrow range. If the protrusion could be stimulated to grow further, the snowman particles

would transform into dumbbell (with equal sized lobes) or even ‘inverted’ snowman particles (protrusion is larger than seed). We show that this is possible by simply increasing the amount of the swelling monomer. For these experiments we picked out the core-shell cross-linked PMMA seeds with 2 wt% cross-link density in which the cross-linker was added between 1.5 and 3.5 h of the reaction. Typical systems are shown in Fig. 6a–d, and the detailed contact angle and radius ratio as a function of swelling monomer weight have been summarized in Fig. 6e and f. Apart from a large increase in the size ratio, the contact angle also increased up to a cross-linker content of 4 g (batch 15 in Table 1). When the amount of the swelling monomer increased to 8 g (batch 16), the inverted snowman (protrusion is bigger than seed) like particles were obtained. Meanwhile, a small secondary lobe was present occasionally, opposite to the main protrusion on the seed particles surface (see Fig. 6d), which aided us to distinguish between the new-formed protrusions and original seeds. To our knowledge, this is the first time the inverted snowman particles are reported. It gives the potential to fabricate inverted snowman shaped particles with an even bigger radius ratio (α) or cone-shaped particles in one step.

Effect of other parameters

In addition, the effect of the PVP concentration on the morphology of the non-spherical particles also was investigated by decreasing the concentration of PVP from 1 wt% to 0.5 wt%, and further to 0 wt% (based on the total suspension mass). When 0.5 wt% of PVP was used (batch 17), the obtained system contained more multi-mers than the system with 1 wt% of PVP did (see Fig. 7a). A similar phenomenon was described in a previous paper,³⁶ that is, a smaller amount of stabilizer led to decreased stability of the system. In that case, swollen seed spheres with liquid protrusions tended to self-assemble into regular colloidal clusters as less stabilizer was present. However, dimers (consisting of two seed particles) and trimers (consisting of three seed spheres) prevailed due to the relatively short stirring time (~ 18 h) in our experiment in the case of 0.5 wt% of PVP. At low swelling ratios (the amount of swelling monomer was 2 g), the interfacial tension compressed the seed spheres to form clusters partially immersed in a liquid droplet. As expected, in the absence of PVP, the system was not able to stay stable any more.

Ethylene glycol dimethacrylate (EGDMA) has two unsaturated bonds and is therefore usually used as a cross-linker to interconnect linear monomers, oligomers and polymers, leading to a cross-linked polymer network. The addition of EGDMA (2 wt% based on swelling monomer mass) in the swelling monomer led to the formation of more branching and a larger volume of cross-linked polymer during polymerization.²⁹ This, in turn, led to particles of a high viscosity with a high degree of chain entanglement, and hence resulted in a smaller degree of phase separation (see Fig. 7b, batch 18). Compared to the previous sample (batch 15 in Fig. 6c) prepared under the same conditions except for the absence of EGDMA, the protrusions in Fig. 7b were less distinct (radius ratio $\alpha = 0.76$, contact angle is $29^\circ \pm 5^\circ$). This indicates that even a small amount of the cross-linker has a strong effect on the formation of the protrusion.

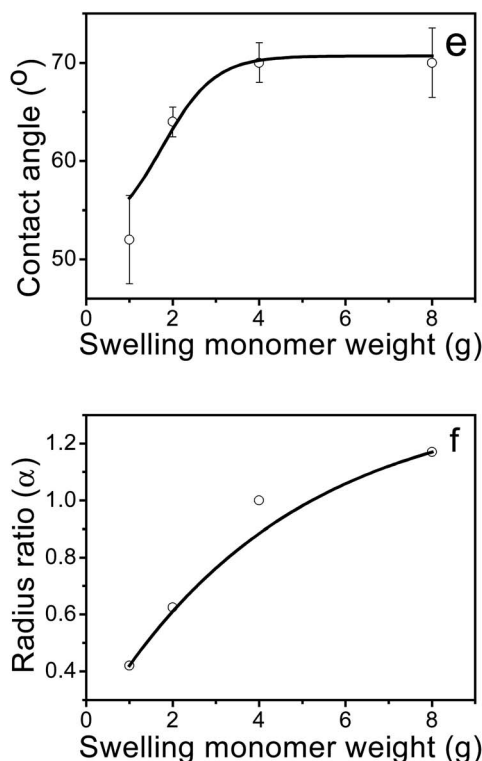
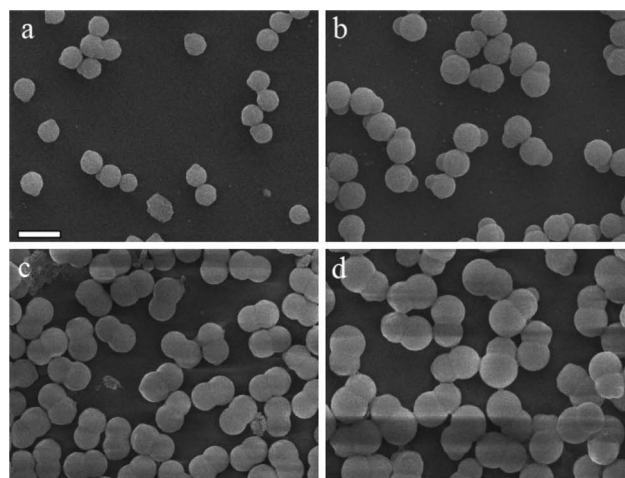


Fig. 6 SEM micrographs of non-spherical PMMA particles swelled by different amounts of MMA, which changed the geometries of the resulting particles (seeds are core-shell cross-linked (the addition of the cross-linker started at 1.5 h and ended at 3.5 h of the reaction) PMMA spheres with 2 wt% cross-link density) (a) 1 g (batch 14 in Table 1); (b) 2 g (batch 9); (c) 4 g (batch 15) and (d) 8 g (batch 16), and the corresponding contact angle (θ) and radius ratio (α) of non-spherical particles as a function of swelling monomer mass (open circles are the experimental data points and the solid lines are a guide to the eye) are in (e) and (f). The scale bar is 2 μm .

Examples of use in real space model studies

To make the non-spherical PMMA particles suitable for confocal microscopy studies, the particles were fluorescently labeled by either a pre- or post-labeling treatment as mentioned above. Results are shown in Fig. 8a and b. The addition of a dye (CAS) in the swelling monomer did not have a significant effect on the

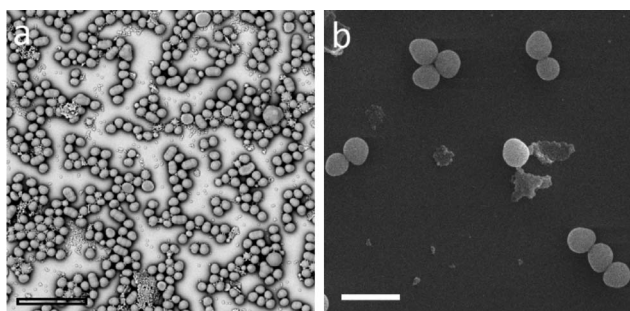


Fig. 7 SEM micrographs of non-spherical PMMA particles were fabricated under various parameters (a) 0.5 wt% of stabilizer (PVP, batch 17), (b) EGDMA (2 wt% based on swelling monomer, batch 18) used as a co-swelling monomer, core-shell cross-linked particles were used as seeds (the cross-link density is 2 wt%) and the amounts of the swelling monomer were 2 g in (a) and 4 g in (b), respectively. The scale bars are 10 μm and 2 μm in (a) and (b), respectively.

formation of the resulting dumbbell shaped particles. Compared to the pre-labeling technique, the dye brought into the polymer phase *via* a post-labeling approach (for details see Experimental part) was easily removed, because the dye was just physically adsorbed by the particles. Just by rinsing the dyed particles which were produced by the post-labeling method with a good solvent for the dye (like ethanol), the dye could readily be removed. Subsequently, these non-fluorescent particles could be fluorescently labeled back by simply repeating the post-labeling treatment. In order to quantitatively study the phase behavior of these non-spherical particles in concentrated dispersions in 3D, light scattering needs to be reduced by dispersing the particles in a refractive index matching solvent (like decalin and/or CHB). Successful transfer of the particles from a polar to an apolar solvent (dielectric constant $\epsilon \sim 2$ like: hexane and decalin) or somewhat more polar but still not too polar solvent ($\sim 2 < \epsilon < \sim 10$) like cyclohexyl bromide (CHB) was achieved by modifying the approach developed by the group of Behrens,²⁵ in which a nonionic surfactant (Span 85) is used. In the solvent CHB, dumbbell particles behaved almost as hard particles, which was caused by not only the creation of sufficient charge on the PMMA to create enough particle repulsion, but also enough ions in the liquid to cause the Debye-Hückel screening length to be short compared to the particle size. The density difference between the solvent (CHB, $\rho \approx 1.33 \text{ g cm}^{-3}$) and particles ($\rho \approx 1.18 \text{ g cm}^{-3}$) caused the particles to float up and gather at the interface of CHB and air. As a result, densely packed dumbbell particles were observed at the interface (Fig. 8c). Note that the particles were aligned side-by-side as in Fig. 8c. Alternatively, randomly oriented dumbbell particles were observed at a lower volume fraction of the particles as shown in Fig. 8d. Unfortunately, only liquid and therefore short-ranged ordered structures were found in the bulk in both cases. On the other hand, when the particles were dispersed in more apolar solvents, such as hexane and decalin, the particles carried not only a significant amount of electric charge but in addition the screening length was several micrometers long, as can be seen from the long range repulsion in Fig. 8e and f. Interestingly, the charged dumbbells showed positional order but orientational disorder in both hexane and decalin, that is, they formed so-called plastic crystals,^{37,38} as shown in Fig. 8e and f. This interesting structure is described in more detail elsewhere.³⁹

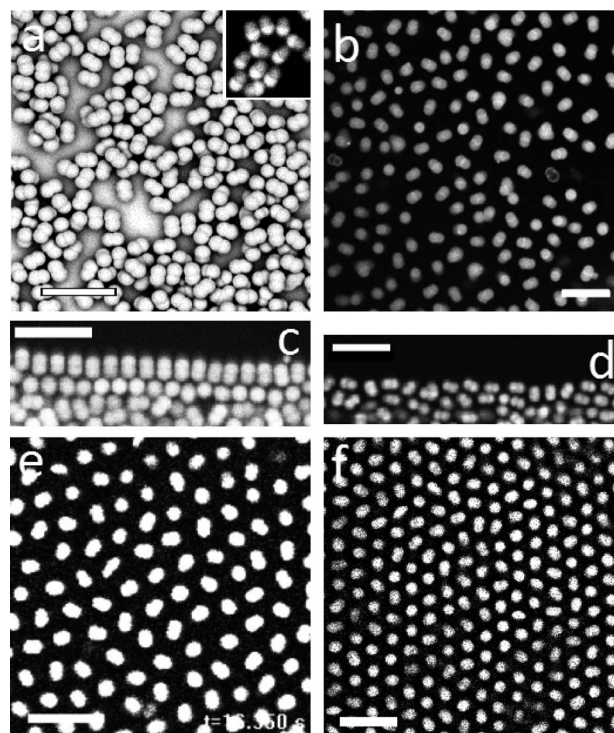


Fig. 8 Scanning electron microscopy (SEM) and confocal micrographs of dyed dumbbell particles: (a) SEM micrograph of fluorescent dumbbell particles (CAS dye) labeled during re-polymerization (pre-labeling), the inset is the corresponding confocal micrograph and (b) confocal micrograph of fluorescent dumbbell particles (RAS dye) labeled after re-polymerization (post-labeling). Confocal micrographs of fluorescently labeled dumbbell particles (stabilized by Span 85 of a concentration of 50 mM) sedimented at the interface of air and CHB, (c) a higher concentration of particles and (d) a lower concentration of particles. Confocal micrographs of dumbbell particles stabilized by Span 85 (50 mM), (e) in hexane and (f) in decalin. All scale bars are 10 μm .

We end with a demonstration of how the as-synthesized particles can be used in a second self-assembly step in which electric fields are used to direct the particles into strings and how a heating step makes the links between the anisotropic particles permanent according to a slight modification of a procedure recently developed in our group.^{29,32} Suspensions consisting of monodisperse non-spherical PMMA particles dispersed in the polar solvent formamide were introduced into a capillary cell with a pair of wires running through the length serving as electrodes. Upon application of a high frequency AC electric field, the induced dipole moment among the particles led to their assembly into strings parallel to the field, and particles were in a head-to-tail arrangement ($E_{\text{rms}} = 0.05 \text{ V } \mu\text{m}^{-1}$, $f = 1 \text{ MHz}$ where E_{rms} is the root-mean-square electric field strength and f is the frequency).³⁸ The electrical field was maintained for 2 h and then switched off (details see ESI†). We noticed that the capillary became rather hot during this time, but not so hot that it caused the boiling of formamide (boiling point is 210 $^{\circ}\text{C}$). After removing the field, more than 80% of the dispersion was converted to permanent strings with a broad distribution in lengths. The permanent bonding was probably caused by the high temperature, similar to the annealing process used to attach PMMA particles to each other in ref. 29, 32, 40 and 41. The

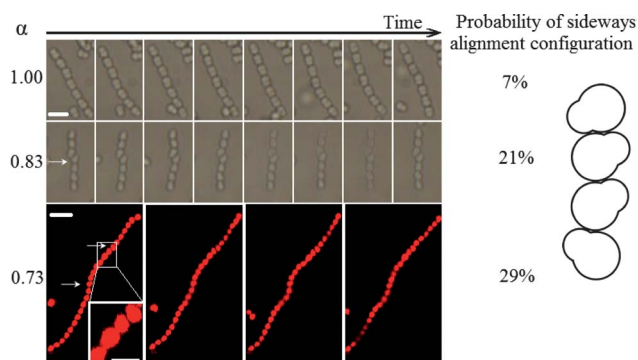


Fig. 9 Time-lapse optical and confocal micrographs of semi-flexible colloidal polymer chains made of non-spherical PMMA particles with different radius ratios α in formamide. The arrows point out the rigid joints in the chains formed by a non-parallel alignment of two neighboring particles. All scale bars are 5 μm except in the inset where it is 2 μm .

chains were not rigid but semi-flexible, similarly to what was observed for strings of the PVP coated PS sphere.³² Fig. 9 shows a time lapse of their Brownian movements. It is clearly seen that with decrease of α , a larger fraction of particles align sideways (see the frequency of sideways alignment configuration of non-spherical particles in Fig. 9). This tendency is in good agreement with computer simulation results.⁴² Moreover, we observed that the chain was much more rigid at such points (shown by arrows in Fig. 9). This is reminiscent of flexible polymer chains in which double bonds may be inserted to form local rigid connections and is presently under investigation.

Conclusions

In summary, we demonstrated a novel approach for fabricating homo-phase snowman or dumbbell shaped PMMA particles by seeded emulsion polymerization. The presented technique allows for precisely tuning the size of the newly formed polymer protrusions by localizing the cross-linker in an outer shell of the seed spheres, and adjusting the swelling monomer content. Moreover, making use of homogeneously cross-linked seeds readily extended this method for making snowman shaped particles to a method for making particles with a tunable roughness. These anisotropic particles were made suitable for real space studies with confocal microscopy by fluorescent labeling and a transfer procedure to apolar index-matching solvents. Electric field driven assembly of these particles into permanently bonded, semi-flexible chains was demonstrated as well.

Acknowledgements

The authors thank Hans Meeldijk for assistance with SEM measurements, Johan Stiefelhagen for helpful discussion, and Marlous Kamp for critically reading this paper. This research was supported by Nanodirect FP7-NMP-2007-SMALL-1, project 213948.

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