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11, 3589

Surface morphology control of cross-linked polymer particles *via* dispersion polymerization

Bo Peng* and Arnout Imhof*

Cross-linked polymer colloids (poly(methyl methacrylate) and polystyrene) with diverse shapes were prepared in polar solvents (ethanol, methanol and water) *via* dispersion polymerization, in which a linear addition of the cross-linker was used during reaction. Apart from spherical particles we found dented spheres or particles covered with nodules, or a combination of both. A comprehensive investigation was carried out, mainly concentrating on the effect of the experimental conditions (e.g., the addition start time and total addition time, cross-linker density and the solvency of the solvents) on particle morphologies. Consequently, we suggest a number of effective ways for the synthesis of regular (spherical) colloidal particles through maintaining a relatively low concentration of the cross-linker during the entire reaction, or forcing the co-polymerization (of monomer and cross-linker) locus to the continuous medium, or using a high quality or quantity of the stabilizer. Moreover, the size of the particles was also precisely manipulated by varying the polarity of the solvents, the concentration of the cross-linker, and the amount and average molecular weight of the stabilizer. In addition, the formation of the heavily dented particles with a very rough surface prepared under a pure or oxygen-‘contaminated’ nitrogen environment was monitored over time. The results accumulated in this article are of use for a better understanding of the mechanism of the polymerization and control over the structure and property of polymer particles.

Received 13th March 2015,
Accepted 16th March 2015

DOI: 10.1039/c5sm00606f

www.rsc.org/softmatter

Introduction

Over the past quarter of a century there has been a strong interest in the synthesis of polymer particles with a narrow size distribution in the micro- or sub-micrometer range because they are used in many applications in a variety of fields that include inks and coatings, chromatography, protein synthesis, biomedical analysis, and medical diagnostics.^{1–7} Particles with sub-micrometer dimensions are most commonly prepared by emulsion or surfactant-free emulsion polymerization. The second approach is particularly effective for preparing functional polymer particles with a very narrow size distribution, with typical diameters in the range of 400–800 nm.^{8–10} Based on the uniform products from surfactant-free emulsion polymerization, micro-sized particles can be made either by the seeded emulsion polymerization developed by Branford and Vanderhoff¹¹ or the activated swelling and suspension polymerization method proposed by Ugelstad *et al.*¹² The ‘dynamic swelling method’ developed by Okubo¹³ is also possible. However, extra time and effort have to be devoted to the separation of the desired products from the mixture due to these multi-step synthesis strategies. Dispersion polymerization is

a relatively simple alternative approach and the resulting products are monodisperse both in size and shape, and the yield can be readily scaled up.^{14–24}

Dispersion polymerization is defined as a radical polymerization reaction in which the monomer is soluble, but the polymer is not. The starting reaction mixture of the dispersion polymerization system is a clear, single phase solution. The polymer begins to precipitate as it is formed. Its mechanism has been widely studied in the 1960s and 1970s and described in detail by Barrett.¹⁴ It is believed to consist of two major stages, that is, nucleation and growth.^{25–28} During nucleation, the initiator decomposes, and the free radicals liberated start reacting with monomers to form oligomer radicals. When the oligomers become sufficiently large, they precipitate from the solvent to form nuclei that are protected by stabilizer. In the second stage, the initial particles swell slightly so that the monomer and initiator are absorbed into the particles. Each particle itself behaves like a small reactor. When all of the monomer has been consumed, the polymerization is complete. In principle, the nucleation stage sets the size distribution and the number of the particles, while in the particle growth stage, unless the reaction conditions are drastically changed, no more nuclei are generated and only particle growth occurs. Dispersion polymerization differs from precipitation polymerization in that it is carried out in the presence of a second soluble polymer as a steric stabilizer. The steric stabilizer becomes attached to the surface of

Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands.
E-mail: pengbo006@gmail.com, A.Imhof@uu.nl; Web: <http://www.colloid.nl>

the precipitating polymer, and stabilizes the precipitate in the form of micron-sized particles.^{14–16,20}

Traditional dispersion polymerization involves a single step reaction with a simple synthesis protocol in which all the reactants are mixed and heated, and often leads to particles with an exceptionally narrow size distribution. The preparation of monodisperse homo-polymer particles in dispersion polymerization has been extensively studied, especially for polystyrene (PS)^{16–18} and poly(methyl methacrylate) (PMMA).^{19,20} Typical reaction conditions consist of monomer and poly(vinyl pyrrolidone) (PVP) as a polymeric stabilizer dissolved in ethanol for PS or methanol for PMMA, and the system is heated in the presence of a free radical initiator. As a result, monodisperse particles are obtained. However, the corresponding co-polymerization reactions are much more troublesome.^{15,16,22} One of the biggest challenges is the synthesis of the cross-linked particles, because the cross-linker has bi-functional vinyl groups (usually divinylbenzene (DVB) is used for the PS system and ethylene glycol dimethacrylate (EGDMA) for the PMMA system).^{16,19} The cross-linker enables the linear polymer chains to branch, leading to a more rigid polymer network. This will hinder a 'healthy' growth of the polymer particles. There are many articles in the literature to attest to the fact that dispersion polymerization fails when cross-linker is present.^{16,19,25–29} Many factors, such as the type and concentration of the monomer, co-monomer, stabilizer, solvent, and initiator, affect the morphology, size and size distribution of the resulting particles. Although several publications have pointed out ways to improve this situation, no full solution has been demonstrated so far.^{28,30,31} Thomson *et al.*^{29,30} reported that monodisperse cross-linked PS spheres could be obtained with less than 0.2 wt% of cross-linker (DVB) present in the initial charge. However, larger amounts of up to 1% DVB could only be incorporated by incremental addition over 7 h after the start of the polymerization. Then, mainly by varying the addition start time, a series of interestingly shaped stable PS particles was obtained: these contained one or more dimples, or were covered by nodules, or both. The relationship between the diverse morphologies and the variation of the addition start time was explained in terms of a more restricted mobility of the stabilizer when cross-linker is added.^{29,31} Moreover, Dullens *et al.*^{27,28} circumvented this difficulty, which they believed was mainly caused by the interference of the cross-linker during the sensitive nucleation stage, by feeding in the cross-linker (EGDMA) during the relatively robust particles growth stage. As a result, core-shell cross-linked (up to 6 wt% based on monomer mass) PMMA spheres of a good uniformity with a smooth surface were obtained. Oddly shaped particles occasionally appeared when a high concentration (for example 6 wt%) of the cross-linker was used. A similar strategy was also adopted by Song *et al.*^{25,32} in the synthesis of core-shell cross-linked PS particles. However, most articles focused on the synthesis of 'regular' spheres. Relatively few words were spent on the description of anomalous results. A particular and deep investigation on the variation of the shape and surface morphology of the polymer particles is still highly desired, not only because it will guide us to a better understanding of the formation of the polymer particles in dispersion polymerization, but also because particles with a more complex shape and structure can be designed this way.

These particles may then be used in various assembly methods. For example, particles with spherical dimples may spontaneously form chains when packed closely together,³³ or when an attractive depletion force is induced between them.³⁴ Moreover, controllable roughness has been shown to be an excellent way to modulate depletion attractions between particles,^{35,36} or parts of particles.³⁷

Recently, we developed a straightforward synthetic strategy for preparing monodisperse fluorescently labelled PMMA colloids with either a heterogeneous or a homogeneous cross-linked structure by simply varying the addition start time of the cross-linker.²⁶ We considered that dispersion polymerization was a two-step reaction in which the fundamental hypothesis was that the nucleation stage was short-lived but very sensitive to perturbation, whereas the particle growth stage was more robust. We were able to prepare monodisperse fluorescently labelled PMMA particles with a core-shell cross-linked structure by delaying the addition until the nucleation stage had completed, and particles with a homogeneously cross-linked structure by beginning to introduce the additives at a relatively low level before the nuclei had formed. Thus, highly cross-linked (as high as 10 wt% of cross-linker, based on the total monomer mass), yet stable PMMA spheres with a smooth surface were obtained.

In the present paper, we describe the circumstances under which our dispersion polymerization technique reproducibly yields particles with a deviating morphology, such as dented or wrinkled spheres and particles covered with nodules. This yields insight into the particle formation mechanism and caters to the need for non-spherical particles in materials science. The shapes are reminiscent to those obtained by Thomson *et al.*^{29,30} for PS in dispersion polymerization and Xu *et al.*³⁸ and Huang *et al.*³⁷ for PS in emulsion polymerization, and probably have a common mechanistic origin, although we arrive at a different formation mechanism.

Experimental section

Materials

All reagents used were of chemical grade unless mentioned otherwise. Methyl methacrylate (MMA, Aldrich) was passed over an inhibitor removal column (Aldrich). Styrene was eluted over a home-made inhibitor removal column which contained aluminum oxide (~150 mesh, Aldrich). After the inhibitor had been removed, MMA was stored in a refrigerator (~4 °C) not longer than one month, while styrene was used at once. Azo-bis-isobutyronitrile (AIBN, Janssen Chimica) was re-crystallized from ethanol before use and was also stored in the refrigerator. Ethylene glycol dimethacrylate (EGDMA, Sigma-Aldrich) and divinylbenzene (DVB, 80% mixture of isomers, Aldrich) were used as the cross-linking agents. Polyvinylpyrrolidone (PVP) with average molecular weights of 10 000 g mol⁻¹ (K-15, Sigma-Aldrich), 40 000 g mol⁻¹ (K-30, Sigma-Aldrich) and 360 000 g mol⁻¹ (K-90, Sigma) was used as the stabilizer. Methanol (Biosolve) and ethanol (J. T. Baker) were used as supplied. De-ionized water was used in all experiments and

was obtained from a Millipore Direct-Q UV3 reverse osmosis filter apparatus.

Procedures for particle synthesis

The cross-linked colloidal PMMA particles with various surface morphologies were synthesized *via* a modified method on the basis of our previous work.²⁶ Briefly, a solvent (or solvent mixture) consisted of methanol or ethanol (or methanol and de-ionized water) containing about 5 wt% (based on the total solvent mass) of the stabilizer (PVP). All monomer (MMA) together with 1 wt% (based on monomer) of initiator (AIBN), was added to two thirds of the solvent mixture (for detailed recipe, see Table 1). The polymerization was carried out in a 250 ml, three-necked flask equipped with a gas supply, a condenser, and a Teflon-coated stir bar. After bubbling nitrogen through the reaction system at room temperature for 30 min, the flask was immersed in a pre-heated silicon oil bath, maintained at 55 °C, and stirred at 100 rpm. The remaining one third of the solvent mixture was mixed with different amounts of cross-linker (EGDMA or occasionally DVB) and fed into the reaction vessel at a constant rate with the aid of a syringe pump. The detailed addition start time and total addition time can be found in Table 1. After the feed had finished, the reaction was allowed to complete for 24 h before cooling to room temperature.

Cross-linked PS particles were prepared in a similar way as the PMMA particles. Typically, 25 g of ethanol, 1 g of PVP (K-30), 5 g of styrene and 0.1 g of AIBN were placed in a 250 ml, three-necked flask equipped with a gas supply, a condenser, and a Teflon-coated stir bar. After a homogeneous solution had formed at room temperature by stirring at 250 rpm, a de-oxygenation process (N₂ was used) was carried out for half an hour. Subsequently, the temperature of the system was increased to 70 °C and the stirring speed was slowed to 100 rpm. Various amounts of cross-linker (DVB) were dissolved in a mixture of 25 g of ethanol and 0.5 g of PVP (K-30). The addition of these mixtures started after the polymerization reaction had run for a certain period (the details can be found in Table 2). The reaction was allowed to maintain at 70 °C for 24 h after the addition had finished.

Table 2 Preparation details of the cross-linked PS latices

Batch	Addition start time (h)	Total addition time (h)	DVB (wt%)	Remark
1	0	12	0.5	Spheres
2	0	12	1	Spheres
3	0	12	2	Spheres
4	0	12	4	Dented spheres
5	1	11	4	Lightly dented spheres
6	0	12	6	Heavily dented spheres

In order to remove the unreacted stabilizer and monomer, all products were washed by three cycles of centrifugation (a Hettich Rotina 46 S centrifuge, at 315g for 20 min) and re-dispersion (a ultrasonic bath, Branson 40 L) in methanol (for PMMA) or ethanol (for PS), and finally dispersed in methanol (for PMMA) or ethanol (for PS) at room temperature.

Characterization of the latex particles

In order to determine the size, polydispersity and surface morphology of the particles, scanning electron microscopy (SEM) was performed with a FEI Phenom scanning electron microscope. The samples were prepared by depositing a droplet of a diluted sample onto a glass slide and allowing the solvent to evaporate at room temperature. The samples were then sputter-coated with a layer of gold (Au) of 10 nm. A number-averaged particle radius (R) and its standard deviation (σ) were calculated on the basis of the surface area of the spheres. The polydispersity (δ) of the colloidal systems was defined as $\delta = \sigma/R$. For some cases of non-spherical particles, it was hard to determine their polydispersities. We just manually measured the size and standard deviation of spheres whose outlines roughly fitted those of the non-spherical particles, and then calculated the polydispersity of them.

Results and discussion

As mentioned earlier, a dispersion polymerization in which the main monomer co-polymerizes another (the co-monomer), in particular a cross-linking monomer (cross-linker), will often

Table 1 Preparation details of the cross-linked PMMA latices

Batch	Methanol (ml)	Addition start time (h)	Total addition time (h)	EGDMA ^a (wt%)	PVP ^c (g)	Remark
1	38.76	1.5	2	1	1.5	Dented spheres with nodules
2	38.76	0.5	4	1	1.5	Lightly rough spheres
3	38.76	1.5	4	1	1.5	Spheres
4	38.76	1.5	4	1 (DVB) ^b	1.5	Rough spheres
5	38.76	0	4	1	1.5	Rough spheres
6	38.76	0	10	1	1.5	Dented spheres
7	31.02 + 6.14 (water) ^d	0	10	1	1.5	Spheres
8	38.76	1.5	2	2	1.5	Dented spheres with nodules
9	38.76	1.5	2	2	3	Rough spheres
10	38.76	1.5	10.5	2	1.5	Spheres
11	38.76	1.5	10.5	2	1.5 (K-30)	Wrinkled spheres
12	38.76 (ethanol) ^e	1.5	10.5	2	1.5 (K-30)	Wrinkled spheres
13	38.76	1.5	10.5	2 (DVB) ^b	1.5	Slightly rough spheres

^a Based on MMA mass (2.5 g). ^b DVB was used as the cross-linker instead of EGDMA in batch 4 and 13. ^c PVP with an average molecular weight of 40 000 g mol⁻¹ (K-30) was used in batch 11 and 12, PVP with an average molecular weight of 360 000 g mol⁻¹ (K-90) was used in the other batches.

^d 6.14 ml of de-ionized water and 31.02 ml of methanol were used as the solvents. ^e Ethanol was used as the solvent instead of methanol.

lead to a poor result. In fact, the presence of a cross-linker (usually >0.5 wt% based on monomer mass) during the nucleation stage usually disturbs the formation of 'normal' nuclei. Nevertheless, our recent work shows that the presence of a cross-linker during the nucleation stage was possible, provided that its concentration was maintained at a relatively low level.²⁶ As a result, homogeneously cross-linked PMMA particles could then be successfully fabricated. Moreover, if the feed of the cross-linker was delayed to a point after the nucleation stage, highly cross-linked (as high as 10 wt%) spherical PMMA particles could also be prepared. Based on this knowledge, an adaptation of our previous method²⁶ was carried out not only on PMMA but also PS. In the following an exhaustive investigation on the varieties of morphologies of the cross-linked polymer particles obtained by varying different experimental parameters will be presented.

Effect of the feeding time

At first, in order to avoid a deleterious influence of the cross-linker on the initial nuclei, a polymerization was carried out by simply delaying the addition start time of the cross-linker to 1.5 h and continuing the feed for 2 h. Meanwhile, pure methanol was used as the solvent and the concentration of the stabilizer was maintained at ~ 5 wt% based on the solvent mass throughout the reaction. When 1 wt% (based on total monomer) of cross-linker was used (for details, see batch 1 in Table 1) in the reaction, particles with a number of large dents and covered with nodules were observed, as shown in Fig. 1A. As mentioned before, the nucleation stage is short and sensitive. In this case, after 1.5 h, the reaction was in the process of particle growth (the evidence for this can be found in the section on the formation mechanism discussion), which implies that the addition of the cross-linker during this period should lead to a core-shell structure. Indeed, the core-shell structure was confirmed by incorporation of a dye along with the cross-linker in our previous work.²⁶ If more cross-linker (2 wt%) was added into the system, fewer dents were present on the surface of the particle, as shown in Fig. 1C. However, the roughness of the surface increased somewhat.

To avoid a deformed surface, we carried out two more experiments in which the EGDMA solution was added continuously over a longer period of time: 4 h for the 1 wt% and 10.5 h for the 2 wt% case, keeping the addition start time at 1.5 h. In this way, the conversion of EGDMA was more evenly spread over the particle growth period (~ 24 h). As a result, cross-linked PMMA spheres with a smooth surface and a narrow size distribution were successfully synthesized (see Fig. 1B and D, respectively). Meanwhile, we observed a reduction in particle size when the cross-linker was added over a longer period: at 1 wt% of cross-linker the size decreased from 2.80 to 2.03 μm when the total addition time increased from 2 to 4 h. Similarly, at 2 wt% of cross-linker the size decreased from 2.93 to 2.43 μm when this time went from 2 to 10.5 h.

In a dispersion polymerization, all chemicals are dispersed homogeneously in the medium (in our case methanol) at the beginning. The monomer and initiator concentrations in methanol

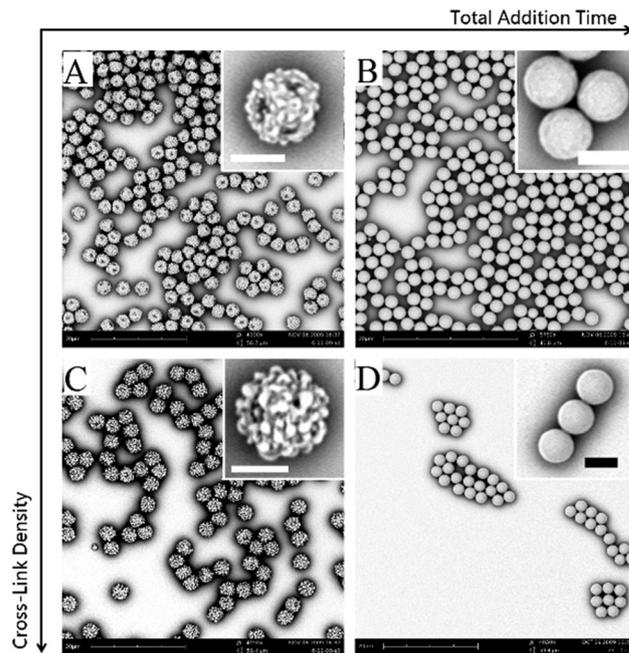


Fig. 1 SEM micrographs of core-shell cross-linked PMMA particles prepared by the post-addition method, with different cross-link densities and total addition times according to Table 1 (the cross-link density and total addition time increased in the direction of the arrows). Key: (A) batch 1, (B) batch 3, (C) batch 8, (D) batch 10. The cross-link densities in (A) and (B) were 1 wt%, and in (C) and (D) were 2 wt%, respectively. The total addition times were 2 h in (A) and (C), 4 h in (B) and 10.5 h in (D), and the addition start time was 1.5 h in all the cases. The scale bars are 20 μm and the insets are 2 μm .

are high, so that the alcohol phase is a major locus of polymerization. The presence of the additive during the nucleation stage will play an unpredictable role in the formation of the nuclei. Therefore, we investigated the effect of the presence of the cross-linker at different stages by simply varying the addition start time. Fig. 2A shows the morphology of particles obtained when the cross-linker feed was started directly after the polymerization reaction had started and continued for 4 h. It is observed that many tiny protrusions are randomly distributed over the particle surface (rough surface) (see Fig. 2A). According to our experience in making regular particles, we extended the total addition time to 10 h. This will lower the cross-linker concentration during the nucleation stage while maintaining some degree of cross-linking in the particle cores. This resulted in particles with a smooth surface and a number of large dents, as shown in Fig. 2B. Alternatively, in order to avoid the perturbation of the sensitive nucleation stage altogether, the addition start time was postponed to 0.5 h (see Fig. 2C), and then further to 1.5 h (see Fig. 2D). This led to particles with increasingly smooth surfaces. In the case of a 1.5 h addition start time the particle surfaces were even completely smooth. The occurrence of particles with a rough or a smooth surface apparently stems from the presence of a high concentration of cross-linker during the sensitive nucleation stage. Therefore, one can infer that either a later addition time, or a longer total addition time, or both are beneficial for producing spherical particles with a smooth surface. On the

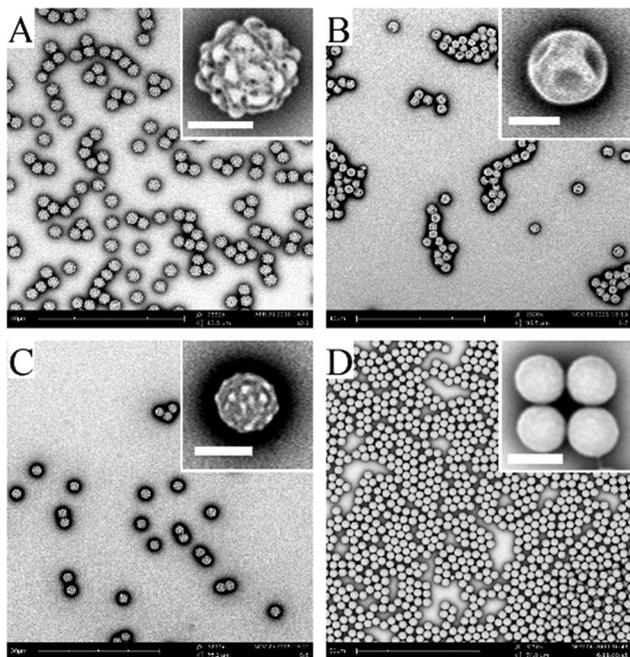


Fig. 2 SEM micrographs of cross-linked PMMA particles with a cross-link density of 1 wt%, prepared with different addition start times and total addition times according to Table 1. Key: (A) batch 5 (0–4 h), (B) batch 6 (0–10 h), (C) batch 2 (0.5–4 h), (D) batch 3 (1.5–4 h). The scale bars in (A) and (B) are 40 μm , in (C) and (D) are 30 μm , and the insets are 2 μm .

other hand, the occurrence of large dents in the particles seems to correlate less well with the cross-linker concentration during nucleation as they may occur both at an addition start time of 1.5 h (see Fig. 1A and C) and at a long total addition time (Fig. 2B). The shape strongly resembles that found after volume reduction of a soft sphere covered by a more rigid shell.^{34,38,39} These rough spheres are very interesting models in studies of self-assembly by means of depletion interactions,^{35,36} and can also serve as seeds for the production of anisotropic non-spherical particles, such as snowman or dumbbell-shaped particles with tunable roughness by seeded emulsion polymerization,^{37–41} or emulsion droplet confinement.^{42,43}

In order to test whether this behavior also applies to another polymer, we similarly produced polystyrene (PS) particles by dispersion polymerization in ethanol. A series of homogeneously cross-linked PS particles was fabricated by the continuous addition method in which the sum of the addition start time and total addition time was kept fixed at 12 h. The recipes are summarized in Table 2. When the concentration of the cross-linker was low (for instance 0.5 wt%, 1 wt% and 2 wt%, based on monomer mass), the obtained particles were smooth and spherical, and the size decreased with increasing cross-linker content. As shown in Fig. 3(A–C), when the cross-link density of the PS particles increased from 0.5 wt% to 1 wt% and further to 2 wt%, the corresponding diameters of the particles decreased from 1.26 μm to 1.20 μm and further to 1.01 μm . These results are in agreement with our previous work on the PMMA system,²⁶ that is, the rise of the cross-link density of the particles results in a size reduction of the particles. Additionally, the success in producing these regular, yet

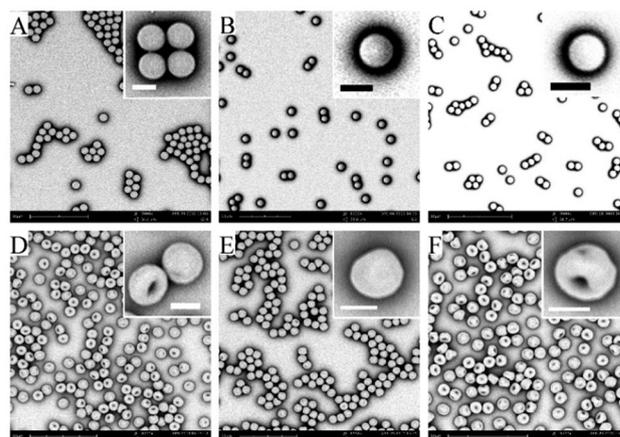


Fig. 3 SEM micrographs of cross-linked PS particles with different cross-link densities, which were prepared by a continuous addition of cross-linker (DVB) (details can be found in Table 2): (A) batch 1 (cross-link density was 0.5 wt%, based on the monomer mass); (B) batch 2 (1 wt%); (C) batch 3 (2 wt%); (D) batch 4 (4 wt%); (E) batch 5 (4 wt%); (F) batch 6 (6 wt%). The addition start time and total addition time were 0 and 12 h, respectively, in all samples except (E) where they were 1 and 11 h. The scale bars are 10 μm and the insets are 1 μm .

homogeneously cross-linked PS particles reveals that the presence of cross-linker at a low level does not disturb the formation of the nuclei, which is probably also applicable to other co-monomers.

However, further increasing the cross-linker content to 4 wt% led to PS particles with a large dent, as shown in Fig. 3D. On close inspection of Fig. 3D, one can observe that a few particles have a secondary, but much shallower dent. It implies that the ideal cross-linker concentration for PS particles with a single dimple is somewhere between 2 to 4 wt%. To obtain regularly shaped particles, the long total addition time (12 h) cannot be further increased because there would be nearly no initiator left over in the final stage. The alternative way is to delay the addition start time (1 h). This way, the obtained particles approach a more spherical shape, as shown in Fig. 3E. We expect that an even later addition start time (> 1 h) would lead to regular shaped particles. On the other hand, when the concentration of the cross-linker was further increased to 6 wt%, the obtained particles were heavily deformed with a large dent and one or two small shallow dimples. In this case, it appears that if the cross-linker concentration is high at the end of the reaction (for example the addition lasted 12 h), a rigid shell will be formed. Then subsequent shrinkage of the monomer-swollen particles causes buckling of the surface.^{44,45}

Effect of the stabilizer (PVP)

In dispersion polymerization, the stabilizer is usually regarded as an anti-coalescence barrier, which has an important influence on the size and size distribution of the particles. Actually, it affects the morphology of the particles as well. For dispersion polymerization in polar media, polyvinylpyrrolidone (PVP) is a highly efficient stabilizer. Initially, three types of PVP were used: PVP K-15, K-30, and K-90. Their corresponding average molecular weights are 10 000, 40 000 and 360 000 g mol^{-1} . The addition start time and total addition time were fixed at 1.5 and

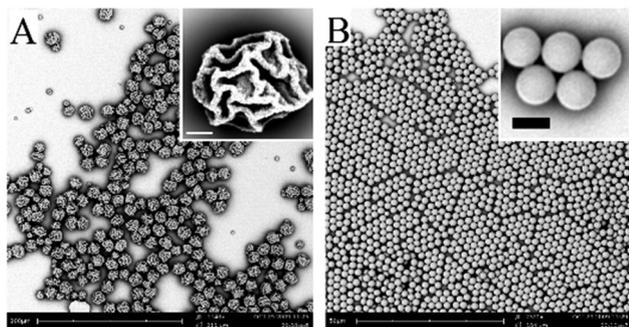


Fig. 4 SEM micrographs of cross-linked PMMA particles (cross-linker density 2 wt%) stabilized by different molecular weight PVP: (A) PVP K-30 (batch 11); (B) PVP K-90 (batch 10). The addition start time and total addition time were 1.5 and 10.5 h, respectively. The scale bars are 100 μm in (A) and 50 μm in (B), respectively, and 2 μm in the insets.

10.5 h, respectively. The batch in which PVP K-15 was used as stabilizer flocculated a few minutes after the addition of the cross-linker (EGDMA). PVP K-30 and K-90 produced stable systems, and the results are shown in Fig. 4. The K-30 stabilized particles were polydisperse (PD = 26.0%) with a severely wrinkled surface, while the K-90 case was monodisperse (PD = 2.1%) with a smooth surface. This clearly reflects the improved efficiency of higher molecular weight PVP in stabilizing the latex. On the other hand, PVP influenced the size of the particles too: the use of high-molecular-weight PVP led to a drop in size of the particles (K-30: $D = 7.89 \mu\text{m}$; K-90: $D = 2.43 \mu\text{m}$). During the polymerization, the PVP is adsorbed on the immature particle, forming a steric barrier. If PVP is not efficient enough to sterically stabilize the particles, a polydisperse system will be obtained as shown in Fig. 4A, or even worse, flocculation takes place as demonstrated by the batch with PVP K-15. The possible reasons for the formation of wrinkled particles will be discussed in the 'effect of solvent' section.

Subsequently, we focused on investigating the effect of the concentration of PVP K-90 on the surface morphology of the cross-linked PMMA particles. In most of the earlier work, the particle size was seen to decrease with increasing concentration of stabilizer.^{16,17,19} This is because nuclei become stable at an earlier stage, so that more are formed, leading to a smaller final particle size. Our results showed the same trend, reflected by a comparison of batches 8 and 9 in Table 1 (also see Fig. 5). There was an obvious size reduction (from 2.93 μm to 1.75 μm) when the concentration of PVP K-90 was increased from 1.5 to 3 g (the other experimental parameters were the same). Moreover, a high concentration of PVP helped to form spherical particles without heavy dents or a wrinkled surface, as shown in Fig. 5, which was probably caused by the size of the particles. As mentioned before, a high concentration of the stabilizer promotes the formation of smaller particles, which are more difficult to deform (*i.e.* more rigid) than large particles. On the other hand, the probability of cross-linker diffusing into the core of small particles is much higher than in big particles, which may lead to a more homogeneous cross-linking. Therefore, the possibility of forming heavy dents decreases with

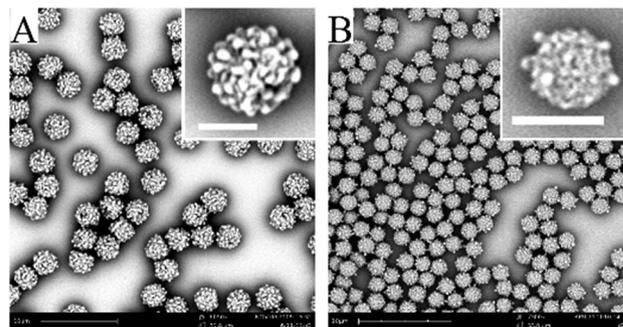


Fig. 5 SEM micrographs of cross-linked PMMA particles with a cross-link density of 2 wt% that were prepared with different amounts of stabilizer (PVP K-90): (A) 1.5 g (batch 8); (B) 3 g (batch 9). The addition start time and total addition time were 1.5 and 2 h, respectively. The scale bars are 10 μm and 2 μm in the insets.

increasing the concentration of the stabilizer. On close inspection of batch 9 in Fig. 5B, the roughness of the particles is non-uniform, with some unusually large protrusions being present. This is reminiscent of the formation of snowman-shaped particles developed by Sheu *et al.*⁴⁶ There, cross-linked seed particles were swollen by a monomer, after which elevation of the temperature led to a shrinkage of the cross-linked polymer network, forcing part of the swelling monomer to form a large number of tiny droplets.^{37,40,41} In our case, during the particle growth stage, the cross-linked immature particles similarly absorbed monomer from the medium, forming swollen particles. Then, as more cross-linker was absorbed by the particles the increase of the cross-link density may have induced a shrinkage of the polymer network, expelling some swelling monomer in the form of relatively big liquid protrusions. Although it is not the focus here, it is worth pointing out that the introduction of heterogeneous materials into polymerization can lead to a rough surface as well.^{47–50}

Effect of the cross-linker

Generally, the cross-linker interferes with the sensitive particle nucleation stage, causing flocculation and deformation. Therefore, in order to circumvent problems we delayed the addition of the cross-linker until the particle growth stage (1.5 h), when it was successively fed into the reaction medium. Two reagents (EGDMA and DVB) were used as to explore the effect that cross-linkers have on the morphology of the particles. When 1 wt% of EGDMA was used, it took a minimum of 4 h of slow addition to obtain spherical particles with a smooth surface and a narrow size distribution (see Fig. 6A). However, the use of the alternative cross-linker DVB produced spherical particles but with a surface covered with nodules under the same circumstances (see Fig. 6B). To investigate, the cross-link density was increased to 2 wt% (Fig. 6C and D). In order to obtain the same appearance (spherical shape and smooth surface) as in the 1 wt% case the total addition time had to be increased to 10.5 h. Again, slightly rough spheres were obtained when EGDMA was replaced by DVB. Thomson *et al.*³⁰ pointed out that commercial DVB was normally a mixture of *para* and *meta* isomers. For the *para* isomer in particular, the first

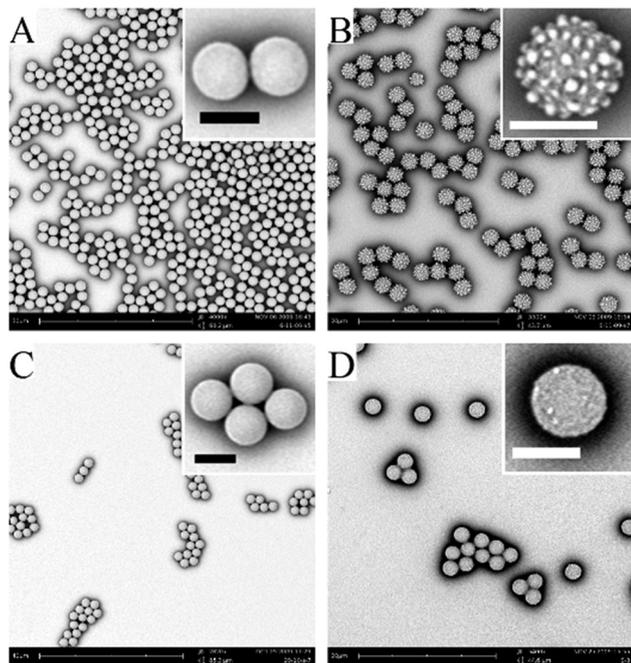


Fig. 6 SEM micrographs of cross-linked PMMA particles prepared by two cross-linkers and two cross-link densities: (A) 1 wt% of EGDMA (batch 3 in Table 1); (B) 1 wt% of DVB (batch 4); (C) 2 wt% of EGDMA (batch 10 in Table 1); (D) 2 wt% of DVB (batch 13). The addition start time and total addition time were 1.5 and 4 h in (A) and (B), and 1.5 and 10.5 h in (C) and (D), respectively. The scale bars are 30, 20, 40 and 20 μm in (A), (B), (C) and (D), respectively, and 2 μm in the insets.

double bond reacts faster than the second and also reacts more rapidly than monomer itself. The preferential consumption of *p*-DVB early in the reaction can be a complicating feature of the use of DVB as a cross-linker. Therefore, the result of the copolymerization of MMA with DVB is a tendency towards the congregation of *p*-DVB units in the MMA chains and a more even distribution of *m*-DVB isomers.⁵¹ After a double bond of DVB has reacted, the pendant vinyl group is less reactive than either monomer. For example, in the copolymerization of styrene with pure *p*-DVB and *m*-DVB, Hild and Rempp⁵¹ observed that the onset of gelation occurred much earlier and at a lower conversion in the *p*-DVB system, strongly suggesting that such pendant groups in the *p*-DVB are more reactive than their *meta*-substituted equivalents. These results point to early consumption of *p*-DVB as the cause of the enhanced deformation of the particle in the dispersion polymerization. In comparison, EGDMA has a slower reactivity in co-polymerization with MMA,⁵² and the reactivities of the two methacrylate groups of EGDMA are essentially identical. As a consequence, one expects that many of the problems encountered when DVB is used as a cross-linker will be suppressed for EGDMA.

Effect of the solvent

The choice of solvent plays an important role in the preparation of polymer particles in dispersion polymerization.^{14,16,19,26,28} At first, two kinds of polar solvents, methanol and ethanol, were compared. The obtained particles are shown in Fig. 7.

The sample (Fig. 7A) prepared in methanol is more heavily wrinkled than the one in ethanol (Fig. 7B). This is probably associated with a difference in their solvency for PMMA. In principle, the solubility of the precipitating polymer is inversely proportional to the difference between the solubility parameters of the dispersing medium and the polymer ($\delta_s - \delta_p$, where the subscripts *s* and *p* stand for solvent and polymer, respectively).^{53,54} This difference is smaller for PMMA ($\delta_p = 19.0 \text{ MPa}^{1/2}$) and ethanol ($\delta_s = 26.2 \text{ MPa}^{1/2}$) than for PMMA and methanol ($\delta_s = 29.7 \text{ MPa}^{1/2}$),⁴⁷ which implies that ethanol has a better solvency for PMMA, shifting the polymerization locus away from the particle phase to the solution. Therefore, when methanol was used as the solvent, the more of the polymerization took place within the particle phase, and more of the monomer and cross-linker were absorbed into the swollen particle increasing the risk of wrinkling of the surface. Additionally, the particles prepared in ethanol were smaller than those in methanol (see Fig. 7), which also suppressed the severely wrinkling.

Mixtures of methanol and de-ionized water have also been tried in our experiments. A pair of representative examples is shown in Fig. 8. The sample in Fig. 8A (batch 6) was prepared in a mixture of methanol/water (80:20 in weight), while the particles in Fig. 8B (batch 7) were synthesized in pure methanol. Due to the presence of the cross-linker during the nucleation stage, the particles in Fig. 8A possess a heavily dented shape. The addition of a poorer^{16,19,26} solvent (water) for PMMA led to smaller, but less deformed particles, because the lower solubility of PMMA causes the critical chain length to decrease, resulting in smaller particles (see the inset in Fig. 8B). As mentioned before, in a system of small particles deformation was less likely. On the other hand, from the point of the solubility parameter, an empirical solubility parameter (δ) of the mixture of methanol-water can be calculated by:⁵⁵

$$\delta = (v_m \delta_m^2 + v_w \delta_w^2)^{1/2}$$

where v_m and v_w are the volume fraction of methanol and water respectively. δ_m (29.7 $\text{MPa}^{1/2}$) and δ_w (48.0 $\text{MPa}^{1/2}$)⁵³ are the solubility parameters of methanol and water, respectively. When the mass ratio between methanol and water is 80:20,

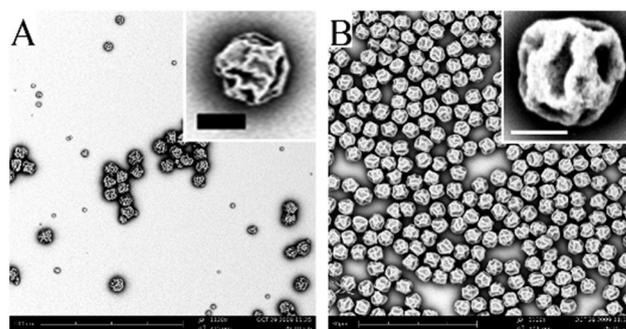


Fig. 7 SEM micrographs of wrinkled cross-linked (cross-link density is 2 wt%) PMMA particles fabricated in different solvents: (A) methanol (batch 11); (B) ethanol (batch 12). The addition start time and total addition time were 1.5 and 10.5 h, respectively. The scale bars are 100 μm in (A) and 30 μm in (B), and the insets are 5 μm in (A) and 2 μm in (B), respectively.

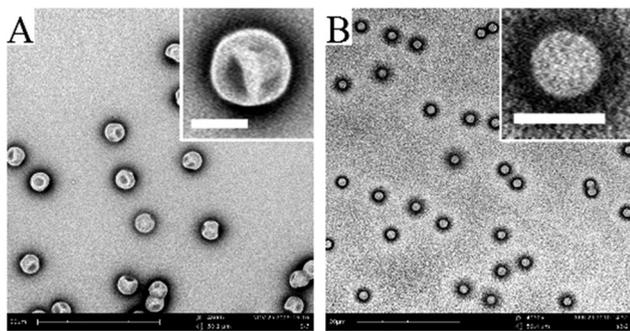


Fig. 8 SEM micrographs of 1 wt% cross-linked PMMA particles at different methanol/water mass ratios: (A) 100/0 (batch 6 in Table 1); (B) 80/20 (batch 7 in Table 1). The addition start time and total addition time were 0 and 10 h, respectively. The scale bars are 20 μm , and 2 μm in the insets.

the corresponding δ is 33.4 $\text{MPa}^{1/2}$, and the difference of the solubility parameter between the mixture and PMMA ($\delta - \delta_p = 14.4 \text{ MPa}^{1/2}$) is larger than that between methanol and PMMA ($\delta_s - \delta_p = 8.9 \text{ MPa}^{1/2}$). It follows that the polymerization locus is away from the medium into particles in the case prepared in the methanol–water mixture, which further indicates more EGDMA will be absorbed along by the particle phase, and in principle, the potential for the formation of the deformed particles is increasing. This is consistent with the results observed by Lacroix-Desmazes *et al.*^{24,56} However, the decrease in size may offset the increasing deformation tendency, and finally result in particles with less deformed surfaces. Combining all factors, one can conclude that the addition of a poor solvent for PMMA results in smaller and less deformed particles. However, further decreasing the methanol/water mass ratio to 70/30 led to coagulation, mainly because of the fast nuclei generation rate.²⁶

Formation mechanism discussion

Dispersion polymerization is used for the production of monodisperse polymeric particles in the micron size range. Both the size and size distribution of the particles can be well-controlled by varying the reaction parameters. Generally, the system is homogeneous prior to the polymerization. As soon as the polymerization is initiated by the decomposition of an initiator, oligomer chains grow in the continuous phase until they reach the critical chain length where they precipitate to form nuclei by a self-aggregative mechanism. The nuclei are unstable and can aggregate with each other. Concurrently, nuclei absorb the PVP-monomer graft stabilizer and become stable particles, which capture oligo-radicals and nuclei from the continuous phase. As long as enough mature particles are formed to capture all the oligomers and nuclei, no new particles are formed and the formation of the particles is completed. However, the addition of the cross-linker often perturbs the dispersion polymerization, leading to a diversity of irregular particles or bad results (*e.g.*, flocculation and agglomeration). In order to successfully produce regularly shaped particles, Dullens *et al.*^{27,28} suggested to feed in the cross-linker after the nucleation had finished for PMMA system in a polar medium. Song *et al.*^{25,32} used a similar strategy for the preparation of the cross-linked

PS particles. Both of them assumed that the nucleation stage was much more sensitive than the particle growth stage. We, too, circumvented potential problems induced by the addition of the cross-linker prior to the formation of nuclei, and selected the particle growth stage as the time during which the feeding of cross-linker was carried out. Nevertheless, we find that this does not yet guarantee that smooth, spherical particles are formed. A case in point is the synthesis of batch 1 (Table 1). During the synthesis of batch 1, the addition of the mixture containing cross-linker was started at 1.5 h and small samples were taken from the reaction flask at intervals. These samples were quenched in a large amount of ‘cold’ (room temperature) methanol, to prevent further growth of the particles. Subsequently, SEM was used to obtain details of the morphology, size and size distribution of the particles at different time marks. The results are summarized in Fig. 9A and 10.

In the first 1.5 hours (1.5 h is the addition start time), the particles retained their spherical shape, which also implies that the nucleation stage had been finished in 1.5 h of the reaction. At the 2.5 h mark, particles seem slightly deformed, but still with a smooth surface. 1.5 hours later (at the 4 h mark), some dimples were visible. We believe this is the time when the formation of the heavy dents started. At this point the cross-linker addition had already finished. At the 5.5 h mark, the dimples became deeper. As this is never observed in syntheses without cross-linker, the deformation must be induced by the copolymerization of the monomer with the cross-linker, which leads to the formation of a cross-linked shell.²⁶ In the final stages of the polymerization the monomer begins to run out and the monomer-swollen soft cores contract, leading to the formation of dents in the more rigid, cross-linked shell that are strongly reminiscent of buckling shapes found in deflated elastic shells.^{38,39,44,45} The tendency of elastic shells to buckle increases as the ratio of shell thickness to radius is lowered.⁴⁴ Feeding in the cross-linker over a more prolonged period therefore avoids the formation of a thin, highly cross-linked shell around a soft core and is therefore more likely to lead to spherical particles. By the same token larger particles are found to deform more readily. However, whether or not the cross-linker feed is started together with the polymerization has little or no influence on the occurrence of this type of deformation.

After the dimples had formed, we also observed the formation of a secondary structure, comprising of distinct bumps of uneven dimension dotted over the entire surface. Ultimately, particles with a lava-like texture were obtained. Apparently, after a sufficiently cross-linked shell has formed smooth growth

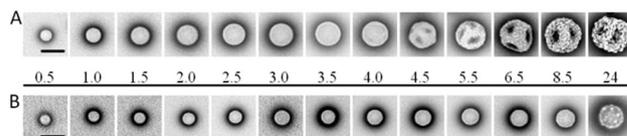


Fig. 9 The SEM micrographs of the formation of the cross-linked (1 wt%) PMMA particles in time (A) in a pure nitrogen atmosphere (batch 1), (B) in an un-pure nitrogen atmosphere (batch 1). Scale bars are 2 μm , the same for all images.

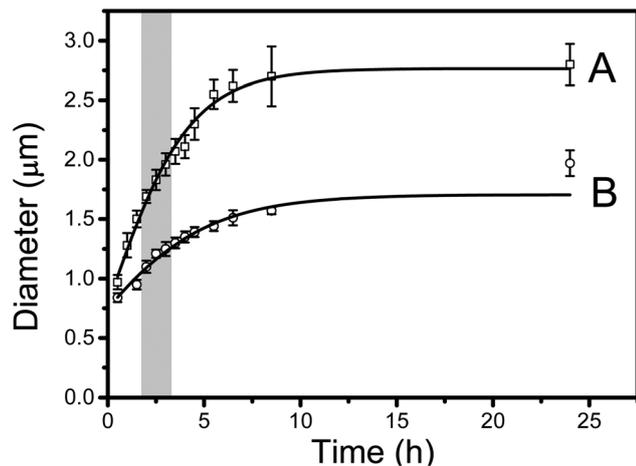


Fig. 10 The growth of batch 1 particles over time, (A) in a pure nitrogen atmosphere, corresponding to the case in Fig. 9A, (B) in a nitrogen atmosphere contaminated with oxygen, corresponding to the case in Fig. 9B. The gray region shows the addition of the cross-linker, which starts at 1.5 h and ends after 2 h. The open squares and circles are the experimental data points, and the solid lines are guides to the eye.

of the particle is impeded. Swelling of cross-linked polymer colloids is often used to induce the formation of one or several large, monomer-filled protrusions, which are subsequently polymerized to produce dimer-shaped particles.^{37,40,41,46} In our work, as well as that of others who observed similarly shaped PS particles, this process of protrusion formation and solidification should constantly be at work and is probably responsible for the observed roughening of the particles. Addition of cross-linker early in the polymerization is expected to enhance this type of unstable growth. Indeed, we observe that smoother particles are formed as cross-linker addition is postponed or spread out over a longer period of time. And use of a cross-linker that polymerizes faster, such as DVB, is found to promote roughening. Note, that small protrusions are also present on the inner walls of the dents, from which we infer that the shell is homogeneously cross-linked. The formation mechanism we propose is different from that of Thomson *et al.*,^{29,30} who described the formation of these particles as being due to the inhomogeneity of the cross-linker in the shell of the particles and the immobilization of the steric stabilizer. Contrary to this, we believe the dimples stem from the contraction of a soft swollen core inside a rigid, uniformly crosslinked shell.

Thomson *et al.*'s paper²⁹ suggests ways for incorporating a high absolute quantity of DVB in a one-pot co-polymerization for PS spheres by decreasing the average length of the polymer chains. Inspired by these suggestions, we repeated the synthesis of batch 1, but allowed in a small volume (~ 1 ml) of air to 'pollute' the pure nitrogen atmosphere (~ 200 ml) during sampling. Samples taken during particle growth were examined with SEM (Fig. 9B). Particle diameters are summarized in Fig. 10. Air contains oxygen which can act as an inhibitor, terminating chain growth and lowering the conversion. This directly resulted in smaller particles. But the resulting lower average molecular weight and reduced cross-linking also

prevented the formation of dents and delayed the appearance of surface roughness.

Conclusions

The dispersion co-polymerization of monomer and cross-linker led to the production of several classes of polymethylmethacrylate (PMMA) colloids with a variety of morphologies. A linear addition of the cross-linker was utilized to avoid instability problems that have often been reported in literature. Despite this, particles with large dimples or with a very rough surface, or both, were often observed. Based on a variation of the addition start time, length of addition, type and amount of cross-linker, and solvent type we conclude that the origin of the large dimples lies in an elastic buckling instability during particle growth when a rigid, cross-linked shell is formed around a soft, monomer-swollen core. Surface nodules, on the other hand, appear to arise from an unstable growth consisting of protrusion formation and solidification taking place at the surface of particles with a cross-linked shell. Although such shapes have been observed before in the dispersion polymerization of polystyrene (PS), they have so far been attributed to different causes. However, as we obtain very similar PS particle shapes using our methods we expect their origin to be the same.

We outline ways to avoid irregular particle shapes, but our results may also be of use for the deliberate preparation of nonspherical and rough, yet monodisperse, particles, as these find increasing use in the assembly of materials from colloidal building blocks.

Acknowledgements

The authors thank Alfons van Blaaderen, Judith Wijnhoven and Johan Stiefelhagen for helpful discussion.

Notes and references

- 1 Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, 2000, **12**, 693–713.
- 2 J. Ugelstad, L. Soderberg, A. Berge and J. Bergstrom, *Nature*, 1983, **303**, 95–96.
- 3 Y. Chen, J. Au, P. Kazlas, A. Ritenour, H. Gates and M. Mc-Creary, *Nature*, 2003, **423**, 136.
- 4 B. Comiskey, J. D. Albert, H. Yoshizawa and J. Jacobson, *Nature*, 1998, **394**, 253–255.
- 5 A. N. Theodore and M. S. Chattha, *J. Coat. Technol.*, 1985, **57**, 67.
- 6 D. Yu, J. H. An, J. Y. Bae, D. Jung, S. Kim, S. D. Ahn, S. Kang and K. S. Suh, *Chem. Mater.*, 2004, **16**, 4693–4698.
- 7 M. Han, X. Gao, J. Z. Su and S. Nie, *Nat. Biotechnol.*, 2001, **19**, 631–635.
- 8 S. A. Chen and S. T. Lee, *Macromolecules*, 1991, **24**, 3340–3351.
- 9 E. Bourgeat-Lami, I. Tissot and F. Lefebvre, *Macromolecules*, 2002, **35**, 6185–6191.

- 10 D. Nagao, T. Sakamoto, H. Konno, S. Gu and M. Konno, *Langmuir*, 2006, **22**, 10958–10962.
- 11 E. B. Branford and J. W. Vanderhoff, *J. Appl. Phys.*, 1955, **26**, 864–871.
- 12 J. Ugelstad, K. H. Kaggerud, F. K. Hansen and A. Berge, *Makromol. Chem.*, 1979, **180**, 737–744.
- 13 M. Okubo and M. Tsujihiro, *US Pat.*, 4,996,265, 1991.
- 14 K. E. Barrett, *Dispersion polymerization in organic media*, Wiley-Interscience, New York, 1975.
- 15 S. Kawaguchi and K. Ito, *Adv. Polym. Sci.*, 2005, **175**, 299–328.
- 16 C. M. Tseng, Y. Y. Lu, M. S. El-Aasser and J. W. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem.*, 1986, **24**, 2995–3007.
- 17 K. P. Lok and C. K. Ober, *Can. J. Chem.*, 1985, **63**, 209–216.
- 18 A. J. Paine, W. Luymes and J. McNulty, *Macromolecules*, 1990, **23**, 3104–3109.
- 19 S. Shen, E. D. Sudol and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 1393–1402.
- 20 S. Shen, E. D. Sudol and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 1087–1100.
- 21 L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, S. Papworth and J. A. Waters, *Colloids Surf.*, 1986, **17**, 67–78.
- 22 K. Takahashi, S. Miyamori, H. Uyama and S. Kobayashi, *J. Polym. Sci., Part A: Polym. Chem.*, 1996, **34**, 175–182.
- 23 P. Lacroix-Desmazes and A. Guyot, *Colloid Polym. Sci.*, 1996, **274**, 1129–1136.
- 24 P. Lacroix-Desmazes and A. Guyot, *Polym. Adv. Technol.*, 1997, **8**, 601–607.
- 25 J.-S. Song, F. Tronc and M. A. Winnik, *J. Am. Chem. Soc.*, 2004, **126**, 6562–6563.
- 26 B. Peng, E. van der Wee, A. Imhof and A. van Blaaderen, *Langmuir*, 2012, **28**, 6776–6785.
- 27 R. P. A. Dullens, M. Claesson, D. Derks, A. van Blaaderen and W. K. Kegel, *Langmuir*, 2003, **19**, 5963–5966.
- 28 R. P. A. Dullens, M. Claesson and W. K. Kegel, *Langmuir*, 2004, **20**, 658–664.
- 29 B. Thomson, A. Rudin and G. Lajoie, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 345–357.
- 30 B. Thomson, A. Rudin and G. Lajoie, *J. Appl. Polym. Sci.*, 1996, **59**, 2009–2028.
- 31 M. T. Elsesser and A. D. Hollingsworth, *Langmuir*, 2010, **26**, 17989–17996.
- 32 J.-S. Song and M. A. Winnik, *Macromolecules*, 2005, **38**, 8300–8307.
- 33 M. Marechal, R. J. Kortschot, A. F. Demirors, A. Imhof and M. Dijkstra, *Nano Lett.*, 2010, **10**, 1907–1911.
- 34 S. Sacanna, W. T. M. Irvine, P. M. Chaikin and D. J. Pine, *Nature*, 2010, **464**, 575–578.
- 35 S. Badaire, C. Cottin-Bizonne and A. D. Stroock, *Langmuir*, 2008, **24**, 11451–11463.
- 36 K. Zhao and T. G. Mason, *Phys. Rev. Lett.*, 2007, **99**, 268301.
- 37 D. J. Kraft, R. Ni, F. Smalenburg, M. Hermes, K. Yoon, D. A. Weitz, A. van Blaaderen, J. Groenewold, M. Dijkstra and W. K. Kegel, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 10787–10792.
- 38 L. Xu, H. Li, X. Jiang, J. Wang, L. Li, Y. Song and L. Jiang, *Macromol. Rapid Commun.*, 2010, **31**, 1422–1426.
- 39 Y. Huang, J. Wang, J. Zhou, L. Xu, Z. Li, Y. Zhang, J. Wang, Y. Song and L. Jiang, *Macromolecules*, 2011, **44**, 2404–2409.
- 40 B. Peng, H. R. Vutukuri, A. van Blaaderen and A. Imhof, *J. Mater. Chem.*, 2012, **22**, 21893–21900.
- 41 B. Peng, A. van Blaaderen and A. Imhof, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4277–4284.
- 42 V. N. Manoharan, M. T. Elsesser and D. J. Pine, *Science*, 2003, **301**, 483–487.
- 43 B. Peng, F. Smalenburg, A. Imhof, M. Dijkstra and A. van Blaaderen, *Angew. Chem., Int. Ed.*, 2013, **52**, 6709–6712.
- 44 G. A. Vliegthart and G. Gompper, *New J. Phys.*, 2011, **13**, 045020.
- 45 J. Yin, Z. Cao, C. Li, I. Sheinman and X. Chen, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 19132–19135.
- 46 H. R. Sheu, M. S. El-Aasser and J. W. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 653–667.
- 47 J. Hu, S. Zhou, Y. Sun, X. Fang and L. Wu, *Chem. Soc. Rev.*, 2012, **41**, 4356–4378.
- 48 M. Chen, L. Wu, S. Zhou and B. You, *Macromolecules*, 2004, **37**, 9613–9619.
- 49 M. Chen, S. Zhou, B. You and L. Wu, *Macromolecules*, 2005, **38**, 6411–6417.
- 50 Y. Sun, Y. Yin, M. Chen, S. Zhou and L. Wu, *Polym. Chem.*, 2013, **4**, 3020–3027.
- 51 G. Hild and P. Rempp, *Pure Appl. Chem.*, 1981, **53**, 1541–1556.
- 52 R. H. Wiley and E. E. Sale, *J. Polym. Sci.*, 1960, **42**, 491–500.
- 53 J. Burke, *AIC Book Pap. Group Annu.*, 1984, vol. 3, pp. 13–58.
- 54 Y. Almog, S. Reich and M. Levy, *Br. Polym. J.*, 1982, **14**, 131–136.
- 55 A. J. Paine, *Macromolecules*, 1990, **23**, 3109–3117.
- 56 P. Lacroix-Desmazes and J. Guillot, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 325–335.