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Cite this: DOI: 10.1039/c0xx00000x

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## COMMUNICATION

## Synthesis of soft colloids with well controlled softness

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

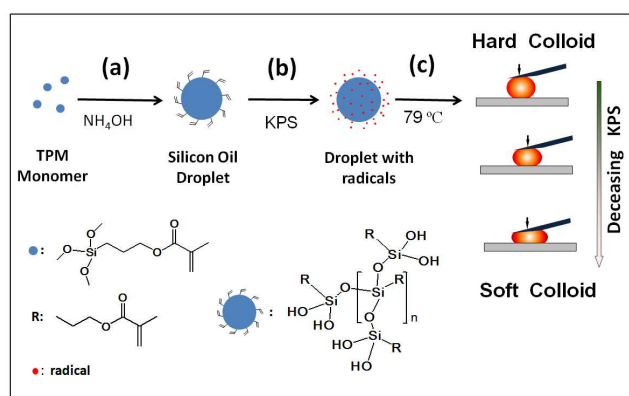
5 We report a novel method to prepare soft colloids with well controlled softness. The softness of the colloids was characterised by atomic force microscopy and rheometry. Possible applications of such soft colloids in uniform particle coating are demonstrated.

Soft colloids, such as star polymers and microgel particles, possess intriguing properties of both polymers and conventional hard colloids, including deformation,<sup>1</sup> stimuli-responsiveness and tunable rheological properties.<sup>2,3</sup> Due to these features, soft colloids have found wide applications in drug release,<sup>4,5</sup> stimuli-sensing,<sup>6</sup> and viscosity modifier,<sup>7</sup> to name a few. In addition, soft colloids display unprecedented complex condensed structures,<sup>8,9</sup> and have become new model systems to mimic the phase behavior of atoms and molecules.<sup>8,9</sup> Following the quest in synthesis and application of soft colloids, here we report a novel method for synthesising soft colloids with well controlled softness. And we demonstrated that, for the first time, soft colloids can suppress the undesirable coffee-ring effect,<sup>10,11</sup> a ubiquitous phenomena in everyday life (coffee stain) as well as in print and coating industries in which colloid deposition plays the crucial role.

Generally, it is difficult to synthesise soft colloids, and it is even more challenging to synthesise soft colloids with well controlled softness. There have been only a few attempts to produce soft colloids, for example, core-shell polymerisation,<sup>12,13</sup> microfluidics<sup>14</sup> and polymerisation with different cross-linkers.<sup>15</sup> Nevertheless, these techniques have some drawbacks, including: (1) sophisticated procedures as in core-shell polymerization, (2) low-throughput production and large particle size, usually in microfluidics fabrication, and (3) lack the ability of well control the softness and/or the monodispersity of the colloids. These drawbacks have greatly limited the application of soft colloids.

In this paper, we break through these limitations, and synthesise soft colloids by emulsion polymerisation of silicon oil droplets, in the presence of different amounts of initiator (Fig. 1). Firstly, stable, monodisperse silicon oil droplets are prepared by hydrolysis and condensation of silane. Then the as-obtained silicon oil droplets are polymerised with the different amounts of initiator. The diffusion of water-soluble initiator into the monomer oil droplet offers an unexpected way of control the polymerisation reaction. By systemically adjusting the amount of initiator, we can prepare colloids with well controlled softness. Furthermore, with emulsion polymerisation, a batch production method in particle synthesis industries, our method has large-scale production ability, which is crucial for practical applications. The as-synthesised soft colloids show intriguing properties of

suppressing coffee-ring effect. In addition, the soft colloids contain functional double bonds on their surface and therefore providing the possibility to introduce desired monomer/polymer onto the surface. For example, the colloids can be modified with thermo-sensitive poly(N-isopropylacrylamide), rendering the particles with thermo-responsive properties.<sup>16</sup> The method are outlined below and the experimental details are given in the *Supplementary Information*.

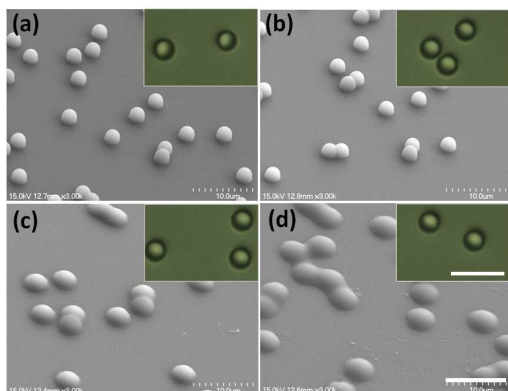


**Fig. 1** Schematic of the synthesis of colloids with various softness. (a) hydrolysis and polycondensation, (b) initiator decomposition and radical diffusion, and (c) polymerisation and particle formation. Insets are the chemical formulas of the monomer and the polymer.

The synthesis of the colloids with tunable softness proceeds in two steps: briefly, we first synthesise silicon oil-in-water emulsion, following the method described by Obey and Vincent.<sup>17</sup> 1.5 ml of 3-methacryloxypropyltrimethoxysilane (TPM) monomer was added to 30 mL of 0.475 M ammonium hydroxide solution (NH<sub>4</sub>OH) under vigorous stirring. Thus slow hydrolysis and polycondensation reaction of TPM led to the formation of TPM oligomers. Then, spontaneous emulsification of the oligomers system produced charge-stabilized silicon emulsion oil droplets.<sup>17,18</sup> The emulsion oil droplets were allowed to grow for 10 h on a rolling incubator. By varying the mixing ratio of TPM and NH<sub>4</sub>OH in this step, we can prepare the monodisperse particles with different sizes (see *Supplementary Information*). In the second step, we synthesise various soft colloids with emulsion

polymerisation. Firstly, 9 ml of  $2.2 \times 10^{-3}$  g/ml sodium dodecyl sulfate solution is mixed with 6 ml of silicon oil droplets emulsion. This mixture, together with different amounts of potassium persulfate (KPS) as initiator, is added to a reaction flask at room temperature ( $\sim 25$  °C). Then the temperature of the mixture is slowly increased to 79 °C at a rate of 5 °C/min. During this process, the KPS progressively and slowly decomposes to generate radicals. In addition, this slow process allows the radicals to diffuse and mixed with monomer in the oil droplet. The majority of the polymerization takes place at 79 °C, and the reaction lasts for 6 h to complete. Longer reaction time yields the same particles (see *Supplementary Information* for more discussions on the syntheses).

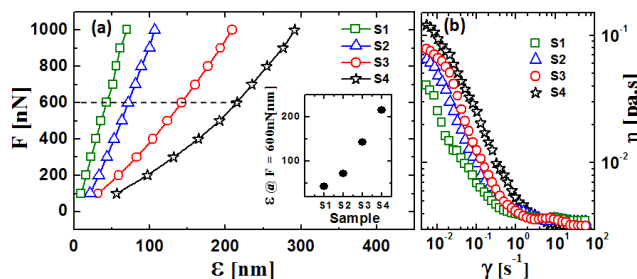
The basic mechanism of the polymerisation is the reaction of methacrylate groups from TMP with the radicals from initiator, KPS.<sup>17,19</sup> As the polymerisation proceeds, TMP forms cross-linked network and liquid droplets become solid particles. The degree of polymerisation is determined by the amount of initiator, which in turn determines the final softness of the colloidal particles. By systemically varying the amount of initiator, we synthesise a series of soft colloids with well controlled softness. It is found that the soft colloids collapse progressively more in the SEM images, Fig. 2a to Fig. 2d, indicating the particles become softer.



**Fig. 2** SEM images of soft colloids with various softness. From (a) to (d), the molar ratios of initiator to monomer are 0.3, 0.2, 0.1 and 0.05, respectively. The insets are bright-field micrographs of the soft colloids dispersed in water. The scale bars are 10  $\mu\text{m}$ .

Specifically, when the amount of initiator, KPS was large, many radicals from the initiator can react with the methacrylate groups of the silicon emulsion oil droplets. Therefore, the silicon oil droplets grow into dense network, and relatively hard S1 colloids are obtained (Fig. 2a). When lowering the concentration of the KPS, fewer radicals attacked the methacrylate groups of silicon emulsion oil droplets. The degree of the cross-linked polymer network was low. Thus, slightly softer S2 particles were fabricated (Fig. 2b). Further decreasing the amount of KPS, the cross-linked polymer network becomes even looser, producing other two softer particles: S3 and S4 particles (Fig. 2c-d). Regardless of the softness, all the soft colloids can be well dispersed in water, behaving as the typical repulsive colloidal spheres (Fig. 2 insets).

In order to quantitatively characterise the softness of the synthesised particles, we measured the elastic response of the particles using the established method of AFM force spectroscopy technique.<sup>20</sup> The method involves the press of particle with AFM tip and monitor the deflection of AFM cantilever (hence the particle deformation). From the AFM force-deformation curves and appropriate model, one can work out the modulus of the particles. From the force-deformation curve, a clear trend can be observed: increasing the softness of silicone particles decreases the resistance of particles to deformation (Fig. 3a). From S1 to S4, there is a significant increase of the deformation at the same force due to softness (see the inset in Fig. 3a). To further evaluate the mechanical properties of the particles, we deduced the modulus according to Hertz model, a typical interaction model for colloids. The Young's modulus of the S1, S2, S3 and S4 particles is 301.2 MPa, 161.9 MPa, 59.0 MPa and 35.7 MPa, respectively. These are between the modulus values of hard silica particles<sup>20</sup> and soft microgel particles,<sup>21</sup> but closer to the microgel. An approximately eight-fold decrease in the Young's modulus was observed from particle hardest particle, S1 to the softest particle, S4. These results quantitatively prove that the synthesised soft colloids have tunable softness (see *Supplementary Information* for details on the force-deformation measurements).

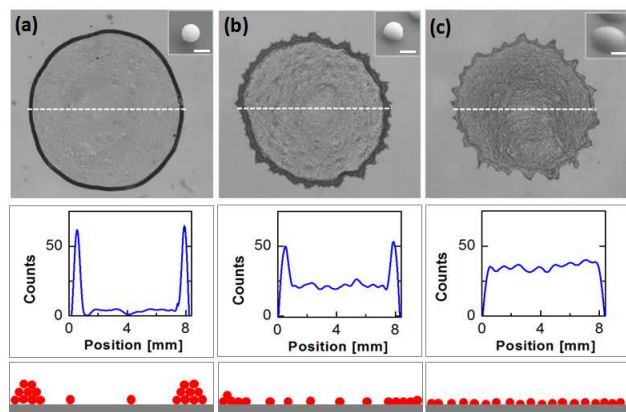


**Fig. 3** Effect of softness on mechanical and rheological properties of the particles, from sample S1 to S4, the softness increases. (a) AFM force-deformation curve, the inset is the deformation at force  $F = 600$  nN, showing the softest particle (S4) has the largest deformation. (b) Shear viscosities for suspensions of soft colloids with different softness.

We further characterise the softness of the colloids with rheometry. It is known that the suspension viscosity of hard and soft colloids are different.<sup>15,22</sup> Here the viscosity of dilute aqueous suspensions (2 % by weight) of soft colloids with different softness was obtained using a rotational rheometer (see *Supplementary Information* for details on rheological measurements). The viscosity plot shows the typical shear-thinning behavior of colloidal suspensions, i.e. the viscosity decreases with increasing shear rate (Fig. 3b). In the low shear regime, at a given shear rate, for example,  $\gamma = 10^{-1} \text{ s}^{-1}$ , the viscosity increase with increasing softness of the particles, which is consistent with the results from microgel colloids.<sup>15</sup> It is believed that the deformation of the soft particles and corresponding energy cost account for this behavior.<sup>15,22</sup> At high shear rate regime, the differences in viscosity among various soft colloids are minimized, as the shear-thinning effect is dominated and all the suspension viscosities reach the level of pure solvent, water.<sup>22</sup>

Colloids have the wide applications in paint, coating, and

ceramic industries. Typically, such applications require uniform coatings after the applied colloidal suspension is dried out. However, when a drop of liquid containing colloidal particles is dried on a substrate, it will leave a thin ring-shaped stain instead of a uniform coating. This phenomenon is known as the coffee-ring effect.<sup>10,11</sup> Adding surfactant can lessen the coffee-ring effect but also introduces impurities and leads to other complications to the colloidal system. Recently, ellipsoid-shaped colloids were found to effectively suppress the coffee-ring effect.<sup>23</sup> Here, we explored the possibility of eliminating the coffee-ring effect with soft colloids. We carried out drying experiments with three kinds of soft colloids with varying softness (Fig. 4).



**Fig. 4** Drying pattern of suspension of soft colloids, with softness of the colloids increases from (a) to (c). Top panel: bright-field micrographs. Middle panel: the profiles of particle distribution, obtain by performing the scans indicated by the dashed lines in the images. Lower panel: schematic side views of the distribution. The insets in the top panel are SEM images of the corresponding particle used in the drying experiments. Dimension of each image in the top panel is 6 x 6 mm and the scale bars in the insets are 2  $\mu\text{m}$ .

We found that hard particle showed the typical coffee-ring effect after drying, with particle deposited mainly near the edge of the droplet (Fig.4a). By contrast, the softest particle achieved a uniform deposition after drying (Fig.4c). There could be multiple mechanisms for this interesting and complicated phenomenon, for example, deformation and/or unique transportation behavior of soft colloids near three-phase contact line<sup>23-24</sup>. However, a conclusive explanation requires a systematical study, which is beyond the scope of this communication. Nevertheless, our results clearly demonstrate that the softness of particle can greatly affect the morphology of the coating, and more uniform coatings can be obtained by using softer particle. So tuning the softness of particles offers an effective way to suppress the undesirable coffee-ring effect.

In summary, we have presented a novel method to prepare polymeric colloids with well controlled softness. Compared to other methods, our approach has the advantages of simple procedures, large-scale production, and softness control ability. AFM and rheological measurements confirm that the soft colloids have tunable softness. Intriguingly, the soft colloids are found to form uniform particle coating when their suspension is dried. Therefore, they have potential applications in the paint and coating industries. In addition, colloids with various softness will

contribute as new models for the research of condense phases in chemistry, physics and material science.<sup>25</sup>

## Acknowledgements

This work was partially supported, the National Natural Science Foundation of China (Nos. 21174101, 1004143, 21374069), by the National Basic Research Program of China (No. 2012CB821500) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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