Supporting Information for

Capillary Force Driving Directional 1D Assembly of Patchy Colloidal Discs

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This PDF file includes:
Materials and Methods
Figures S1 to S14
References (38-40)
Materials and Methods:

Materials.
Styrene (St), polyvinylpyrrolidone (PVP, K-30), decane and tetraethyl orthosilicate (TEOS) were obtained from Sigma-Aldrich. The other chemicals we used were purchased from Sinopharm Chemical Reagent (Shanghai, China). 2,2'-azobisisobutyronitrile (AIBN, Reagent grade) was purified by recrystallization with methanol. Styrene was purified by passing through basic alumina column to remove the inhibitors. All other chemicals were of analytical grade.

Preparation of polystyrene (PS) particles:
1.54 g of PVP (K-30), 10.0 g of styrene and 0.1 g of AIBN were dissolved in 90 g of ethanol. The solution was bubbled with nitrogen for about 20 min and then stirred at 70 °C for 24 h. The obtained PS particles were washed in turn with ethanol and water and have an average diameter of 1.58 ± 0.05 µm. For 1.36 ± 0.03 µm PS particles, 1.54 g of PVP (Mn = 40000), 10.0 g of styrene and 0.1 g of AIBN were used. For 1.95 ± 0.04 µm PS particles, 1.54 g of PVP (K-30), 10.9 g of styrene and 0.1 g of AIBN were used. And for 2.85 ± 0.05 µm PS particles, 1.0 g of PVP (K-30), 13.7 g of styrene and 0.15 g of AIBN were used.

Preparation of theta-shaped PS disc dispersion:
The synthesis of theta-shaped PS disc dispersions was performed by following a reported procedure.30,35 0.25 g of PS seed particles, 0.0625 g of EHMA, 8.2 mg of AIBN, 0.1 g of PVP and 1.25 g of decane were added into 12.0 ml of mixed solvent of methanol/water (10/2), and the reaction mixture was deoxygenized with nitrogen flow for 10 min. The reaction was performed at 60 °C for 24 h. The formed droplets have an aspect ratio about 1.1 and the averaged diameter of PS discs is 2.20 ± 0.12 µm. And these droplets are called “theta-shaped PS disc droplets” and each droplet consists of a PS disc sandwiched by two attached decane droplets. The other PS disc dispersions were synthesized along a similar procedure.

Preparation of patchy PS disc dispersion with controlled liquid amount in the patches:
Typically, a given amount of anhydrous ethanol was slowly added into theta-shaped PS disc dispersions, and the dispersion was shaken immediately for several tens of seconds. The ratio of ethanol/methanol/water (E/M/W) was controlled to prepare PS discs containing different amount of decane in the patches. Two typical ratios are 2.4/1.0/0.2 and 6.0/1.0/0.2. The former was used for the 1D assembly via sedimentation, and the latter was used for the 1D assembly via centrifugation.

Silica coating of PS disc dispersion to prove the existence of decane on PS discs:30:
Three patchy PS disc dispersions were firstly prepared with E/M/W = 0.6/1.0/0.2, 2.4/1.0/0.2 and 6.0/1.0/0.2. The PS discs were separated from the mixed solvents by centrifugation and the supernatants were removed as much as possible. By this way, the decane dissolved in the continuous phase should
have been removed and only the decane attached on PS discs left. The precipitates were re-dispersed in 8.69 g of methanol containing 3.78 g of water, 0.25 g of CTAB, 0.625 ml of ammonia solution, and then 0.4 ml of TEOS was added. The reaction was performed at 30 °C for 1 h. When there is decane on PS discs, two hollow champers should be seen by TEM imaging after silica coating. That indeed is the case as shown in Figure S5 in this file.

1D assembly into colloidal chains by sedimentation:

10.0 ml of anhydrous ethanol was added into 5.0 ml of theta-shaped PS disc dispersion and the mixture was shaken for a few seconds. The new dispersion was concentrated by sedimentation so that the expected particle concentrations were obtained. The sedimentation time for concentrating was short so that no or only a few short chains formed. Once the short chains formed, the short chains were removed by sedimentation again to ensure the obtained dispersion containing only individual discs. The PS disc concentrations we used are 2.5 mg/ml to 15.0 mg/ml. Tetrabutylammonium chloride (TBAC) was added so that the salt concentration is 50 mM in the system. The volume of the dispersion is 1.0 ml and the sedimentation was done in a regular 2 ml centrifuge tube.

1D assembly into colloidal chains by (repeated) centrifugation:

500 µl of anhydrous ethanol was added into 100 µl of theta-shaped PS disc dispersion in a regular 2 ml centrifuge tube, and the mixture was centrifuged with a given centrifugal force and time. The precipitate was re-dispersed with the help of ultrasonic for a few seconds for repeated centrifugation.

Characterization

Scanning electron microscopy (SEM) imaging was performed in a field emission scanning electron microscope (FE-SEM, Hitachi S-4800), and the working voltage is 10 kV. Before measurements, the samples were dropped on to silicon wafer and sputtered with around 10 nm of Pt layer on a JFC-1600 auto fine coater (20 mA, 180 s).

Transmission electron microscopy (TEM) imaging was performed in a JEOL JEM-1011FS transmission electron microscope, operating at an accelerating voltage of 160 kV. The samples were firstly dispersed into a solvent and then dropped onto carbon-coated copper grid for measurements.

Optical microscopy was performed on an Olympus IX73 microscope that was equipped with a CMOS camera.

$^1$H NMR was performed in Bruker Advance III HD 400 MHz spectrometer and the solvent was Deuterochloroform.

Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM). The samples was covered a Pt layer ($25 \times 25 \times 1 \mu m^3$) by in situ ion beam-induced deposition (IBID). The Pt layer can protect the surface during slicing to achieve sharp upper edges and minimize curtaining artifacts. The FIB system (type Nanolab G3 CX) consisted of a dual beam unit equipped with an electron column and an ion column.
The ion column operated at accelerating voltages of up to 30 kV, gallium was used as the liquid metal ion source to produce cross-sections of the particles. SEM imaging conditions were kept low to prevent potential damage of the layer by the beam, typical imaging conditions were 2 kV and 0.21 pA.

The contact angle was measured on DSA 100 Drop Shape Analyzer. The volume of droplets is about 5-10 μl.

The average lengths of the formed chains were measured with open software ImageJ based on optical microscopy images. Typically, about 500 ~ 1200 chains were counted for each value of $L_{\text{chain}}$. 
Estimation of the capillary force between two colloidal discs:

The attractive capillary force between two colloidal discs can be expressed as the sum of two forces: one is the contribution from the interfacial tension acting on the contact line and another is the contribution from Laplace pressure across the curved interface.

The expression can be written as:

$$F_{cap} = 2\pi R \gamma \sin \theta + \pi R^2 \gamma \left(\frac{1}{r} + \frac{1}{l}\right)$$  \hspace{1cm} (1)

where $R$ is the radius of the interface area between the liquid (PEHMA decane solution) and colloidal disc, $\gamma$ is the interfacial tension, and $\theta$ is the contact angle. The radius $l$ of the neck of the liquid bridge is given by:

$$l = R + r \sin \theta - r$$  \hspace{1cm} (2)

and $d$ is given by:

$$d = 2r \cos \theta$$  \hspace{1cm} (3)

The values of the parameters used in our calculations: $R = 1.1 \ \mu m$ and the contact angle is taken as a constant $30^\circ$. The real contact angle was estimated to be between $15^\circ$ and $30^\circ$, which is estimated from the measurements of contact angles by using 33.0 wt.-% PEHMA decane solution wetting on PS-coated glass slides in the mixed solvents with E/M/W = 2.4/1.0/0.2 and 6.0/1.0/0.2. The pictures are shown Figure S12. The interfacial tension was estimated to be the order of tens of $\mu$N/cm by measuring the equilibrium interface curvature by mixing a PEHMA decane solution (33.0 wt.-% ) and the continuous phase (E/M/W = 6.0/1.0/0.2) with equal volumes.\cite{36}

Estimation of van der Waals force between two colloidal discs:

The van der Waals attractive potential between two semi-infinite surfaces is given by:

$$F = -\frac{A}{6\pi d^3}$$  \hspace{1cm} (4)

and $d$ is the separation, $A$ is calculated by the following expression by considering retardation effect.\cite{39}

$$A = A_{\text{non}}/(1+5.3d/100 \ \text{nm})$$  \hspace{1cm} (5)

where $A_{\text{non}}$ is taken as $1.2 \times 10^{-20}$ J, estimated by the Lifshitz theory.\cite{40}
Here the subscript 1 refers to PS phase, and 3 refers to the continuous phase, which is ethanol for simplification. The values of the parameters used in our calculations: $\varepsilon_1 = 2.55$, $\varepsilon_3 = 26$, $n_1 = 1.557$, $n_3 = 1.333$, $\nu_e$ is the main electronic absorption frequency in the UV and $\nu_e$ is taken as $2.3 \times 10^{15}$ s$^{-1}$, $h$ is Planck’s constant $6.626 \times 10^{-34}$ J.s. For the calculation of van der Waals force, we considered two pure PS discs as two semi-infinite surfaces with a parallel configuration with a separation $d$. 

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A_{\text{non}} = \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3h\nu_e (n_1^2 - n_3^2)^2}{16\sqrt{2} (n_1^2 + n_3^2)^{3/2}}
\]
Figure S1. Optical microscopy images of theta-shaped PS disc droplets (a) and patchy PS discs with two liquid patches (b,c). The ratios of ethanol/methanol/water (E/M/W) are 2.4/1.0/0.2 in (b) and 6.0/1.0/0.2 in (c). The images show that the particles are stable and do not form any aggregations. Scale bars are 10 μm in all images.

Figure S2. 1H NMR spectrum of PS, PEHMA and PS discs. The peaks (j) corresponds to the characteristic chemical shifts of the hydrogen atoms in benzene rings, and the peaks (e) corresponds to chemical shift of hydrogen atom of CH group in PEHMA. The mass ratio of PEHMA/PS for each PS disc was estimated by the formula:

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\frac{0.07}{1.66} \times \frac{198.3}{104.2} = 0.40
\]

Therefore, PEHMA content for each PS disc is 0.286.
Figure S3. SEM images of the dried patchy PS discs on silicon wafer. The ratios of ethanol/methanol/water (E/M/W) are 2.4/1/0.2 in (a) and 6.0/1/0.2 in (b,c). The halos of rough structures surrounding each particle can be clearly observed. Scale bars are 1.0 μm in all images.

Figure S4. SEM images of theta-shaped PS disc droplets, which corresponds to the droplets shown Figure S1a and were dried on silicon wafer. The halos of rough structures surrounding each particle can be clearly observed. From Figure S1, the attached PEHMA decane on PS discs of these droplets can also clearly observed by optical microscopy. Scale bars are 1.0 μm in all images.
Figure S5. (a) Optical microscopy images of patchy PS disc dispersions. (b) TEM images of the particles shown in (a) were coated with a layer of SiO$_2$. (c) FIB-SEM images showing the inner structures of the corresponding particles in (b). (1): E/M/W = 0.6/1/0.2; (2): E/M/W = 2.4/1/0.2; (3): E/M/W = 6.0/1/0.2. The yellow arrows show the positions of hollow chambers, which can be further proved by FIB-SEM images. Because silica was coated on the surface of decane, therefore, the presence of hollow chambers suggested that decane was there during the SiO$_2$ coating. When PS discs without decane were used for SiO$_2$ coating along a similar procedure, no hollow chambers were observed. Also, the sizes of the hollow chambers gradually decreased when more and more ethanol was added into the system, corresponding to the decrease of the content of decane in liquid patches.
Figure S6. (a) Optical microscopy image of patchy PS discs with two liquid patches obtained from the system of E/M/W = 6.0/1.0/0.2. (b-f) Optical microscopy images of patchy PS discs shown in (a) after a rotational mixing for three days at different TBAC salt concentrations. (b) 0.0 μmol; (c) 10.0 μmol; (d) 50.0 μmol; (e) 10.0 mmol; (f) 50.0 mmol. The samples in (b-f) were diluted with the same solvent for better observations under optical microscopy. The images show that the particles are stable and do not form any aggregations. Scale bars are 10 μm in all images.

Figure S7. 1D colloidal assembly of patchy PS discs via colloidal sedimentation. SEM images of colloidal chains from increasing initial disc concentration (Φ₀): (a) Φ₀ = 2.5 mg/ml, (b) 7.5 mg/ml and (c) 15.0 mg/ml. Scale bars are 20 μm in all images.
Figure S8. 1D colloidal assembly of patchy PS discs via colloidal sedimentation. (a) The average length of the chains $L_{\text{chain}}$ as a function of initial disc concentration $\Phi_0$; (b) The corresponding probability density function of the distribution of $L_{\text{chain}}$.

Figure S9. 1D colloidal assembly of patchy PS discs via colloidal sedimentation. (a) The average length of the chains $L_{\text{chain}}$ as a function of sedimentation time $T_{\text{sedi}}$; (b) The corresponding probability density function of the distribution of $L_{\text{chain}}$, with $\Phi_0 = 10.0$ mg/ml and the inset is for $\Phi_0 = 3.0$ mg/ml.
Figure S10. 1D colloidal assembly of patchy PS discs via centrifugation. (a) The average length of the chains $L_{\text{chain}}$ as a function of centrifugal force; (b) The percentage of colloidal discs that are individual (hollow) and that participated the formation of chains (Solid); (c-d) The corresponding probability density function of the distribution of $L_{\text{chain}}$ in (a) for 1 time centrifugation (c) and for 10 repeated centrifugations (d).

Figure S11. The probability density function of the distribution of $L_{\text{chain}}$ of the formed chains shown in Figure 2f in the main text.
Figure S12. The wetting of PEHMA decane droplets on PS substrates. The measurements were performed in the mixed solvents of E/M/W = 2.4/1.0/0.2 (a) and E/M/W = 6.0/1.0/0.2 (b) and in air (c). The obtained contact angles are 20.6 degree from (a), 16.6 degree from (b) and 32.9 degree from (c) by fitting the shapes.

Figure S13. The comparison of capillary and van der Waals attraction between two parallel discs. The contact angles are set to a constant 10 degree (a) and 60 degree (b). The calculated range of interfacial tensions is between 0.001 and 0.1 mN/cm.
Figure S14. SEM image of the jagged chains that are shown in Figure 3d(3). They are shown here in a larger image size. Scale bar is 20 μm.

References: