Preparation of Monodisperse Polymer Particles Having Cylindrical Shape and Its Applications

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平成３１年1月

神戸大学大学院工学研究科

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棒状形態を有する単分散高分子微粒子の合成とその応用

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Wei Li

Contents

General Introduction

Generally, polymeric particles prepared in a heterogeneous polymerization system tend to become spherical in shape as the interfacial free energy between particles and medium should be minimized[1].

$$\Delta G = \frac{4}{3}\pi r^3 \cdot \Delta G_v + 4\pi r^2 \cdot \gamma$$

At the situation of same volume, a spherical shape has the smallest interfacial free energy, thus, the spherical polymer particle should be the most stable particle in heterogeneous system.

Unlike spherical particles, non-spherical particles usually have some additional properties including rheological, optical, bioactive and mechanical properties[2-5]. Since the middle of 1970s, non-spherical particles have been reported in literatures and have attracted considerable attentions. Utilizing these properties, non-spherical particles are hopeful to be used in many fields such as colloidal crystal, smart fluids, drug delivery system and cosmetics[6-9].

To date, non-spherical particles are mainly prepared via polymerization or mechanical processes. Okubo et al. reported the preparation of a various of non-spherical particles with complex

morphologies such as mushroom-like and disc-like (Figure 1a, b) by utilizing the non-equilibrium between kinetics and thermodynamics[10,11]. In the preparation of disc-like particles, PS as a seeded particle was added in polymerizable EHMA/decane-water system and initiated by AIBN. After the obtained particle having a humbugger-like morphology extracted by 1-butanol for removing PEHMA, the disc-like part of PS was remained (Figure 1b).
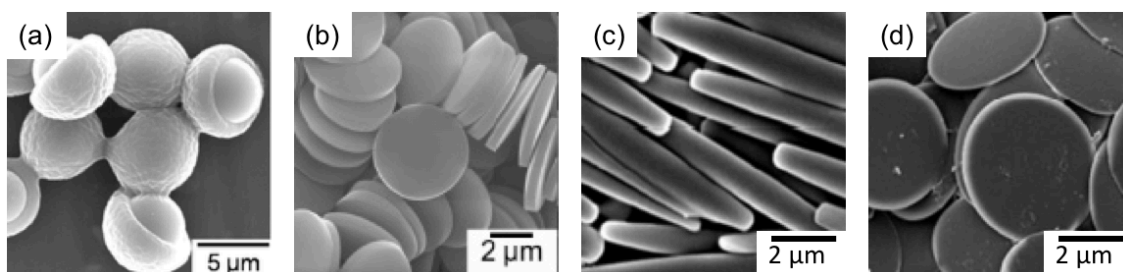
Figure 1. SEM images of non-spherical particles prepared by non-equilibrium polymerization or mechanical deformation: (a) mushroom-like, (b) disc-like, (c) rod-like and (d) disc-like particles.

Another method to prepare non-spherical particles is proposed by Ho et al[12,13]. The Spherical polymeric particles were embedded in a proper polymer matrix, and after heating upon to glass-transition temperature of spherical particles while below to the matrix, we can easily deform the spherical polymeric particles by stretching. Choosing the good solvent for particles as a plasticizer is also a wise method to plasticize the spherical particles. When the plasticized particles were stretched by uniaxial tension,

the rod-like particles can be obtained (Figure 1c), while disc-like particles would be obtained by biaxial tension (Figure 1d).
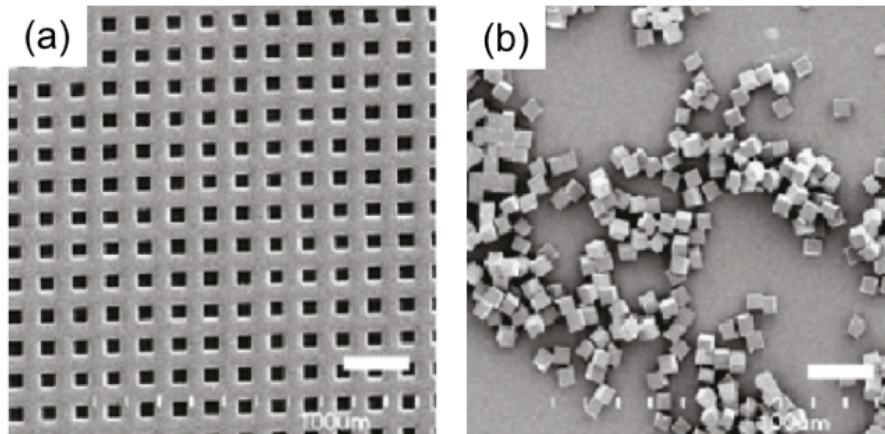
Figure 2. Non-spherical particles prepared by template method. The SEM images of (a) mould and (b) non-spherical particles after demoulding.

A more universal way to prepare the non-spherical particles is template method proposed by DeSimone[14-16]. The melting polymer was injected in a non-wetting mould with different shape, a kinds of non-spherical particles can be obtained after cooling solidification.

In these non-spherical particles, rod-like particles have an abundant academic researches due to it as a kind of typical non-spherical particles is quite similar to cylinder in geometry that the characteristics of rod-like particles can be speculated by simulation in mathematics and physics, and that will benefit to be more effectually used in engineering and actual applications. Consequently, the application of rod-like particles have already been reported in rheology, simulation, biology[17-21].

However, the preparation of rod-like particles usually includes multi-step and procedure is still complex, it seriously limited the improvement of research about the rod-like particles.

1. Applications of rod-like particles

(i) Drug delivery system

Recently, mechanism for the formation of mesoporous silica rod-like particles has been proposed in reports. Importantly, magnetite/silica composite ellipsoids were prepared through a nano casting route and can be used as building blocks to organize into ordered arrays in response to an external magnetic field[22]. In addition, after functionalized with amino-groups, the amino-modified anisotropic magnetite/silica ellipsoids can be further used as carriers for delivering oligo-DNA-Cy3 into tumor cells, showing potential application in fields of self-assembly and drug/gene delivery system[23, 24].

(ii) Simulation

Mitragotri et al. and other groups reported the use of polymeric particles with different geometries as the model particles to stimulate some

functional cell such as macrophages[25,26]. The macrophages cell demonstrated the different sensitivities to the particles with different geometric shape, especially, macrophages cells were more sensitive to the rod-like (ellipsoidal) particles owing to their larger specific surface area, which was expected to improve sustained release agents and target therapy[27,28].

(iii) other application

Rod-like particle as his anisotropy has a great number of unique properties such as electrical and rheological properties. Sun's group reported rod-like SnO_2 particles as an addition in Ag matrix can greatly improve the electrical property of composite to low electrical resistivity $(2.227\mu\Omega\times cm)$[29]; Co-researcher Armes and Saunders proposed a facile and versatile low shear approach for assembling hydrogels containing aligned rod-like particles that demonstrated a pH-responsive ability[30]; The research by Stebe et al. indicated that the curvature-driven capillary migration of rod-like particles displayed a difference from the spherical particles, and it can be applied in smart fluid[31]. Yunker et al. also mentioned that the rod-like particles have a different assemble behavior in coffee ring effect, and implied the specificity of anisotropic particle in rheology[32,33]. Moreover, rod-like particles also exhibit a lot of other unique properties including

optic, chemical and mechanical property, that it is hopeful to be applied in structure coloring, catalysis and so on[34,35].

Furthermore, rod-like particle as a kind of simplest non-spherical particles is similar to cylinder in shape which have been thoroughly researched in geometry and physics[36-39]. Through the discussion of cylindrical shape in mathematics and physics, we can speculate some actual characteristics of rod-like particles and it is significant for us to increase the understanding of behavior and theory of higher anisotropic non-spherical particles.

2. *Preparation of rod-like particles*

(i) *Particle replication in non-wetting templates (PRINT*[TM]*)*

Particle replication in non-wetting templates (PRINT[TM]) method proposed by professor DeSimone et. al. is a powerful tool, in which the melting polymer is cast in non-wetting mold, used for preparation of a various of non-spherical particles, such as rod-like, cubic-like and disc-like particles[22-25].

PRINT[TM] as a universal and versatile method for preparing kinds of non-spherical particles have been applied several years, however, it is mainly used for preparation of non-spherical particles in a large-sized from

several micro-meter to dozens micro-meter.
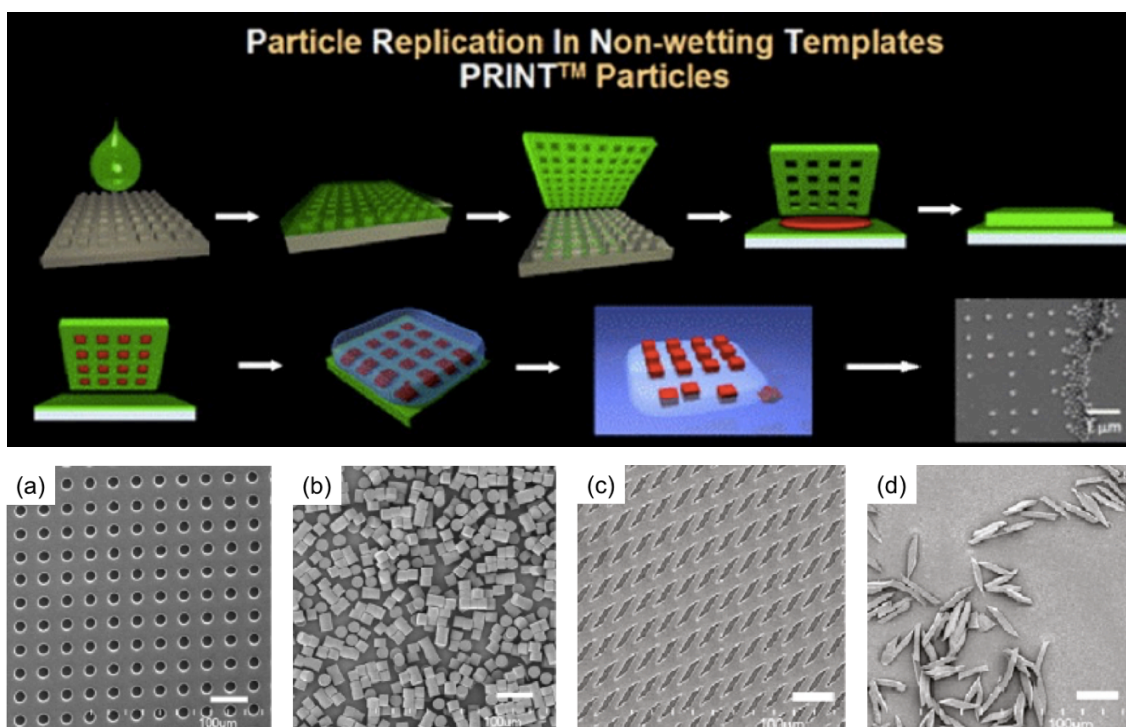
Figure 3. Procedure of particle replication in non-wetting templates (PRINT^{TM}) method. SEM images is (a), (c) mould and (b), (d) polymeric particles after demoulding

Both in figure 3b and 3d, the size of particles is larger than 20 µm. Moreover, the non-wetting mould in this method was made by photolithographic technology that have to utilize the technique of photoetching, ultraviolet curing and fluoride coating at least, resulting in it is difficult to be applied in most laboratories and large scale producing.

(ii) Stretching method

The rod-like particles can also be prepared by a more facile approach

which called stretching method. The method has been proposed by Ho et al.[12,13] in 1993 that was known as an economical method to prepare rod-like particles only and used in most laboratories. Recently, Mitragotri et al.[25,26] improved the method and created a kinds of non-spherical particles.
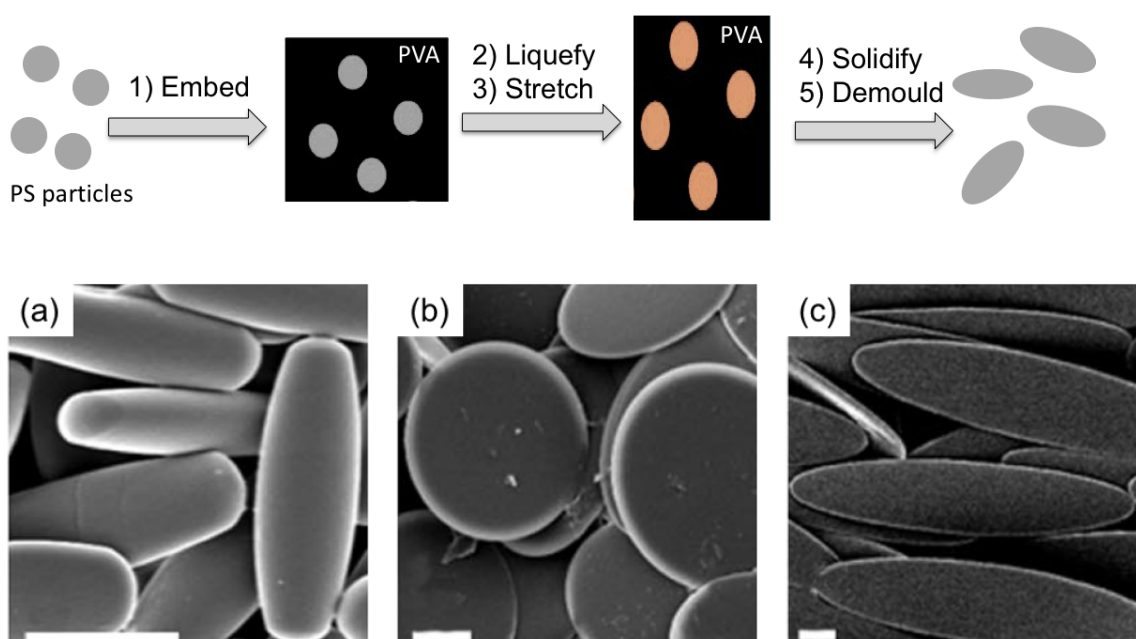
Figure 4. Procedure of stretching method and the SEM images of particles after stretching: (a) rod-like particles, (b) disk-like particles and (c) elliptic disk particles.

Firstly, polymeric spherical particles were embedded in a proper matrix, usually used poly vinyl alcohol. After liquefying via heating upon to the glass-transition temperature of particles but below to the polymeric matrix, the softened particles were stretched with the polymeric matrix by uniaxial tension. After solidifying and demoulding, the rod-like particles can be obtained (Figure 4a). If the particles were stretched by biaxial

tension, the particles would be extended at two directions in planar resulting in the formation of the disc-like particles as Figure 4b, c shown. Plasticizing the particles by a good solvent is also a wise way that can be avoid the glass-transition temperature between particles and matrix is approximate. Since 90s, professor Ho proposed stretching method, it have been widely used as a facile approach to prepare the micro-sized rod-like particles at laboratory-scale. However, the preparation of sub-micron sized particles has not been reported until now, as well as, the preparation amount was still less.

Although PRINT^{TM} and stretching method provides an approach to fabricate rod-like polymer particles, it remains a lot of disadvantages such as multi-step procedure, complex operation and difficult to prepare rod-like particles in industrial scale.

Recently, we unexpectedly discovered a facile and novel method to prepare "cylindrical" monodisperse polystyrene (PS) particles using a stirring method. The spherical PS particles prepared via dispersion polymerization were simply stirred in a polyvinyl pyrrolidone (PVP) aqueous solution. As a result, the spherical particles were deformed to a cylindrical shape maintaining monodispersity. Compared with previous researches, the obtained shape of particles in this method was completely cylindrical instead of ellipsoidal shape that has two slender heads. This

method provides a facile and highly efficient approach for preparing the cylindrical particles without using a complex procedure; the method also provides a high yield, with the formation of particles in this method being quite different from the rod-like and ellipsoidal particles describe in previous reports.

In this study, the influence of a various methodological conditions on the formation of cylindrical particles was investigated including the stirring pattern, time, speed and the kind of dissolved polymers in aqueous solution. The mechanism of deformation was also discussed and it is quite different from other method.

Moreover, the application of cylindrical particles was also considered and we demonstrated a super stable Pickering emulsion using cylindrical particles as a particulate surfactant. The arrangement of cylindrical particles on the surface is diverse that it can generate a net-work structure to maintain the stability of droplet as well as closely packing the droplet.

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Chapter 1

Preparation of Cylindrical Polystyrene Particles by Stirring Method
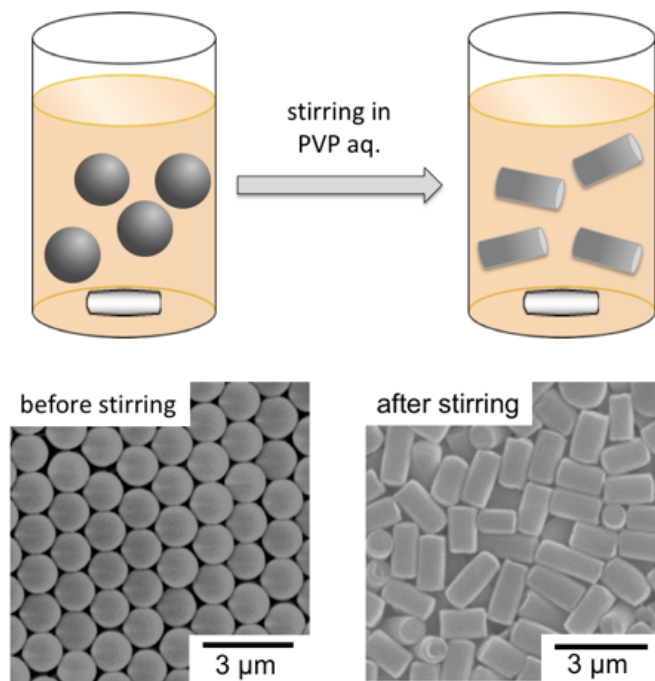
Introduction

    A facile and novel approach for preparation of monodisperse polystyrene (PS) particles having a "cylindrical" shape was discovered. Different from the particles prepared by stretching method or PRINT^{TM} method, the particles prepared by stirring method have a completely

cylindrical shape in geometry that distinguished from the so-called rod-like particles which have two slender heads.

The proposed stirring method merely involved to stir spherical PS particles in a polyvinyl pyrrolidone (PVP) aqueous solution for several hours using a magnetic stirrer. The spherical PS particles were synthesized via dispersion polymerization with a monodispersity. In the presence of PVP, the spherical PS particles deformed into cylindrical shapes following stirring, while maintaining monodispersity; The deformation can be greatly affected by stirring pattern: regular cylindrical particles can be obtained in laminar fluid while irregular particles were obtained in turbulent fluid. In the situation of using vortex and shaking bed, the particles even can not deform. This method not only provides a facile and highly efficient approach for preparing cylindrical particles without adopting a complex procedure, but also provides a high yield of deformation, and the particles formed by this method are quite different from the rod-like particles described in previous reports.

Experimental Section

Materials

Styrene and methyl methacrylate (Nacalai Tesque Inc., Kyoto, Japan)

were purified by distillation under reduced pressure in a nitrogen atmosphere; reagent grade 2,2'-azobisisobutyronitrile (AIBN, Nacalai Tesque Inc., Kyoto, Japan) were purified by recrystallization in methanol. Polyvinyl pyrrolidone (PVP, weight-average $M = 4.0 \times 10^4$, Nacalai Tesque Inc., Kyoto, Japan), poly acrylic acid (PAA, weight-average $M = 2.5 \times 10^4$, Sigma-Aldrich Co. LLC., German), hydroxypropyl cellulose (HPC, 3-6mPa·S, 2% in water at 20˚C, Tokyo Chemical Industry Co., LTD.), methanol and ethanol (Tokyo Chemical Industry Co., LTD.) was used as received. The deionized water used in all experiments was obtained from an Elix UV (Millipore Co., Ltd., Japan) Purification system and had a resistivity of 18.2 MΩ·cm.

Preparation of Spherical PS Particles

PS with stabilizer PVP were prepared via dispersion polymerization[6]. Recipe for dispersion polymerization of styrene, initiator AIBN and methanol media under the conditions listed in Table 1. Firstly, monomer styrene, stabilizer PVP and initiator AIBN was dissolved in the media methanol, and put into a glass tube. Then the glass tube was degassed with vacuum/nitrogen recycle several times, and sealed. The polymerization was conducted in the sealed glass tube placing in water bath at 60 °C for 24 hours with horizontally shaking at 80 cycles/min (3 cm strokes).

Preparation of Cylindrical PS Particles

Table 1. Preparation of polystyrene particles via dispersion polymerization

Ingredients		PS$_{PVP}$ particles
Styrene	(g)	1.0
Polyvinyl pyrrolidone	(g)	0.2
AIBN	(g)	0.01
Methanol	(g)	6.0

The cylindrical particles were prepared by stirring in a PVP aqueous solution using a typical procedure, which is as follows: a spherical particles suspension (1.5 g, 2.0 wt%) was added into the PVP aqueous solution (1.5 g, 2.0 wt%), and stirred in a 15ml glass vial for 24-72 hours using a magnetic stirrer (360 round/min) at room temperature. After the stirring process, the resultant cylindrical particles were removed from the PVP solution by washing in ethanol and water 3 times respectively via centrifugation.
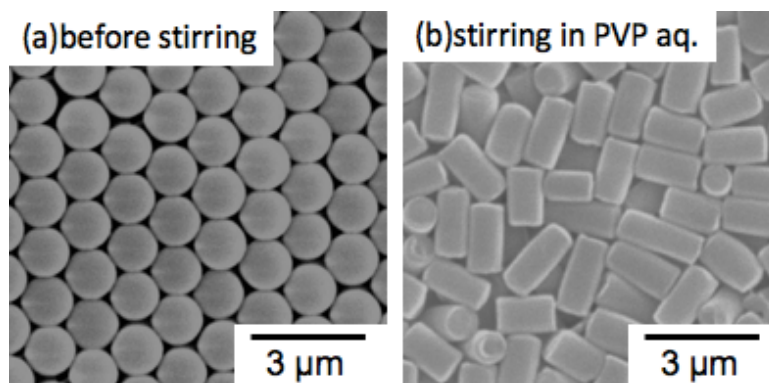
Results and Discussion

Figure 1. SEM images of polystyrene particles via dispersion polymerization (a) before and (b) after stirring.

Figure 1 shows spherical PS particles prepared via dispersion polymerization with high monodispersity using PVP as a stabilizer (PSPVP particles, Dn=1.2 mm, Cv=4.2%) before and after stirring. The particles were stirred in the presence and absence of PVP in the aqueous solution using a magnetic stirrer at room temperature for 48 h. Following stirring, in the presence of PVP in the medium, the PS particles were obviously deformed from spherical to cylindrical shapes. The yield of cylindrical particles was almost 100% after stirring for 48 h. In contrast, in the absence of PVP in the medium, deformation of the PS particles was not observed, indicating that the presence of PVP in the medium is crucial for the formation of cylindrical particles. The volume of the cylindrical particles (Vcy= 0.98 mm^3, which was estimated by counting more than 200 particles

in the SEM images using an analysis software (WinROOF, Mitani Co., Ltd., Japan)), was consistent with that of the spherical particles (Vsp=0.91 mm^3) prior to stirring, indicating that one cylindrical particle was deformed from one spherical particle without coagulation.
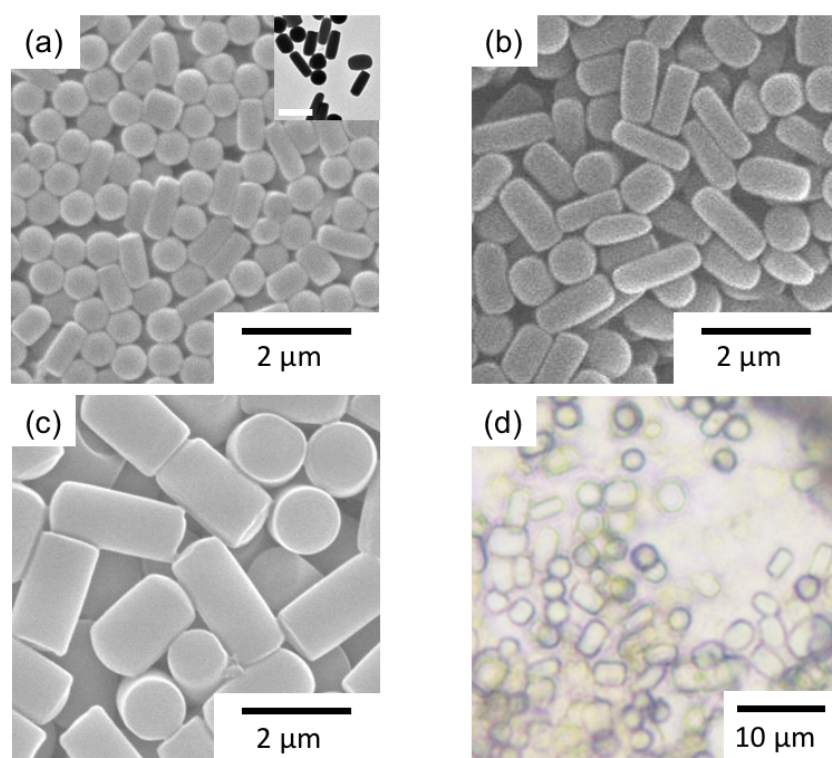

Figure 2. The PS particles with different size deformed after stirring in PVP aqueous solution after 12-48 hours: (a) 370nm, (b) 800nm, (c) 2μm and (d) 4μm.

Stirring method is also a universal method for preparing cylindrical particles with different sizes. From figure 2a – 2d, all the particles can be deformed by stirring at a range of 370 nm to 4 µm.

Different from rod-like particles prepared by stretching or PRINT^{TM}

method[1-5], particle using stirring method have a completely cylindrical shape instead of the spindle shape with two slender shape. It indicated that the mechanism of stirring method as a novel approach should distinguishes from previous researches. It is meaningful to investigate the mechanism of deformation that may help us to create a number of novel particles by stirring method.

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Chapter 2

Deformation of Spherical Particles by Mechanical Shear Force in Fluid

At chapter 1, we have demonstrated a facile and efficient method to prepare cylindrical particles, which is quite different from stretching method and PRINT[TM] method[1-5]. Particles by stirring method proposed in this study have completely cylindrical shape instead of the spindle shape.

Stirring patter as an important procedure can greatly effect on the consequence of experiment. To discuss stirring pattern how to influence on the deformation of the spherical particles, the particles stirred in a series of stirring pattern have been conducted.
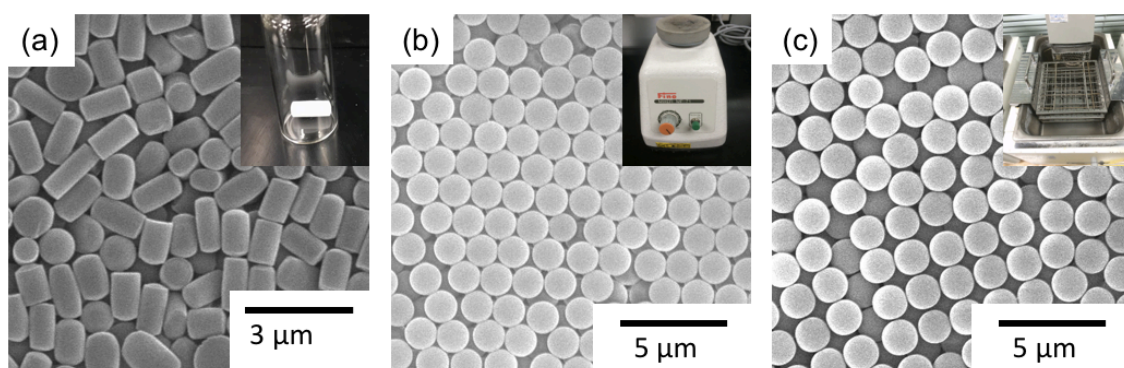

Figure 1. SEM images of the spherical particles stirred in different pattern: (a) stirred by magnetic stir bar, (b) vortex and (c) shaking table.

Figures 1a-c show SEM images of PS particles after stirring with different pattern, indicating that only stirring by a stir bar deformed the particles, and deformation was not observed in the pattern vortex and shaking methods. In the case of figures 1b, not only medium but also particles were driven by gravity, the shear force between the medium and the particles is so weak that the deformation cannot be occurred.

In the case of figures 1c, as the flow pattern was oscillatory, the shear force was isotropic, resulting the stress on spherical particles at stochastic directions and mutually counteracting.

In the situation of stirrer, the shear force was anisotropic, and the directional force deformed the spherical particles in the direction of the fluid[6-8]. It is also the reason why the cylindrical particles prepared by stirring method without two slender heads. It can be attributed to the shear force between the PS particles and the PVP aqueous solution, in which equal shear force should stress on the spherical particles. In comparison, the force distribution should not be homogeneous in the stretching method[9-11].
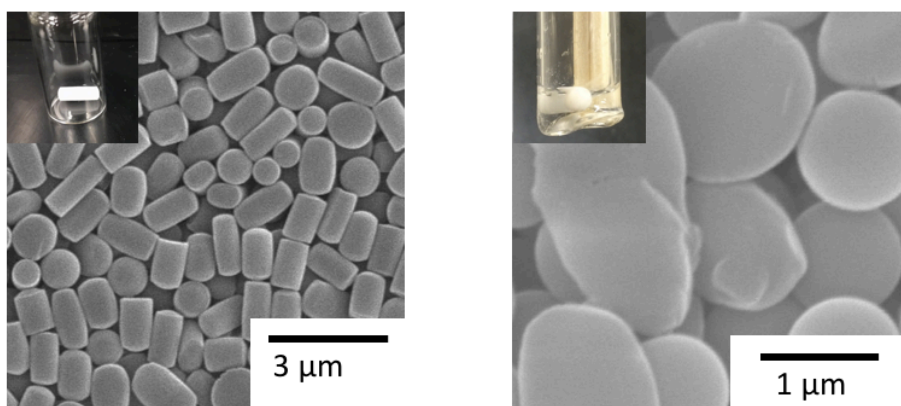
Figure 2. The spherical particles were stirred by magnetic stir bar in sample bottle (a) with regular shape and (b) irregular shape.

Interestingly, in the case of the glass vial with irregular shape, the obtained particles also became irregular (Figure 2b) owing to the turbulent fluid generated in the irregular shaped glass vial and disordered shear force result in the irregular shaped particles. The consequence indicated that the directional fluid was crucial for the formation of cylindrical particles.
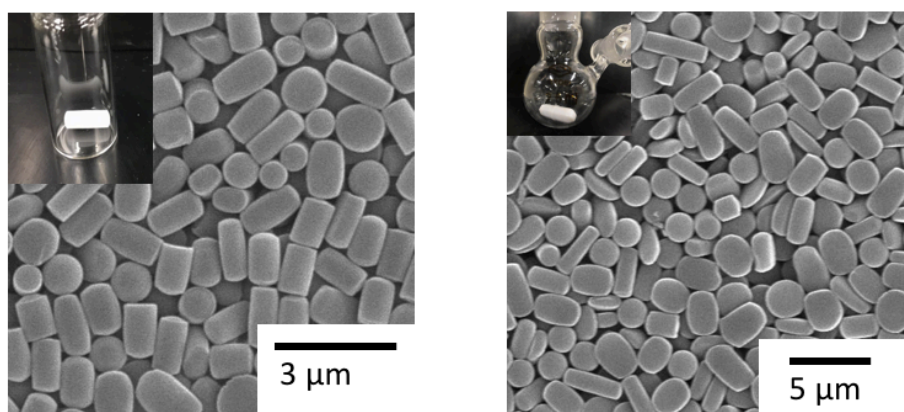

Figure 3. The spherical particles were stirred in two kinds of different glass vial: (a) the glass cylindrical vial with a flat-bottom and (b) the Schlenk flask with a cambered bottom.

The spherical particles also deformed in the Schlenk flask with a magnetic stirrer (Figure 3b), in which the stir bar did not touch with the bottom of the flask. This result strongly suggested that the PS particles should not deformed by friction between the stirrer and the bottom of glass vial.
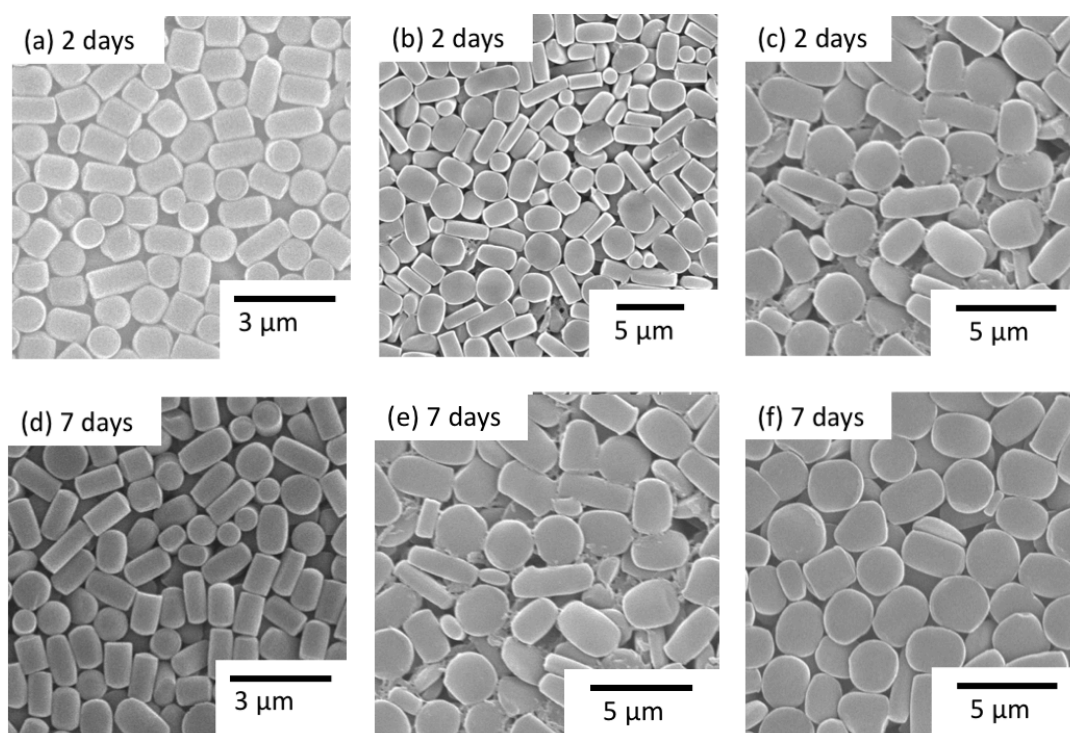
Figure 4. The spherical particles were stirred at different speed will deform in different shape: at 360 rpm after (a) 2 days and (d) 7 days; 1000 rpm after (b) 2 days and (e) 7 days; 1400 rpm after (c) 2 days and (f) 7 days.

We also investigated more details of experiment from standpoint of fluid mechanics. Stirring spherical particles at different speed, the particles with different shape will be obtained. Comparing with particles stirred at

360 rpm (figure 4a), the particles stirred at higher speed (figure 4b, c) would be deformed in disc-like shape partially. Following stirring, the percentage of disc-like particles was increasing that indicated that the disc-like particles should probably deform from cylindrical particles, instead of deforming from spherical particles. Notably, there should be a threshold of stirring speed between deformation of cylindrical and disc-like particles, otherwise, the particles stirred at 360 rpm for a long time should become disc-like shape as well.
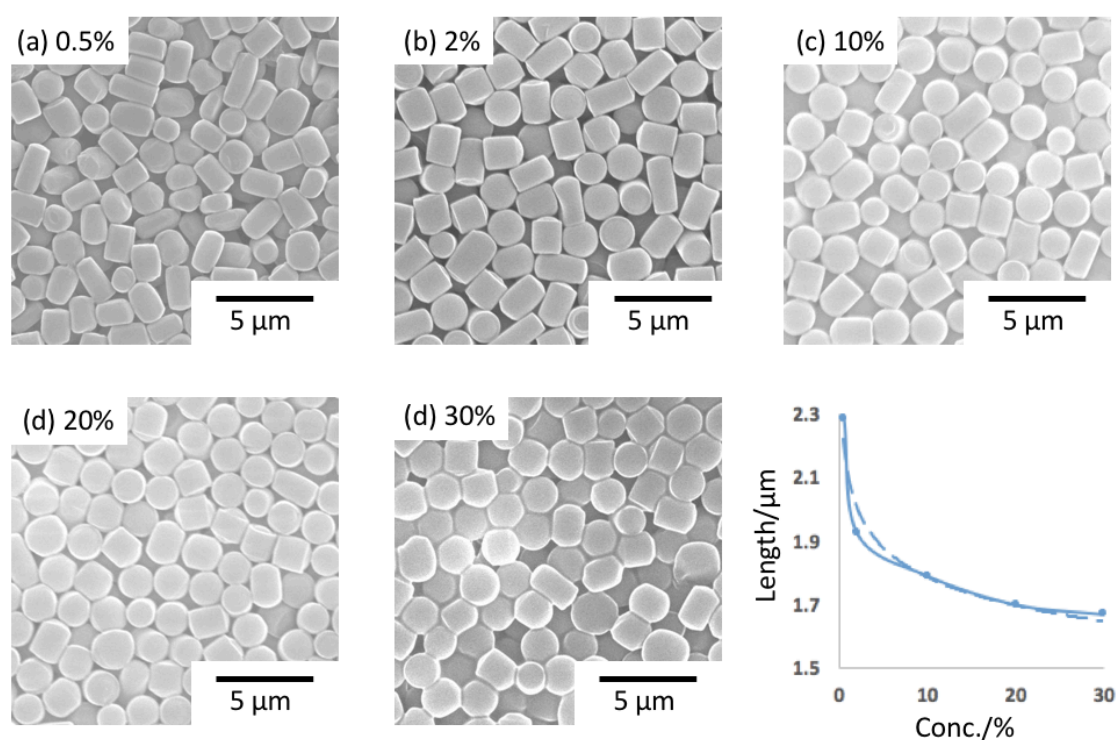

Figure 5. The SEM images of cylindrical PS particles. The spherical particles with different concentration were stirred in 5% PVP aqueous solution: (a) 0.5%, (b)   2%, (c) 10%, (d) 20% and (d)30%. The chart demonstrated the relation between the length of cylindrical particles and the concentration of particles.

The concentration of particles can also effect on the formation of cylindrical particles. At the higher particle concentration, we can observe that particles are difficult to deform even though almost the most particles were spherical shape (Figure 5e), while the particles at the lower concentration were easily deformed after stirring. It should be due to the particles at a higher concentration have not enough space to deform.
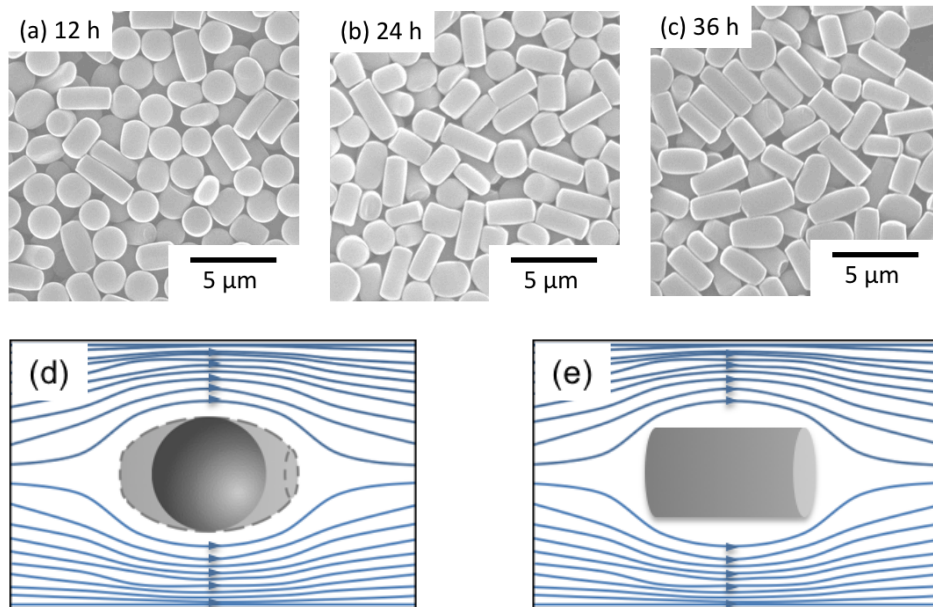
Figure 6. The SEM images of the particles after discontinuous stirring: (a) 12 hours, (b) 24 hours and (c) 36 hours. The diagram shows the particles deformed in a fluid (d) and continue to stretch at the direction of fluid (e).

Benefiting from the cylindrical particles always flowed with the fluid, the cylindrical particles can even be obtained at a discontinuous stirring. Figure 6a showed that the particles have been deformed after 12 hours, furthermore, the deformation percentage can continue to increased with

time while irregular shaped particles have not been observed (Figure 6b, c), because that the cylindrical particles can flow with the fluid and be stretched at the direction of fluid once the particles became cylindrical shape.
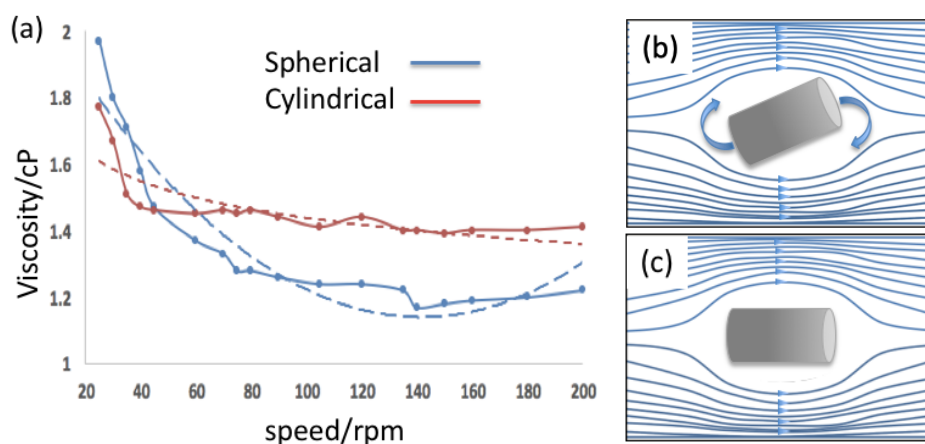

Figure 7. The relation between the stirring speed and the viscosity of two kinds of particle suspensions (4.4 wt%): (red line) spherical particles, (blue line) cylindrical particles. The diagrams illustrate the arrangement of cylindrical particles in a fluid.

As the anisotropy of cylindrical particles, it has been demonstrated some interesting properties in this work, which one is viscosity. From figure 7a shown, the fluid with cylindrical particle has a higher viscosity than that of spherical particles after stirring speed upon 40 rpm. Through linear fitting to viscosity of fluid with cylindrical particles at different stirring speed, we can also find that the fluid with cylindrical particles has more stable viscosity. It can be considered that anisotropic cylindrical particles were always on the state of flowing with the fluid (Figure 7c),

result in system should provide excess energy to maintain the cylindrical particles being horizontal in fluid. As the special property of cylindrical particles, it is hopeful to be applied in preventing the fluid from shear thinning by addition of cylindrical particles.

Conclusions

From the above discussions, it is concluded that the spherical PS particles were deformed by the shear force generated between the particles and the medium: comparing the deformation in laminar and turbulent flow, cylindrical particles only forming in laminar flow prove that stable and directional shear force is significant for the formation of cylindrical particles. Concentration, stirring time and speed can also effect on the consequence of experiment, but above all, it can be attributed to the properties of flow.

Moreover, the cylindrical particles as the anisotropy demonstrated a unique property in flow, which is quite different from spherical particles. As the cylindrical particles always flow along with the micro-flow, when the cylindrical particles stirred in fluid the system should provide more energy to enable the cylindrical particle horizontally flow along with the micro-flow, resulting in the viscosity of cylindrical particles dispersion larger than spherical particle.

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Chapter 3

Plasticization of Particles in PVP Aqueous Solution

Until now, we have concluded that the spherical PS particles were deformed by a shear force generated between the particles and the medium. However, PS as a plastic has a high glass-transition temperature above 100°C. Based on the data of differential scanning calorimetry (DSC, Seiko Instruments Inc., Japan), the glass-transition temperature of spherical PS particles in aqueous suspension occurred at 112°C. It is impossible for the PS spherical particles deformed at room temperature just by stirring, unless the PS spherical particles are plasticized.
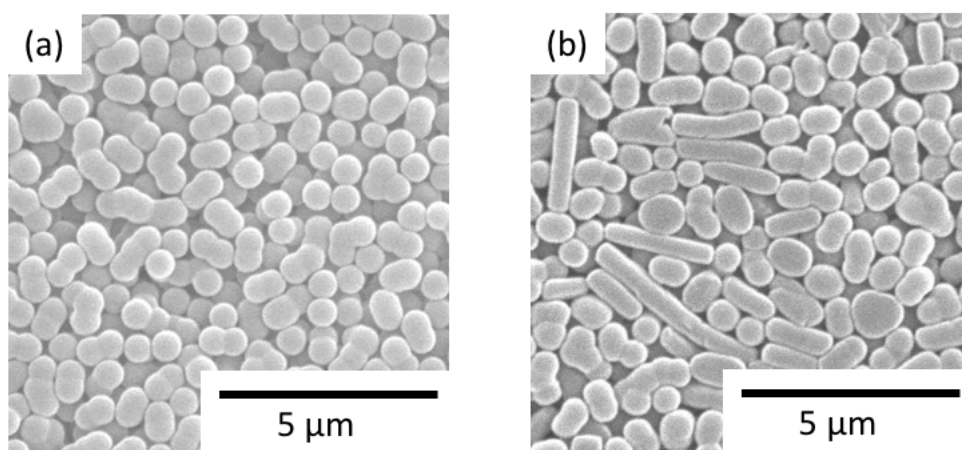

Figure 1. The SEM images of deformation of patchy particles in PVP aqueous solution by stirring method: (a) before stirring and (b) after stirring.

Another evidence is that the patchy PS particles can also deform in PVP aqueous solution by stirring. As shown in figure 1b, deformation of patchy particles illustrate that the formation of cylindrical particles is not only due to mechanical deformation by shear force[1-5]. If mechanical deformation is the only reason why cylindrical particles can be formed, a fracture at the neck of patchy particles should happen owing to the stress concentration is the highest in the zone of neck.
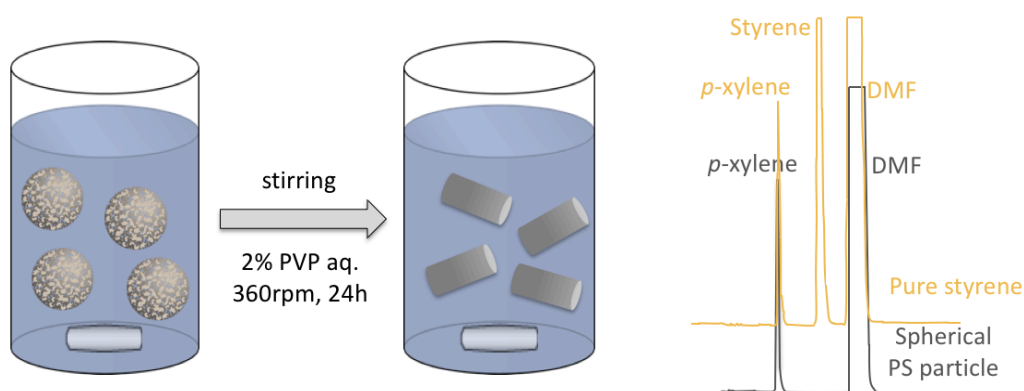
Figure 2. The possible mechanism (left diagram) and the gas chromatography of monomer styrene and PS spherical particles (right curve).

At beginning, we assumed that the plasticization might be due to the unreacted monomer styrene remained in the spherical particles and plasticized them. The plasticized spherical PS particles have a lower mechanical property and deformed into cylindrical shape by shear force at last. However, residual monomer has not been detected via analysis of gas chromatography (Figure 2 right curve).

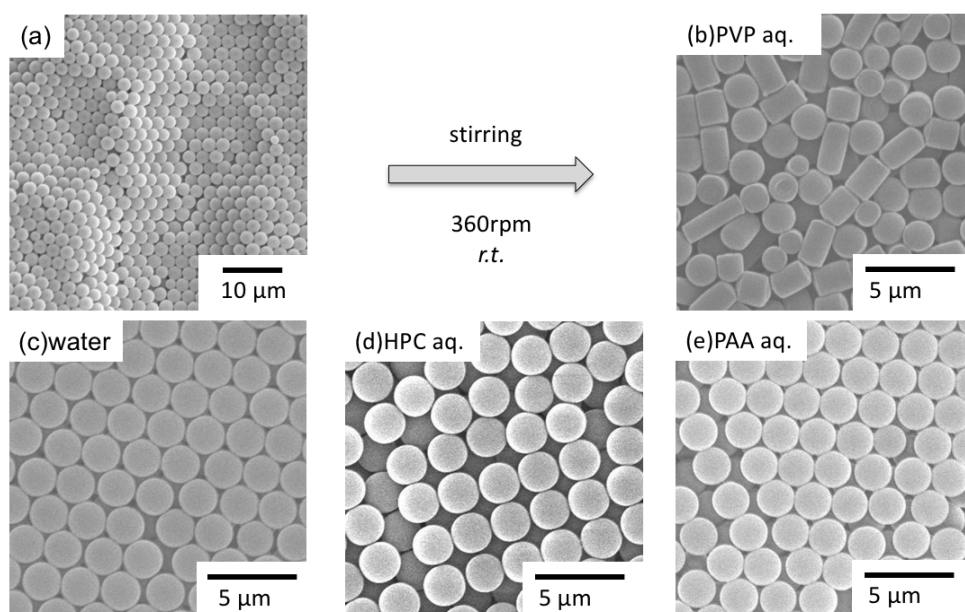**Figure 3.** The SEM images of spherical PS particles (a) stirred in: (b) PVP aqueous solution, (c) pure water, (d) hydroxylpropyl cellulose and (e) poly acrylic acid aqueous solution.

An interesting phenomenon is that the spherical particles can easily deform in PVP aqueous solution. If we remove PVP and stir the spherical particles in pure water, the particles can not deform, even though after 5 days stirring (figure 3c). Similarly, the spherical particles can not deform in other polymer aqueous solution such as hydroxypropyl cellulose (HPC) and poly acrylic acid (PAA) aqueous solution (figure 3d, e). The PVP as a key point may help us to understand the mechanism of plasticization.
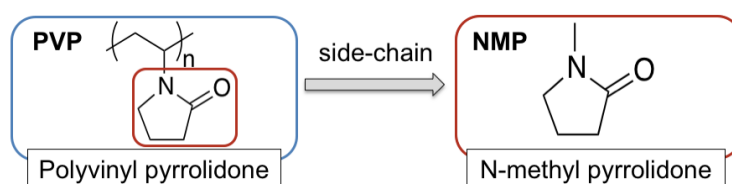

Figure 4. The molecular structure of Polyvinyl pyrrolidone (PVP) and N-methyl

pyrrolidone (NMP).

Figure 5. The dissolving ability of N-methyl pyrrolidone (NMP) to a various of polymer. To most polymers, such as polystyrene, poly methyl methacrylate and others, can be dissolved in NMP.

In fact, as shown in figure 4, the side-chain of PVP is similar in the structure of N-methyl pyrrolidone (NMP), which is a good solvent for many polymer including polystyrene, poly methyl methacrylate, polyvinyl pyrrolidone and others (Figure 5). We assume that the side-chain of PVP dissolved in aqueous solution probably act as a good solvent to plasticize the spherical PS particles.

If the side-chain of PVP can plasticize the spherical PS particles, the negative peak of plasticization should be detected by DSC, however, the peak can not be observed. It might because that he side-chain of polymer PVP represent the collective behavior which is quite different from small molecules.
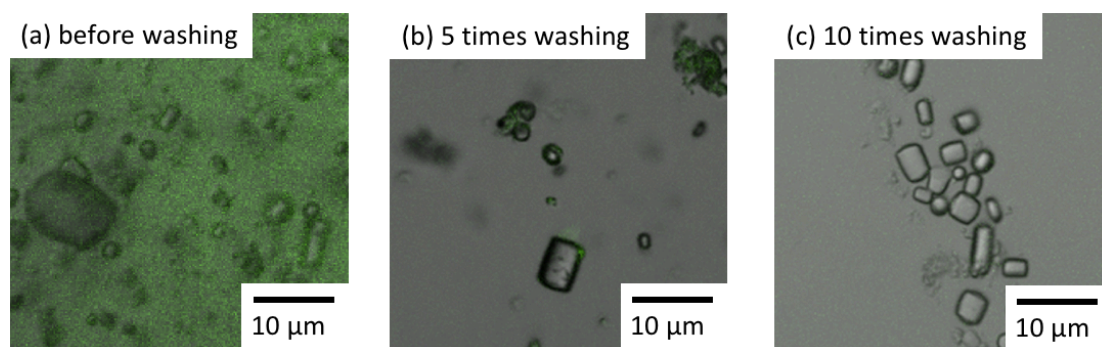
Figure 6. The Confocal laser scanning microscopy (CLSM) photos of (a) the PS particles stirring in PVP aqueous solution and after washing by centrifugation (b) 5 times, (c) 10 times.

Subsequently, we synthesized fluorescent PVP as a label to indicate the trace of PVP. The fluorescent PVP was synthesized by a solution polymerization as following recipe shown: monomer vinyl pyrrolidone (1.9 g), fluo-vinyl pyrrolidone (0.1 g) and AIBN (0.05 g) was dissolved in ethanol (20 g) and put into a schlenk flask. Then the flask was degassed with vacuum/nitrogen recycle several times, and sealed. The polymerization was conducted in the flask placing in water bath at 60 °C for 6 hours with stirrer at 160 cycles/min.

As figure 6a shown, the fluorescence from PVP can be observed in the PS particles before washing indicating that the PVP actually penetrated into the PS particles. However, the fluorescence in PS particles become weaker and weaker with several times washing by centrifugation (Figure 6b, c). It should be considered that the carbonic side-chain of PVP

penetrated into the PS particles while the main-chain still remained at outside of the PS particles, and after washing, the side-chain was finally extracted from PS particles with the main-chain of PVP.

Until now, all the PS spherical particles we have used are stabilized by PVP. Stabilizer PVP used in synthesis of particles might influence on the consequences of experiment, as PVP were also used in aqueous solution at the step of stirring. To get rid of the interference of stabilizer PVP, we synthesized PS particles by other stabilizer. Recipe for dispersion polymerization of styrene, initiator AIBN and methanol media under the conditions listed in Table 2.

Table 2. Preparation of polystyrene particles by different stabilizer

Ingredients		PS_{PVP}	PS_{PAA}	PS_{HPC}
Styrene	(g)	1.0	1.0	1.0
Stabilizer	(g)	0.2	0.2	0.15
AIBN	(g)	0.01	0.01	0.01
Methanol	(g)	6.0	4.8	3.0
Water	(g)	-	1.2	3.0

Firstly, monomer, stabilizer and initiator was dissolved in the media, and put into a glass tube. Then the glass tube was degassed with vacuum/nitrogen recycle several times, and sealed. The polymerization was conducted in the sealed glass tube placing in water bath at 60 °C for 24 hours with horizontally shaking at 80 cycles/min (3 cm strokes).
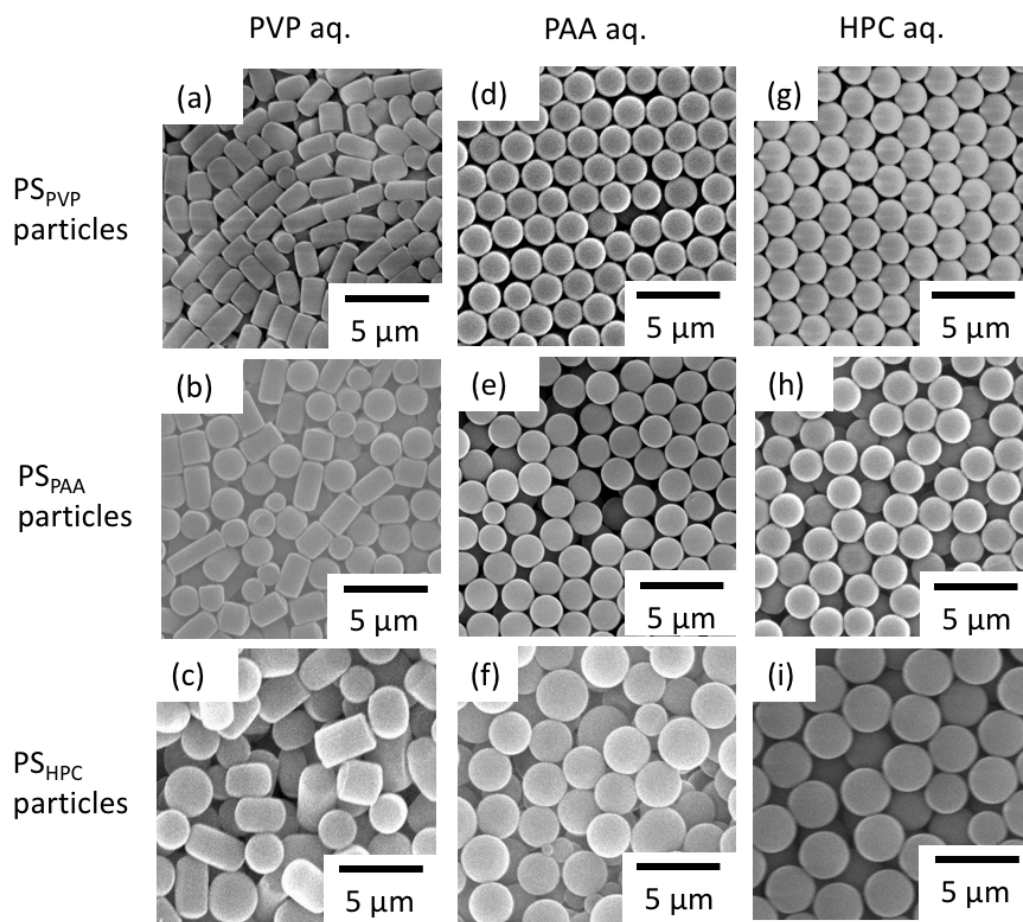
Figure 7. The PS particles with different stabilizer were stirred in polymer aqueous solutions. (a) – (c) The PS particles stabilized by PVP, PAA and HPC (PS$_{PVP}$, PS$_{PAA}$, PS$_{HPC}$) were stirred in PVP aqueous solution; (d) – (f) the PS particles were stirred in PAA aqueous solution; (g) – (i) the PS particles were stirred in HPC aqueous solution.
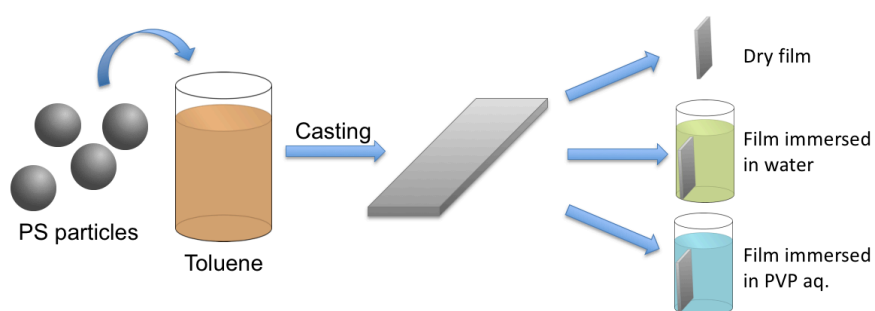

Figure 8. Preparation of PS films by casting the PS particles toluene solution. The films

treated by different liquid were estimated by tensile test.

If the PS particles were plasticized by PVP aqueous solution, the mechanical properties of the PS particles should be affected after a treatment with PVP aqueous solution. To estimate the mechanical properties, tensile testing was conducted using the PS films prepared from the PS particles. As figure 8 shown, the PS films were prepared by casting a PS toluene solution (5 *wt%*) that from dissolution of spherical particles.
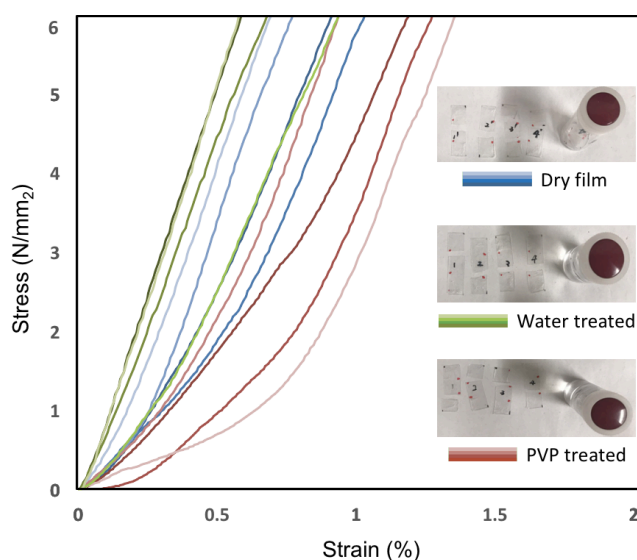
Figure 9. Tensile test of the PS films with different treatments: (blue lines) PS films without any treatment, (green lines) PS films immersed in pure water for 48 hours, (red lines) PS films immersed in PVP aqueous solution.

Figure 9 shows the curve of tensile testing of PS films with different treatments. Comparing the PS films without any treatment (blue curves), the mechanical property of PS films obviously decreased after immersing

in a PVP aqueous solution (red curves). In order to suppress the interference of medium water, the mechanical strength of PS films immersing in pure water also be tested and has not decreased. These results suggested that the PVP dissolved in medium actually decrease the mechanical strength of PS particles and act as an important role of plasticizer in stirring process.
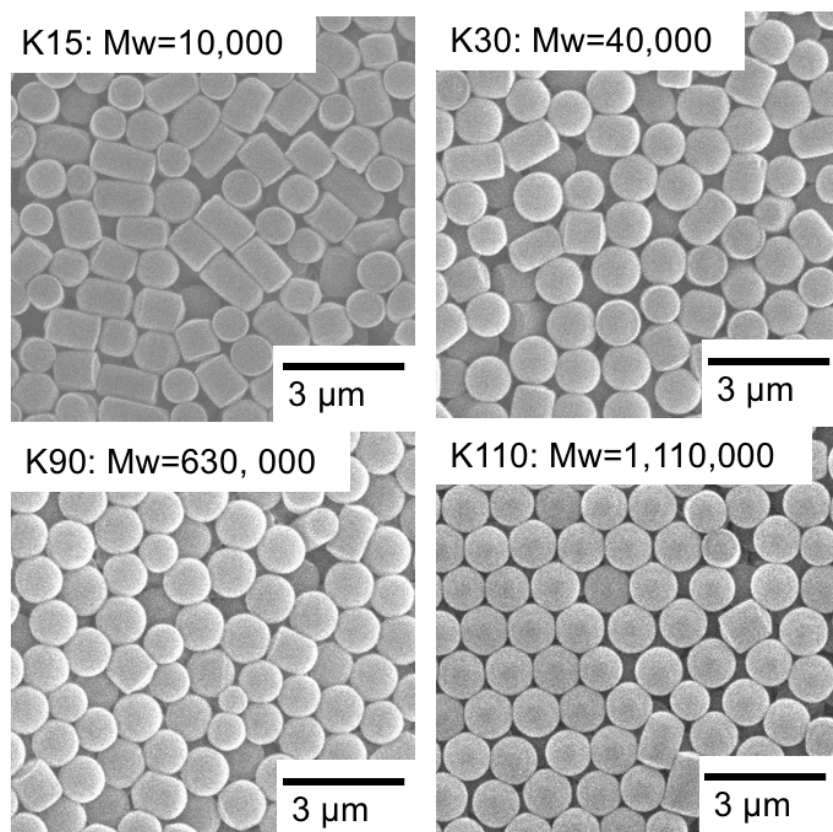

Figure 10. SEM photographs of spherical PS particles stirred in PVP aqueous solutions with different molecular weights: (a) K15, Mw = 10,000, (b) K30, Mw = 40,000, (c) K90, Mw = 630,000 and (d) K110, Mw = 1,110,000.

Besides, molecular weight of PVP dissolved in water would also

influence on the deformation of particles. With the increasing molecular weight of PVP, deformation became difficult even though can not deform. It can be considered that side-chain of PVP have a better freedom at lower molecular weight and even approach to micro-molecular NMP.

Table 3. Preparation of poly methyl methacrylate particles via dispersion polymerization.

Ingredients		PMMA$_{PVP}$
Methyl methacrylate	(g)	1.0
Polyvinyl pyrrolidone	(g)	0.15
AIBN	(g)	0.01
Methanol	(g)	7.0
Water	(g)	3.0

Similarly, we also synthesized PMMA spherical particles via dispersion polymerization as table 3 shown. Firstly, monomer methyl methacrylate (1.0 g), stabilizer PVP (0.2 g) and initiator AIBN (0.01 g) was dissolved in the media of ethanol (6.3 g) and water (2.7 g), and put into a glass tube. Then the glass tube was degassed with vacuum/nitrogen recycle several times, and sealed. The polymerization was conducted in the sealed glass tube placing in water bath at 60 °C for 24 hours with horizontally shaking at 80 cycles/min (3 cm strokes). After centrifugal washing by ethanol and water 3 times respectively, 2 *wt*% PMMA particles aqueous suspension was added in 2 *wt*% PVP aqueous solution and stirred at 360 rpm for 72 hours.
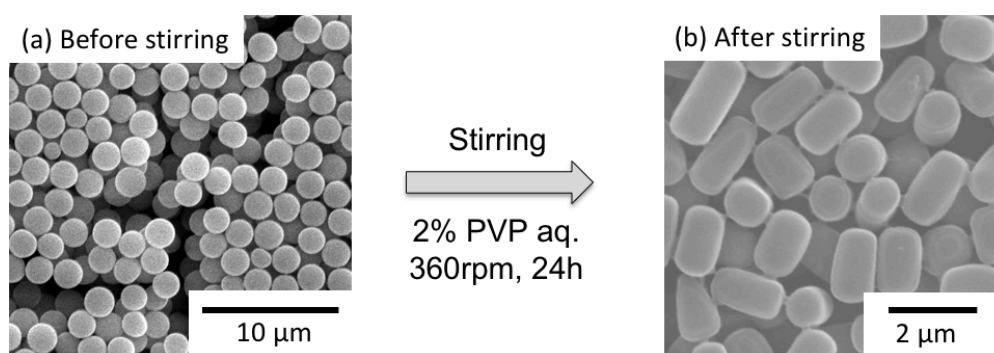
Figure 11. SEM images of PMMA particles (a) before and (b) after stirring in PVP aqueous solution.

Figure 11a showed that monodisperse PMMA particles were successfully prepared by dispersion polymerization and cylindrical PMMA particles actually deformed after stirring in a PVP aqueous solution (Figure 11b) that proved plasticization effect of side-chain.

Table 4. Preparation of cross-linked polystyrene particles via dispersion polymerization.

Ingredients		
Styrene	(g)	1.0
Divinyl benzene	(g)	0.05
Polyvinyl pyrrolidone	(g)	0.2
AIBN	(g)	0.01
Ethanol	(g)	6.0

An interesting phenomenon is that cross-linked PS particles were also able to deform in PVP aqueous solution by stirring method, although cross-linked particles is difficult to deform. The cross-linked PS particles were synthesized through addition of cross-linking agent divinyl benzene (DVB) via dispersion polymerization: monomer styrene (1.0 g),

cross-linking agent DVB (0.05 g), stabilizer PVP (0.3 g) and initiator AIBN (0.04 g) was dissolved in the media of ethanol (16.0 g) and water (1.8 g), and put into a glass tube. Then the glass tube was degassed with vacuum/nitrogen recycle several times, and sealed. The polymerization was conducted in the sealed glass tube placing in water bath at 60 °C for 24 hours with horizontally shaking at 80 cycles/min (3 cm strokes). After washing by centrifugation, 2 *wt*% cross-linked PS particles aqueous suspension was added in 2 *wt*% PVP aqueous solution and stirred at 360 rpm for 1 weeks.
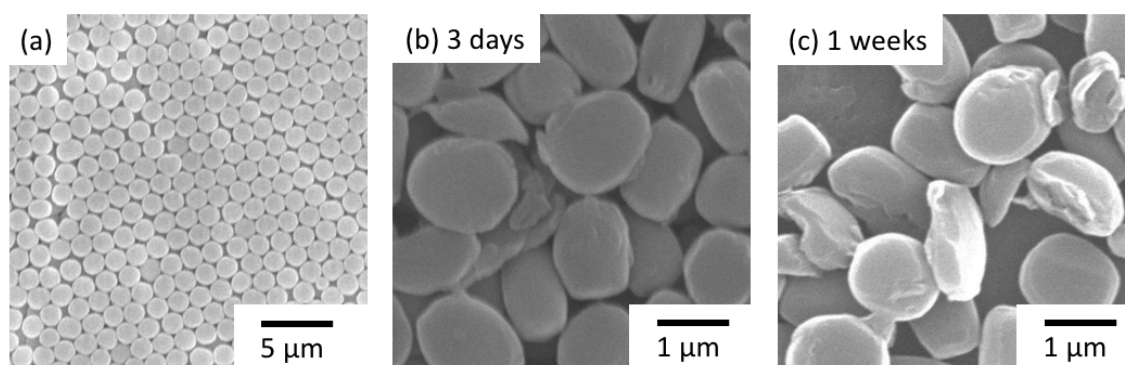
Figure 12. SEM images of cross-linked PS particles (a) before and after stirring in PVP aqueous solution for (b) 3 days, (c) 7 days.

From figure 12a shown, monodisperse cross-linked PS particles were successfully prepared by dispersion polymerization. After stirring in PVP aqueous solution, cross-linked particles have also deformed obviously just after 3 days (figure 12b). Especially, deformed particles reveal a raw edge which looks like a linear PS was extracted from cross-linked particles

(figure 12c). It proved that deformation of particles is not only due to the shear force, but also exist an interaction between particles and PVP aqueous solution at molecular scale.

Conclusions

Herein, we can conclude that a facile method to prepare cylindrical particles was proposed. The stirring method is a universal method can be used for preparing cylindrical particles with different sizes at a range of 370 nm to 4 μm, as well as different materials including PMMA. And more materials will be discussed in later works.

The mechanism of formation of cylindrical particles can be concluded two important process: the plasticization by side-chain of PVP dissolved in aqueous solution and the deformation by shear force generated between particles and medium.

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Chapter 4

Preparation of Pickering Emulsion Using Cylindrical Particles in Oil/Water System

60 μm
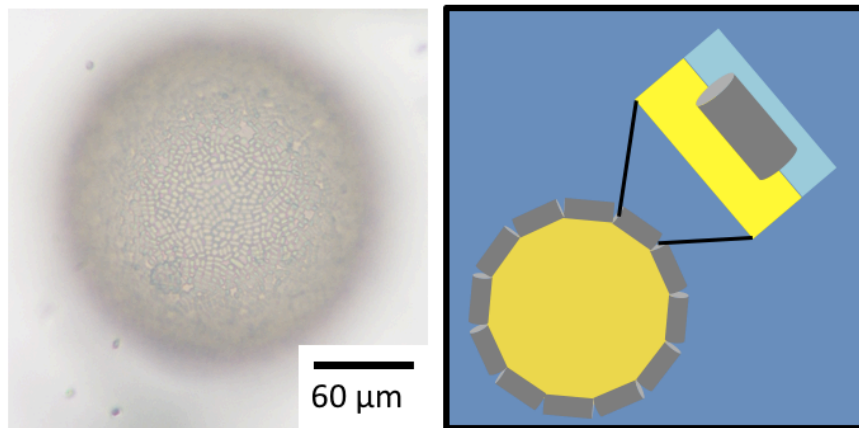
Introduction

Usually, emulsion is a mixture including two or more kinds of immiscible liquid/gas. In order to maintain the stability of emulsion system, the molecular emulsifier was used as a surfactant to stabilize the heterogeneous system. Especially, after functionalization, it was widely applied in many different field such as polymerization, pharmaceutics, cosmetics, food industry and so on[1-7]. At 1903, Ramsden et al. discovered

an interesting phenomenon that sulphur particles can stabilize oil droplets in water medium without conventional molecular surfactant[8], afterwards, Pickering et al. also reported the emulsion stabilized by solid particles in details[9]. As the excellent works about this type of emulsion, the emulsion that stabilized by solid particles such as silica, metal oxide, clay and polymer particles was named "Pickering emulsion"[10]. Comparing with a conventional emulsion using low molecular weight surfactant, the Pickering emulsion is more stable due to high desorption energy of the particulate particles.

Recently, Pickering emulsion is widely used in oil recovery[11], emulsion polymerization[12], responsive materials[13,14] and drug delivery system[15-18]. Fujii et. al. has reported to use polymeric particles as a particulate surfactant to fabricate the Pickering emulsions[19,20] and applied them in multi-cavity materials[21], responsive materials[22,23]. Typically, the authors utilized the hydrophobic polyaniline particles as a surfactant and prepared a liquid marble with a light-responsiveness.

Recently, non-spherical particles exhibit many excellent properties including optical, rheological and mechanical properties[24-27]. Utilizing these properties, non-spherical particles have been widely applied in colloidal crystal, microfluids, and cosmetics[28-31], The Pickering emulsion using non-spherical particles has been reported[32-35], however, investigation

of many details such as the stability of Pickering emulsion, the absorption behavior of particle at interface still remained. Recently, we found novel non-spherical polymer particles having unique cylindrical shape in which Pickering emulsion using the cylindrical particles as a particulate surfactant exhibited excellent stability as comparison with the system using spherical particles.

In this chapter, preparation of Pickering emulsion using the cylindrical particles was introduced. We mainly discussed more details about the stability of Pickering emulsion and the different experimental condition such as pH, particle concentration how to effect on the consequences.

Experimental Section

Materials

PS particles aqueous suspension (5 *wt*%) was prepared via stirring method after washing by centrifugation 3 times; sodium hydroxide (Nacalai Tesque Inc., Kyoto, Japan), hydrochloric acid (35%-37%, Wako Pure Chemical Ltd., Osaka, Japan), sodium hydroxide (Nacalai Tesque Inc., Kyoto, Japan), hydrochloric acid (35%-37%, Wako Pure Chemical Ltd., Osaka, Japan).

Preparation of Pickering emulsion

A typical preparation of Pickering emulsion as following. PS particles aqueous suspension (1.0 g, 5 *wt*%) was added into decane/water system (w/w, 0.8 g/2.4 g). After mixing by homogenizer at 6000 rpm for 5 minutes, the Pickering emulsion was observed by optical microscope.
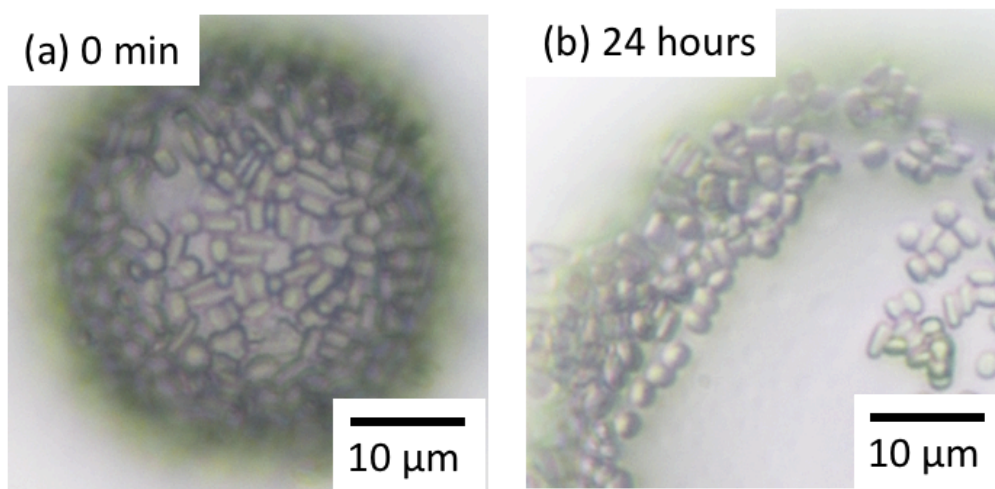
Results and Discussion

Figure 1. Optical microscopy photographs of (a) Pickering emulsion. (b) Just after 1 days, Pickering emulsion destroyed.

As figure 1a shown, Pickering emulsion using cylindrical particles was successfully prepared. The cylindrical particles were laying on the surface of oil droplet and act as a particulate surfactant, however, the stability of Pickering emulsion was not well. At room temperature, Pickering emulsion destroyed just after 1 days and the oil droplets were exposed as some particles dropped off (Figure 1b). We considered that the stabilizer of cylindrical particles in this experiment is PVP, that the side-chain of PVP has a larger stereospecific blockage that it will repel with each other, resulting some particles dropped off from droplet. By interfacial decoration to cylindrical particles, it probably be able to improve the stability of Pickering emulsion.
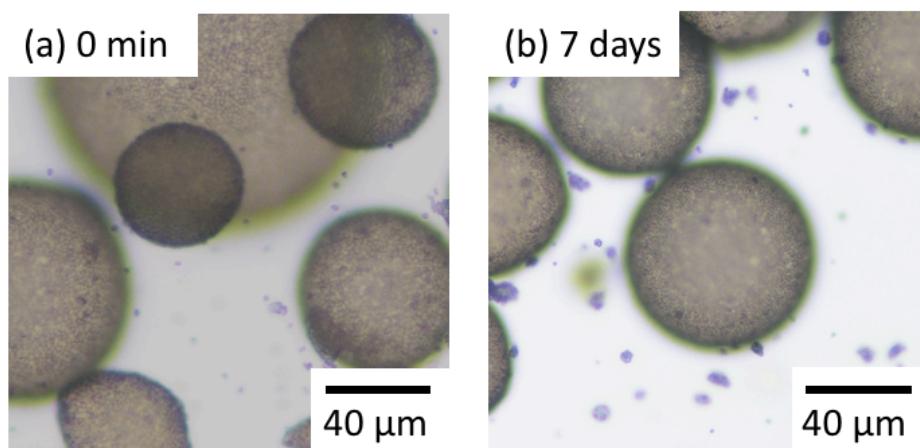
Figure 2. Optical microscopy photographs of the Pickering emulsion using cylindrical PS$_{PAA}$ particles(a). The Pickering emulsion after 7 days (b).

Subsequently, we used PS cylindrical particles stabilized by PAA as the particulate surfactant. As the side-chain of PAA can form hydrogen-bond via its carboxyl group, the cylindrical particles on surface of oil droplet may connect with each other to maintain the stability of Pickering emulsion. Actually, even though after 7 days, the Pickering emulsion using PS$_{PAA}$ cylindrical particles still maintain a better stability.

The concentration of particles can also influence on the stability of Pickering emulsion. In the preparation of Pickering emulsion, we altered the concentration of particles suspension to 10 *wt*%, 2 *wt*% and 1 *wt*%. From figure 3b and 3c, we can find that the Pickering emulsions were also able to generate, however, stabilities were not well. After one week, in the Pickering emulsion using 2 *wt*%, the oil has split out form droplet (Figure 3e) while in the concentration of 1 *wt*%, the Pickering emulsion has been

destroyed (Figure 3f).
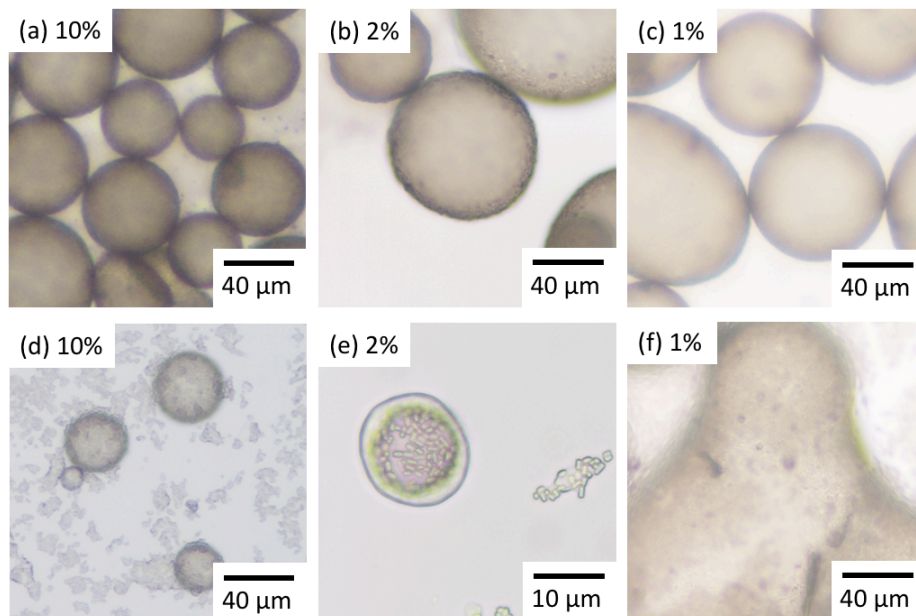
Figure 3. Optical micrographs of Pickering emulsion using cylindrical PS particles with different concentration (a) – (c). (d) – (f) is after 7 days.

It is because that in an excessively low concentration, there are not enough particles to encase droplet. On the contrary, if we increase the concentration of particle suspension, an excess particle will disperse in continuous phase (Figure 3a, d). Moreover, with the shortage of particles, the size of droplet is also decreasing with the decreasing concentration of particles.

Conclusions

The Pickering emulsion using cylindrical particles can be prepared by homogenizer. The stability of Pickering emulsion can be effected by many factors such as stabilizer and concentration of cylindrical particles. By optimizing the conditions of preparation, the droplet of Pickering emulsion can maintain the stability upon one week.

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Chapter 5

Stability of Pickering Emulsion Using Cylindrical Particles and Its Surficial Absorption Behaviour
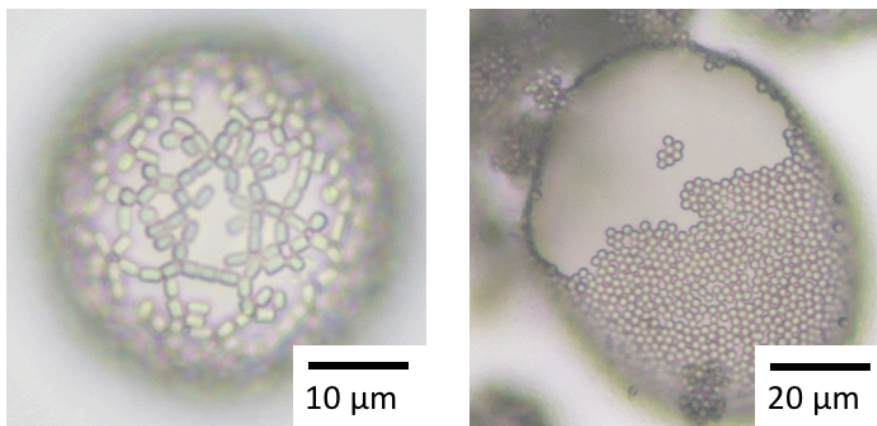
A robust structure of Pickering emulsion as a prerequisite is crucial for exhibiting its functions. Colloidal particles owe to their special property that is facile to fit different emulsion system by surface decoration, is most researched. Fujii et. al. attempted to use polymeric particles to fabricate a Pickering emulsion[1,2] and applied them in multi-cavity materials[3], responsive materials[4,5].

Recently, non-spherical particles as their asymmetry have demonstrate

many excellent properties including optic, rheological and mechanical properties[6-9]. Utilizing these properties, non-spherical particles have been applied in colloidal crystal, smart fluids, cosmetics, however, less in Pickering emulsion. Although some researches of the Pickering emulsion using non-spherical particles has been reported, the stability of emulsion is not well[10-13].

The stability of Pickering emulsion is relative to many factors such as the surficial property of particles, the arrangement of particles on droplet and the characteristic of liquid[14,15]. In this study, we mainly investigated the influences of particles on the stability of Pickering emulsion. In previous works, the reason why the stability of Pickering emulsion using a non-spherical particle is not well, was considered that the non-spherical particles can not closely pack onto the surface of droplet. There exited the interfacial free energy between uncovered portion of droplet and continuous phase. We prepared non-spherical cylindrical PS particles as particulate surfactant to fabricate the Pickering emulsion, and discovered that under certain circumstance the Pickering emulsion can maintain the stability even the uncovered portion of droplet contacted the continuous phase.

In this chapter, we discussed that the Pickering emulsion using PS_{PAA} cylindrical particles as a particulate surfactant can maintain the stability in

a long time even upon 4 months, due to stabilizer PAA can connect with each other by hydrogen bond of carboxyl group. Especially, carboxyl group as his proton, can buffer the effect of pH in Pickering emulsion system by protonating or deprotonating.

Herein, we prepared a Pickering emulsion at acid or alkaline environment as table 1 shown.

Table 1. Recipe for preparation of Pickering emulsion using cylindrical PS_{PAA} particles.

Ingredients		Acid	Neutural	Alkaline
PS_{PAA} suspension	(g)	1.0	1.0	1.0
HCl (1mol/L)	(g)	0.1	-	-
NaOH (1mol/L)	(g)	-	-	0.1
Water	(g)	2.4	2.5	2.4
Decane	(g)	0.8	0.8	0.8

The hydrochloride acid or sodium hydroxide (0.1 g) was added into aqueous suspension of PS_{PAA} cylindrical particles (1.0 g, 5 *wt*%) at stirring, and the particle suspension was added into water/decane (w/w, 2.4 g/ 0.8 g) system. After mixing by homogenizer at 6000 rpm for 5 minutes, the Pickering emulsion was obtained and observed by optical microscope.
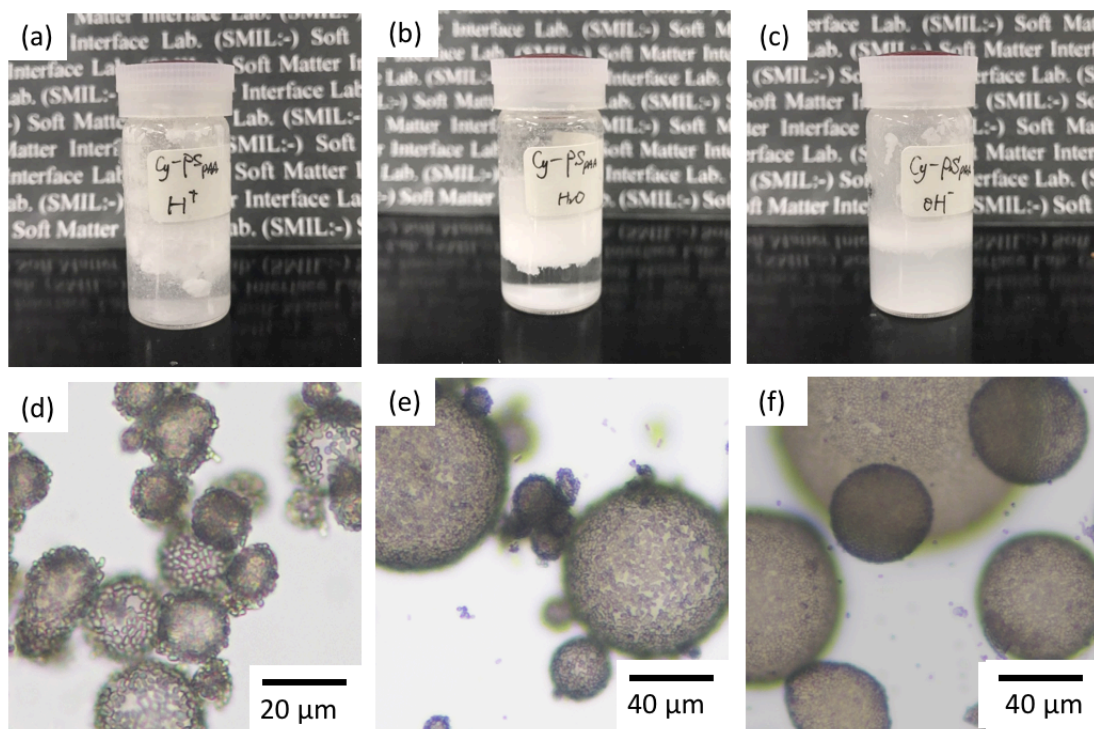
Figure 1. The Pickering emulsion using cylindrical PS$_{PAA}$ particles in different environment: visual images of Pickering emulsion in (a) acid, (b) neutral and (c) alkaline environment; optical microscope photos of Pickering emulsion in (d) acid, (e) neutral and (f) alkaline environment.

The figure 1a – c actually showed Pickering emulsion can be prepared in different environment. The oil phase decane was dispersed and caged by the cylindrical PS$_{PAA}$ particles. As the density of decane was lower than water, we can adjudge that the creamy and flocculent part was oil phase and transparent part was aqueous phase. As the pH in three samples is different, the morphologies is also different. In acid environment, as the carboxyl group of stabilizer PAA of particles severely connected with each other by hydrogen bond, the droplet of Pickering emulsion almost

aggregated. Moreover, due to the aggregated droplets was strongly stirred by homogenizer, the aggregated part was easily peeled out from droplet. From figure 1d shown, we can also observe that a lots of droplets were naked in aqueous phase. In neutral and alkaline environment, the droplets were dispersed in aqueous phase and wrapped by PS$_{PAA}$ cylindrical particles. Especially in alkaline environment, the droplets almost did not aggregate.
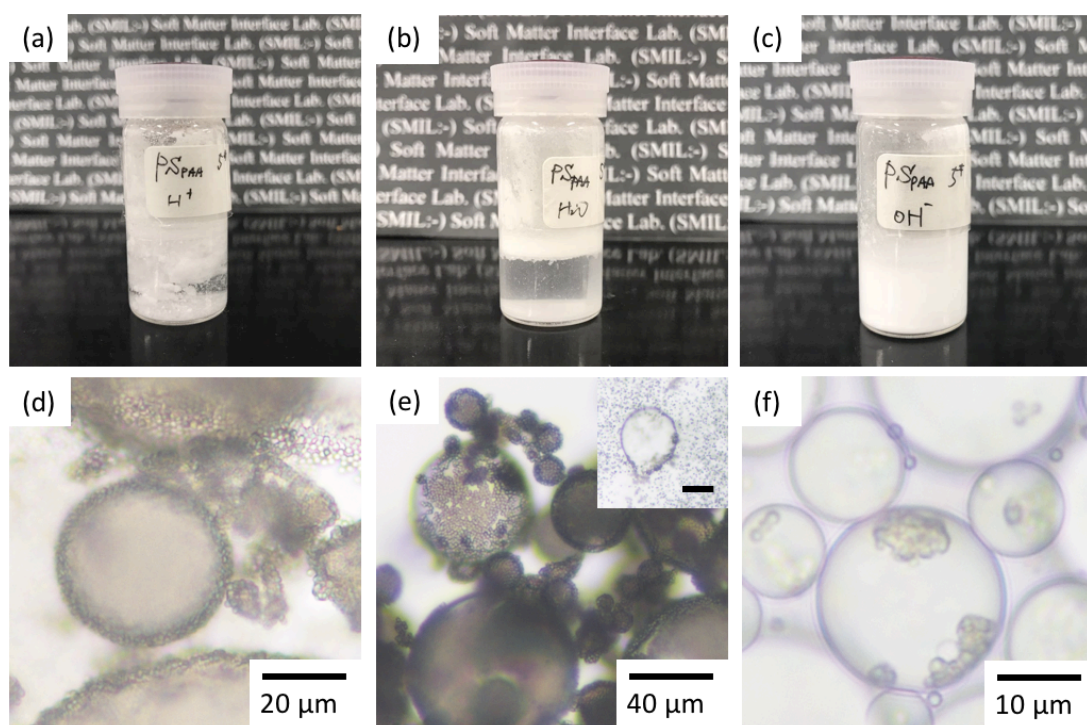

Figure 2. The Pickering emulsion using spherical PS$_{PAA}$ particles in different environment: visual images of Pickering emulsion in (a) acid, (b) neutral and (c) alkaline environment; optical microscope photos of Pickering emulsion in (d) acid, (e) neutral and (f) alkaline environment. The inset in (e) is Pickering emulsion after 3 days and scale bar is 40 μm.

However, in the case of Pickering emulsion using spherical PS_{PAA} particles, the stability was not well. Even though, the Pickering emulsion can be prepared in acid and neutral environment, the droplets of oil phase were seriously aggregated as figure 2d and e shown. And the droplets were also unstable and destroyed in neutral environment just after 3 days (Figure 2e inset). Moreover, the Pickering emulsion even can not generate in alkaline environment. From figure 2f shown, although the droplets were generated after stirring by homogenizer, the droplets were almost exposed in aqueous phase without any package of PS_{PAA} particles (Figure 2f). It could be owed to the carboxyl group of stabilizer PAA of particles was deprotonated in alkaline environment, and negative charged stabilizer was mutually repulsed resulting in PS_{PAA} particles can not connect with each other. Just after 30 minutes, the oil droplets coalesced and fused to one phase as the interfacial minimization rule. The differences of stability between the spherical and the cylindrical PS particles could probably explained by the contact area. Observing two kinds of different Pickering emulsion, we can find that the arrangement of particle on the surface of droplet is quite different.
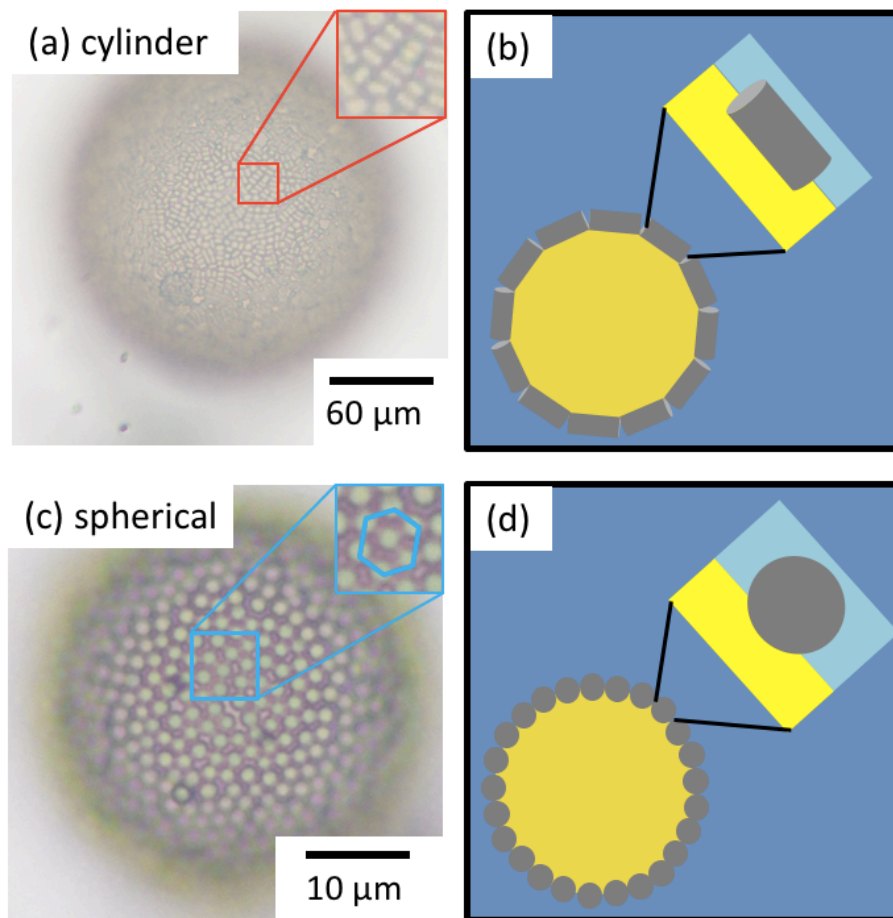
Figure 3. Optical micrographs of Pickering emulsion using (a) cylindrical particles and (c) spherical particles. The diagraphs show the arrangement of (b) cylindrical and (d) spherical particles on the surface of oil droplets.

In the situation of cylindrical particles, the particles are laying on the surface of oil droplet and the contact area between cylindrical particles and oil droplet is quite lager than that of spherical particle. It is the reason why stability of Pickering emulsion using the cylindrical particles was better than the spherical particles[16-19].
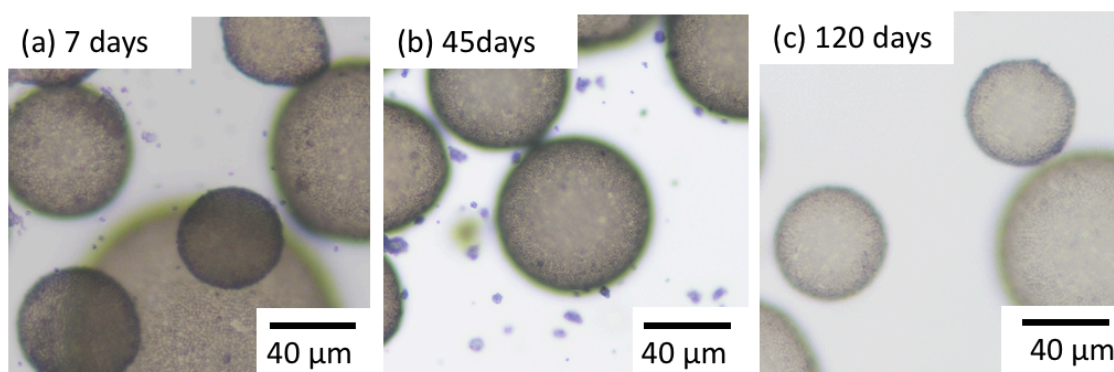
Figure 4. Optical micrographs of Pickering emulsion using the cylindrical PS particles after (a) 7 days, (b) 45 days and (c) 120 days.

From figure 4, we can also find that the Pickering emulsion using cylindrical particles demonstrated a more excellent stability than that of spherical one. Even after 120 days, the droplets still maintain a better stability.
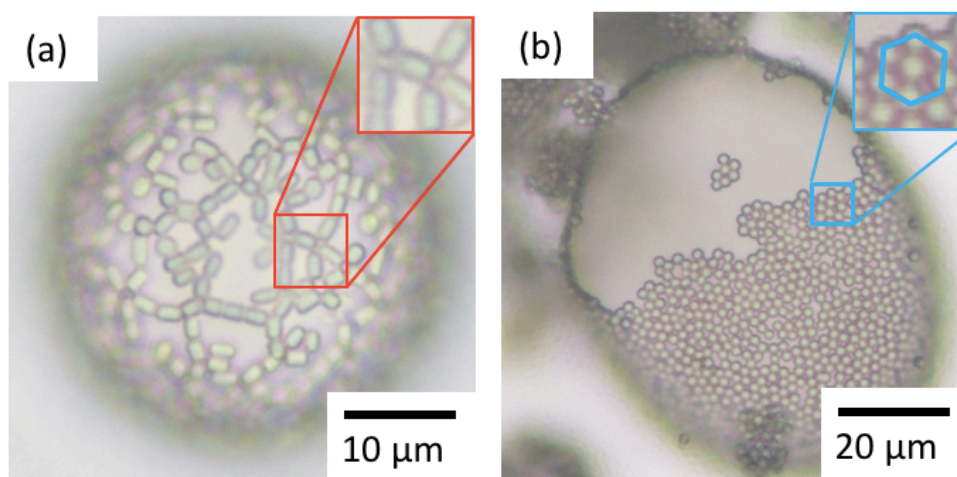

Figure 5. Optical micrographs of Pickering emulsion using the (a) cylindrical and (b) spherical PS particles.

Interestingly, in the sample of Pickering emulsion using a PS_{PAA}

cylindrical particle, we find some emulsion droplet which have special structure. The Pickering emulsion using cylindrical particles can also maintain the stability by exchanging configuration to form network as figure 5a shown. When cylindrical particles drop out from surface, the cylindrical particles will exchange configuration of self to connect with each other and generate the network to cage the oil droplet.

Even the most portion of oil droplet have been exposed into the aqueous phase. It is quite different from a previous perspective that the destruction of Pickering emulsion was owing to the interfacial free energy between exposed droplet and continuous phase. However, in the Pickering emulsion using cylindrical particles, the interfacial free energy was offset by a connection of cylindrical particles. Oppositely, in Pickering emulsion using the spherical particles, the oil droplet will destroy if it exposed in continuous phase (Figure 5b).

Moreover, when the Pickering emulsion stabilized by cylindrical particles was forcibly destroyed by heating or a mechanical method (e.g., pressing the cover class when observing the sample with the microscope), the cylindrical particles assembled in string-like structures (figure 6a, b), due to the particles moved with the micro-fluid at interface. In Figure 6c and d, the SEM images of the cylindrical particles after arrangement are shown.
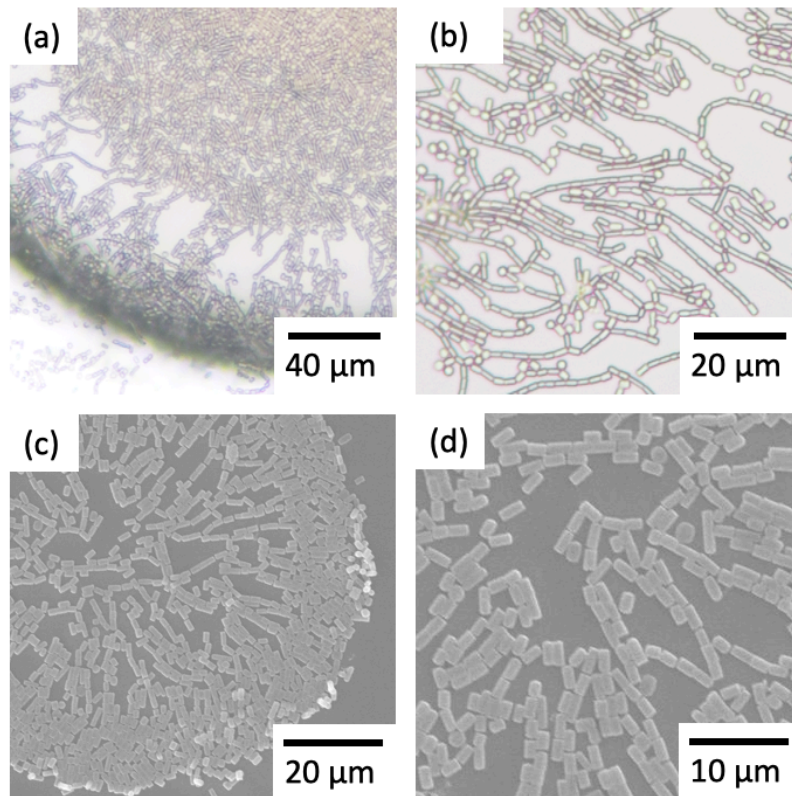
Figure 6. Optical micrographs (a, b) and SEM images (c, d) of the Pickering emulsion stabilized by cylindrical particles after destruction.
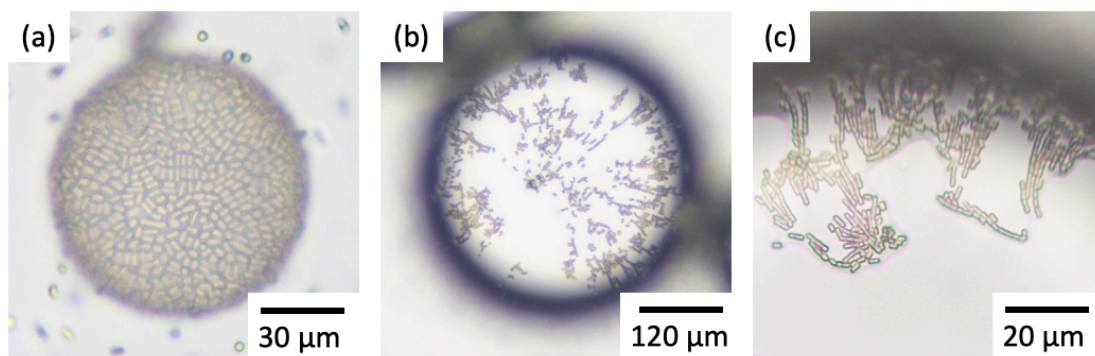

Figure 7. Optical micrograph of cylindrical particles on the surface of droplet: (a) droplet before puffing and (b), (c) after puffing by heating.

The droplet can also be destroyed by heating. With the increasing

temperature, micro-flow on surface of droplet became rapid and

result in the cylindrical particles arranged along with the micro-flow.

Conclusions

Pickering emulsion using cylindrical particles have been successfully prepared by homogenizer. As the contact area between oil droplet and cylindrical particles lager than that of spherical particles, the Pickering emulsion using cylindrical one demonstrated an excellent stability. Moreover, cylindrical particle as its anisotropy can exchange the configuration of self to form a network structure for caging the oil droplet. Even though tremendous interfacial free energy was generated between exposed droplet and continuous phase, the special structure can still exist.

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Conclusions

In this study, a facile and novel approach to prepare polymer cylindrical particles was proposed, which merely need to stir spherical particles in 2 *wt%* polyvinyl pyrrolidone aqueous solution at 360 rpm for 24 hours. As the simplification of this stirring method, it can be used in industrial manufacture at a large amount. It is meaningful to the fields of theoretical research and application that need to use cylindrical particles.

And obtained particles via stirring method has a completely cylindrical shape, which is quite different from two slender heads of rod-like shape. It because of the shear force generated between particles and medium can homogeneously stress on the particles, while particles prepared via stretching method or PRINT^{TM} method has two slender heads.

Moreover, mechanism of deformation should be also different from stretching method or PRINT^{TM} method, which is merely mechanical deformation. In the case of stirring method, we infer that there should be a plasticization before deformation of particles. The detail of mechanism of plasticization will be discussed in later work.

At last, cylindrical particles as a particulate surfactant can be used for preparation of Pickering emulsion. As the stabilizer of cylindrical particles, the Pickering emulsion can exist in acid environment and alkaline

environment. Interestingly, Pickering emulsion using cylindrical particles can maintain the stability by exchanging a configuration of the particles and form a network structure to cage the oil droplet.

Curriculum Vitae

Conferences

2016.12.13th – 16th (Fukuoka, Japan)
The 11ᵗʰ SPSJ International Polymer Conference   Poster presentation

2017.5.29th – 31st (Chiba, Japan)
66th SPSJ Annual Meeting   Poster presentation

2017.6.23rd – 30th (Bilbao, Spain)
International Polymer Colloids Group Conference 2017
                                    Poster presentation   **(Post award)**

2017.9.20th – 22nd (Matsuyama, Japan)
66th SPSJ Symposium on Macromolecules
                                    Poster presentation   **(Post award)**

2018.3.7th – 9th (Fukui, Japan)
The 6th Asian Symposium on Emulsion Polymerization and Functional Polymeric Microspheres   Poster presentation   **(Post award)**

2018.5.23rd – 25th (Nagoya, Japan)
66th SPSJ Annual Meeting   English oral presentation

2018.7.1st – 5th (Cairns, Australia)
IUPAC Macro2018   Poster presentation

2018.12.4th – 7th (Hiroshima, Japan)

The 12th SPSJ International Polymer Conference   Poster presentation

2018.12.15th (Tokyo, Japan)

1st Glowing Polymer Symposium KANTO   English oral presentation

Papers

Chapter 1, 3

A Facile Method for Preparation of Polymer Particles Having a "Cylindrical" Shape

Wei Li, Toyoko Suzuki, Hideto Minami

Angew. Chem. Int. Ed., **57**, 31(2018)

Chapter 2

The Formation Mechanism of Cylindrical Particles in a Fluid

Wei Li, Ohmura Naoto, Hideto Minami

In preparation

Chapter 4, 5

Pickering Emulsion Using a Cylindrical Particle as Surfactant and The Absorption Behavior at Interface

Wei Li, Hideto Minami

In preparation