동적 상분리법을 이용한 이방성 도토리형상 입자 제조

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Anisotropic Acorn-like Particle Fabrication Via a Dynamic Phase Separation Method

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요   약: 이방성 입자는 독특한 물리적 특성 때문에 다양한 분야에서 발표되고 있다. 여기서, 이방성 도토리구조 나노 입자를 제조하기 위해 새로운 동적 상분리 방법이 도입된다. 동적 상분리 방법은 용제 증발 및 무용제에 의한 침전으로 구성된다. 하부층은 비용매 회석제로서 물을 공급함으로써 제어되며, 상부층의 상분리는 휘발성 용매의 확산 및 증발에 의존한다. 이 상태에서, 도토리 형 입자가 제조되었다. 물이 채워진 밀폐된 상자(자발적 상분리)하에서, 단분산 폴리스틸렌 입자가 합성되었다. 동적 상분리와 자발적 상분리가 공존할 때, 캡과 입자의 크기가 변경되었다. 또한, 폴리스틸렌 용액의 부피는 입자 형상에 영향을 미친다. 독특한 구조가 다양한 응용 분야에 활용될 수 있기 때문에 멤브레인 기반의 제어된 물 공급과 같은 첨단 기술이 개발되면 단분산의 도토리와 같은 입자가 제조될 수 있을 것이다.

Abstract: Anisotropic particles have been issued in various fields due to their unique physical properties. Herein, a novel dynamic phase separation method (DPS) is introduced to fabricate anisotropic acorn-like nanoparticles. DPS consists of two dynamic conditions; solvent evaporation and nonsolvent induced precipitation. The bottom layer is controlled by feeding the water as a non-solvent diluent, and the phase separation of the upper layer relies on the diffusion and evaporation of a volatile good solvent. At this condition, the acorn-like particles were fabricated. Under a closed box filled with water (spontaneous phase separation), monodisperse polystyrene (PS) particles were synthesized. At the coexistence between DPS and spontaneous phase separation, the sizes of cap and particle were changed. Also, the volume of PS solutions influences on the particle shape. Since the unique structures could be utilized into various applications, if advanced techniques such as membrane-based controlled water feeding is developed, monodisperse acorn-like particles could be tuned.

Keywords: anisotropic particle, acorn-like particle, phase separation, polystyrene

1. Introduction

Polymeric nano-/microparticles have been widely studied in a variety of fields such as electronics, drug delivery, fluids with respect to the size[1-3]. With the ad-

ditional functions, many groups have tried to create core/shell as well as Janus particles with more attractive physical properties[4]. Thus, if advanced functional structures in particle morphology/structure can be found, novel physical properties could be unveiled for the next

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generation of functional materials[5]. Recently, those particles were used for precise pore size membrane. For example, Qiugen *et al.* reported the free-standing nanoporous membrane using PS nanoparticles[6]. The nanoparticles could be used for pore formation agents after removal so that it could be also microfiltration membrane[7]. When Breath-Figure method is combined with assembly nanoparticles, three-dimensional inherent membrane can be synthesized[8]. Those intrinsic unique structure could be used as supports for interfacial polymerization[9-12].

Traditionally, methods for fabricating polymeric particles could be subdivided into two groups: top-down and bottom-up methods. The bottom-up method (e.g., emulsion and suspension polymerization) is generally selected to synthesize narrow size distribution in the nano-size[13]. However, it might have some drawbacks in terms of the kind of the polymer (limited selection in the monomers). Top-down methods can be relatively simply achieved by preparing polymer solutions with good solvents, based on its phase diagram. Thus, it holds great potential for commercialization[14].

To induce the phase separation for nucleation/growth, there are two major methods; precipitation methods through miscible non-solvent additions and evaporation method of atomized droplets. Typically, spraying methods is preferentially considered for particle generation because the method is simple and cost-efficient. Also, interesting particle structures (e.g. torus, hollow, or core/shell) can be generated by controlling the consolidation mechanism with complicated evaporation of good solvents on/in the size-restricted droplets[15].

In other methods, polymers are prepared with good solvents at a certain concentration at the first stage. And then, the solution is dropped into a non-solvent[16]. If the composition ratios of three components passes beyond a binodal point (at a certain critical concentration) in phase diagram, the polymeric chains are aggregated (nucleation step) and then polymer chains in the thermal fluctuation attaches and grows on the nuclear (growth step). Typically, it is difficult to well control the kinetic aspect because of fast mixing rate
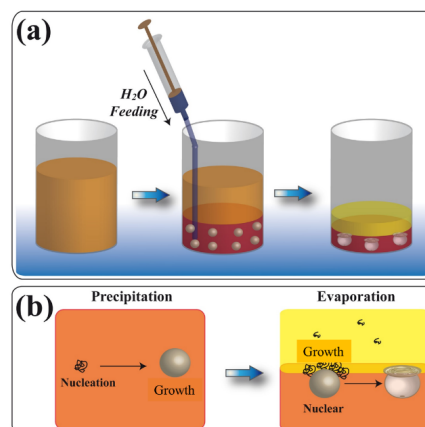

Fig. 1. Schematic illustration of a dynamic phase separation method.

between the good solvent and poor-solvent. Recently, as one of the developed method to solve the limitation, Shimomura *et al.* reported an improved method to synthesize monodisperse nano-/microparticles[17]. Furthermore, as controlling both kinetic and thermodynamic aspect, they produced various interesting structures such as stacked lamellar, onion, Janus and core/shell structures, which is called the phase-separated technology [17-19].

Thus, current developed methods provide us some of ideas how to create novel functional particles. Herein, we introduce the novel combination method, which is referred as to a novel dynamic phase separation method (DPS) as shown in Fig. 1.

The polymeric solutions with organic good solvents have density lower than water density of 1 kg/m³. Let's consider the precipitation method. When the miscible non-solvent is added into the polymer solution, it is diffused and polymer chains are aggregated at a certain critical concentration. However, we can observe a layered structure anywhere when a solvent with different density is very carefully pumped on/under a solution without any vigorous stirring. Thus, a heavier miscible non-solvent is pumped into a polymer solution, we can introduce separated two layers and the polymer particle might be generated at the bottom layer. The particles hold specific ability to stabilize the interface[20]. In other hands, synthesized particles might move into the

interface between different density layers, and then the diffusion rate is probably decreased. At this time, if there is no any external energy to mix the solution, the two layers might be stable even though a non-solvent is miscible. After that, if a non-solvent have volatile properties, we can expect the phase-separated methods as introduced by Shimomura group[17-19]. Thus, as controlling the kinetic of the upper layer as well as the precipitation at the bottom layer, various structures could be produced. Therefore, this study is to prove the possibility of our suggestion for the next generation of functional material as a simple process to be commercialized.

2. Experimental

As one of a model polymer, polystyrene (PS, Mw = 350,000 g/mol, PDI = 1.05) was purchased from Sigma-Aldrich (USA). Tetrahydrofuran (THF) as a HPLC grade was received from J.T. Baker (Germany). The second distilled water was used as a miscible non-solvent. The polymer was dissolved with THF at 0.1 wt%.

For very careful feeding, a KD100 science pump (KDS Science Co.) was used at a proper feeding rate to generate the two-layered structure. The stainless steel nozzle (I.D. = 0.2 mm, O.D. = 0.41 mm, Ban Seok, South Korea) was connect to the syringe (5 mL, Becton, Dickinson and Company, USA), and the tip was located the bottom of a container (1 × 1 × 4, W × L × H cm^3) with 2 mL of polymer solutions. To control the evaporation rate of THF, the ambient temperature was controlled in a home-made closed box at 25°C.

After the feeding of distilled water at various feeding speed, the container was deposited for 24 hours to remove the volatile solvent of THF. Synthesized particles were collected on the slide glass and dried in the vacuum oven at an ambient temperature (~25°C).

The scanning electron microscopy (SEM) images of the particles were obtained using S-4800 (Hitachi, Japan) at 4 kV. All the samples were sputter-coated with platinum (Pt) at 3 nm thickness.
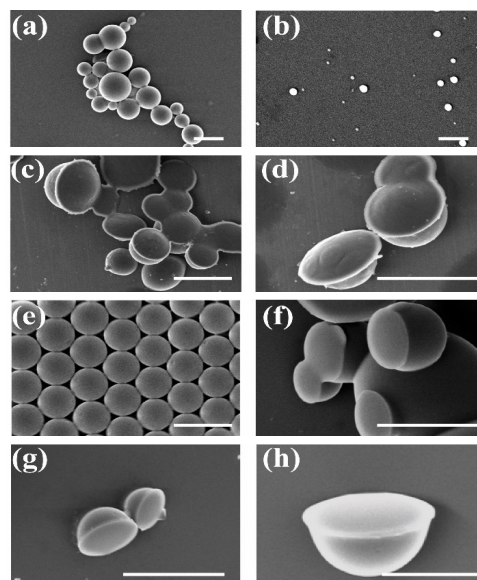

Fig. 2. SEM images of PS particles produced (a) at the feeding rate (5 mL/h) with vigorous stirring (b) at the feeding rate (0.04 mL/h) with vigorous stirring into 2 mL PS solution, (c), (d) at the slower feeding rate (0.04 mL/h) without vigorous stirring into 2 mL PS solution, (e) in a home-made closed box with external water environment, (f) at feeding rate (0.04 mL/h) and in a home-made closed box into 2 mL PS solution, (g) at feeding rate (0.04 mL/h) and in a home-made closed box into 1.5 mL PS solution, and (h) at feeding rate (0.04 mL/h) and in a home-made closed box into 1 mL PS solution. The scale bar respond to 500 nm.

3. Results and discussion

One of the simplest methods to generate polymeric particles is the precipitation methods using a non-solvent based on a phase diagram. The conventional method is relatively well described in previous results[16]. The current results also show the similar trend that the feeding of non-solvent water for PS can induce the nuclear at a certain critical concentration and generate particles. The nucleation relies on the feeding rate because of unsteady-state non-equilibrium. In other hands, the number of nuclear might increase with increase the feeding rate so that the particle size can be controlled by the feeding rate. At the relatively fast feeding rate (5 mL/h) with vigorous stirring, the particle size is about 400 nm (Fig. 2(a)). However, at the slower feed-

ing rate (0.04 mL/h), the particle size is below 100 nm (Fig. 2(b)).

As mentioned before, if the non-solvent is feed into the good solvent under different density without any external energy to mix, the nucleation/growth at the mixing bottom layer might be produced. Herein, 0.1 mL of non-solvent water (0.04 mL/h) was inserted at the bottom. At that time, the Brownian diffusion was observed. Especially, the bottom layer became clear. During feeding, the reactor was under an open system. Thus, THF was evaporated continuously at a certain rate. After 24 hours, almost particles wear the caps as shown in Fig. 2(c, d).

The results give us more questions if the evaporation is well controlled as suggested by Shimomura. Without water feeding, the THF solution was exposed in a home-made closed box with external water environment. This system might be a good well-controlled condition for the fabrication of the homogeneous particle because THF can be diffused into external water, and gaseous water can also be diffused into PS solution. Similar to Shimomura, PS particles (~250 nm) have homogeneous size distribution as shown in Fig. 2(e). Thus, our system can be combined with Shimomura method. The water-feed solution was combined with the home-made closed box. When non-solvent water (0.04 mL/h) was feed into PS solution, the particle size (Fig. 2(f)) is larger and the cap size is smaller than PS particle produced as Fig. 2(c, d). When the volume of PS solution was reduced up 1.5 mL, the PS particles (Fig. 2(g)) have oval structure with cap. When the volume of PS solution (Fig. 2(h)) was reduced up to 1 mL, the PS particle has hemisphere structure with cap.

Unfortunately, we could not supply the clearly detailed explanation about the dynamic phase separation mechanism that combines between evaporation and precipitate phase separation. However, we could suggest a possible mechanism; PS particles produced in the bottom layer are floated around the interface because an absorbed good solvent (tetrahydrofuran) reduces the density of particles. Therefore, PS particles act as the nuclear. Herein, the PS particles do not have any Brownian motion and PS chains could not diffuse into bottom layer. From this interesting phenomenon, the secondary PS chains are growing on the PS particles existing at the interface zone.

The structures of synthesized PS particles are undoubtedly very unique. There are many chance to observe and tune the structure. For example, if the water semipermeable membrane is assembled into the dynamic phase separation mechanism instead of needle feeding, we could expect to produce the homogeneous and monodisperse capped particles. Also, a certain material is simultaneously feed with water, the composite particles can be synthesized.

4. Conclusion

This study exhibit how to produce asymmetric polymeric particles via dynamic phase separation mechanism. When the non-solvent water vapor is supplied into PS solutions, the particles has monodisperse shape. When the non-solvent water is supplied into PS solutions through needles at a certain feeding rate, the PS particles wear the cap. When the size of cap seem to be reduced. More interestingly, as reducing the volume of PS solutions, the structure of PS particles change into semi-sphere.

Acknowledgements

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