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Morphology control of anisotropic nonspherical functional polymeric particles by one-pot dispersion polymerization

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ABSTRACT

A feasible and versatile route for a large-scale synthesis of monodisperse nonspherical functional polymer particles by one-pot dispersion polymerization was demonstrated. The particle morphology could be precisely tuned by varying the divinylbenzene (DVB) concentration, the start feeding time of DVB, the total feeding time of DVB, the styrene (St) mass ratio of stage I/stage II, and the solvent polarity. Sphere-like, polyhedron-like, and red blood cells (RBC)-like particles with dimples or smooth surface were obtained. In addition, the formation mechanism of these nonspherical particles was ascribed to the phase separation induced by the uneven distribution of cross-linked network. Because of the incompatibility between St homopolymer chain and cross-linked network, St homopolymer chain was forced to move to those zones where the blend was allowed. The particle surface was forced to distort, leading to the formation of particles with various morphologies.

1. Introduction

The use of polymeric particles as elements, through their proper assembly, to construct desired structured materials is a strategy widely applied in practice. For anisotropic, nonspherical particles, since charges, van der Waals forces, hydrophobicity, and curvature are inhomogeneously distributed on the surface, thus supplying more dimensions for us to generate materials of rather different structures through aggregation, gelation, and self-assembly. Recently, an increasing research interest has been drawn for the design and synthesis of monodisperse nonspherical particles in the micron and submicron size range because of the potential applications in functional coatings [1–4], anisotropic photonic crystals [5–7], drug carriers [8–10], biological sensors [11], and complicated assembled structures [12,13]. Nevertheless, the precise control of morphology has been a key challenge during the preparation of nonspherical particles as the surface tension promotes the formation of spherical particles for minimizing the surface energy.

In general, different methodologies have been used to fabricate nonspherical latex particles, including the deformation of spherical particles [14,15], lithography combining with microfluidic technique [16–20], and emulsion polymerization [21–26]. Certainly, the deformation of spherical particles is an effective method for fabricating ellipsoidal-based particles. Champion et al. [15] obtained different nonspherical particles (such as rectangular disks, rods, worms, and so on) by the stretching of spherical particles. Lithography combined with a microfluidic technique is a newly developed approach for fabricating the particles with diverse shapes. Min et al. [19] demonstrated a microfluidic approach to create uniform anisotropic microparticles with dimpled core-shell, spherical core-shell, and acorn-shaped structure by using phase separation of polymer blends confined in emulsion droplets. However, a common limitation of these two synthesis methods is high cost, low yield, and a complicated synthesis process or difficulty to control morphology. Emulsion polymerization is a conventional and typical method for the synthesis of spherical and nonspherical particles; this method allows the control of not only surface morphology but also chemical and physical properties of nonspherical particles. Huang et al. [24] demonstrated a facile control of cavity structures of the latex particles by varying the feeding method of divinylbenzene (DVB) during emulsion polymerization. Kim et al. [27] generated the dumbbell-type particles with well controllable shape and surface chemistry based on the seeded polymerization technique. Yet, the dispersion polymerization approach toward anisotropic particles has some advantages. First, the synthesis process is simple and straightforward. Second, the morphology, size, structure, and composition of particles can be tuned easily. Finally, the introduction of functional monomer makes it possible to functionalize anisotropic particles [28,29]. Thomson et al. [30] investigated the effect of cross-linker on particle morphology by dispersion copolymerization of styrene and DVB, producing particles ranging from classic smooth-surfaced spheres at low DVB concentrations to node-covered cups and heavily dented spheres at higher levels. Liu et al. [31] presented a simple one-step dispersion polymerization approach to prepare particles with

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a combination of anisotropies in morphology, surface roughness, structure and composition. Shi et al. [32] prepared the thermal-sensitive poly(*N*,*N*-diethylacrylamide)-grafted poly(acrylonitrile/styrene) (PDEA-g-PAN/PSt) polymeric microspheres with raspberry-like morphology by dispersion copolymerization of PDEA macromonomer, styrene, and acrylonitrile.

In addition, the formation mechanism of nonspherical particles has been rarely reported in the past [5,22,24,33,34]. Certainly, the main formation mechanism is the heterogeneous phase separation. Masayoshi Okubo et al. [35] proposed that the formation of anomalous polymer particles with red blood corpuscle shape was attributed to the evaporation of unpolymerized DVB and toluene, resulting in pressure difference between interior and exterior of the particles. Xu et al. [5] ascribed the possible formation of the cavities of the mushroom-cap-shaped particles to phase separation because of the preference of hydrophobic PDVB upon the surface toward the interior of particle core part. Huang et al. [24] illustrated the possible formation of the particles with various cavity structures. This was mainly attributed to the single or multilocation of PDVB at the surface of particles, which resulted in a controllable phase separation. According to a previous work [5,24], the research on the formation mechanism of nonspherical particles focused only on single cavity and multicavity structures, and phase separation was the main reason for the formation of nonspherical particles.

In our previous research, we synthesized monodisperse red blood cell (RBC)-like PS particles and briefly illustrated the possible formation mechanism of RBC-like PS particles [36]. Herein, we designed and synthesized monodisperse, anisotropic, and nonspherical polymeric particles by dispersion copolymerization of St and DVB monomers, where DVB was used as a cross-linker. The desired morphology and size were realized by tuning the thermodynamics and kinetics at the oil–water interface. We mainly investigated the effects of DVB concentration, the start feeding time of DVB, the total feeding time of DVB, the St mass ratio of stage I/stage II, and the solvent polarity on the resulted morphology of particles. Moreover, we proposed a possible formation mechanism of nonspherical particles. The formation of various morphologies was mainly attributed to uneven distribution of P(DVB-St) nuclei on the surface of particles and further development into a heterogeneous cross-linked network. Thus, the results of this study can lead not only to substantial contributions to the theory of colloidal science and engineering, but also to methodologies in design and preparation of the functionalized polymeric particles and their industrial applications.

2. Experimental section

2.1. Materials

All reagents used were of analytical grade. Styrene (St, Damao Chemical Reagent Co., Ltd.) was purified by treating with a 5% NaOH aqueous solution. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Tianjin Kermel Chemical Reagent Co., Ltd.) was recrystallized from ethanol before use. DVB (80% isomer, Alfa Aesar (Tianjin) Reagent Co., Ltd.) was used as a cross-linker. Polyvinylpyrrolidone (PVP, K29-32, Aladdin Reagent Co., Ltd.) with an average molecular weight of 58,000 $g \cdot mol^{-1}$ was used as a stabilizer. Anhydrous ethanol (>99.7%, Guangdong Guanghua Science and Technology Ltd.) was used as a solvent. Deionized water was used in all experiments.

2.2. One-pot dispersion polymerization

The nonspherical polystyrene particles with various surface morphologies were synthesized by one-pot dispersion polymerization. The preparation detail of nonspherical particles is given in Table 1. All experiments were performed in a 250 mL four-necked round-bottom flask equipped with a Teflon mechanical stirring blade, a condenser, and a nitrogen gas inlet. First, St, AIBN (0.2 g), PVP (2.0 g), ethanol, and deionized water were charged into the four-necked round-bottom flask, where the feeding mass of St, ethanol, and deionized water in stage I was listed in Table 1. After a homogeneous solution was obtained at ambient temperature by stirring at 200 rpm, a deoxygenation process (N_2 was utilized) was performed for 30 min. Subsequently, the mixture was placed in a water bath thermostated at 70 °C with stirring. The feeding of the prepared mixture consisting of DVB, St, ethanol and deionized water was started by a peristaltic pump after the polymerization process was run for a period of time, where the composition of the prepared mixture in stage II was also listed in Table 1. The polymerization reaction was maintained at 70 °C for 24 h. The resultant product was centrifuged at 8000 rpm for 10 min, and the sediment was then washed three times with anhydrous ethanol and deionized water to remove the residual monomer and stabilizer, respectively.

Table 1
Preparation detail of nonspherical particles.

Batch	Start feeding time (h)	Total feeding time (h)	Stage I[a] St (g)	Ethanol (g)	H_2O (g)	Stage II[b] St (g)	DVB[c] (wt%)	Ethanol (g)	H_2O (g)
1	1.5	5	10	50	0	10	0–10	50	0
2	1.5–9.0	5	10	50	0	10	2	50	0
3	1.5	2–10	10	50	0	10	1	50	0
4	1.5	5	13	50	0	7	2	50	0
5	1.5	5	15	50	0	5	2	50	0
6	1.5	5	18	50	0	2	2	50	0
7	1.5	5	19	50	0	1	2	50	0
8	1.5	5	20	50	0	0	2	50	0
9	1.5	5	10	45	5	10	2	45	5
10	1.5	5	10	40	10	10	2	40	10
11	1.5	5	10	35	15	10	2	35	15
12	1.5	10	10	50	0	10	2	50	0

[a] The addition mass of reagents before polymerization.
[b] The addition mixture after polymerization run for a period of time.
[c] On the basis of the total St mass.

2.3. Characterization of the particle morphology

The particle morphology was characterized by field-emission scanning microscopy (FE-SEM, ZEISS ULTRA 55). The samples for SEM characterization were first prepared by depositing a droplet of a diluted sample on aluminum foil and allowing the solvent to evaporate. Subsequently, the samples were sputtered with platinum. Transmission electron microscope (TEM, HITACHI H-7650) was used to characterize the particle morphology operating at 80 kV.

3. Results and discussion

3.1. Morphology control of particles

3.1.1. Effect of DVB concentration on morphology

The DVB concentration is a key parameter to control the surface morphology of colloid particles [30,33]. Therefore, we performed a series of experiments to explore the DVB concentration effect on the surface morphology, where DVB concentration was based on total St monomer mass in all cases. Fig. 1 shows the SEM micrographs of as-prepared polymeric particles. As shown in Fig. 1, nonspherical particles with various morphologies were obtained when the different DVB concentration was introduced. Monodisperse spherical PS particles could be prepared without the addition of DVB (Fig. 1a). However, when 0.2 wt% DVB was added, the morphology was retained as monodisperse spherical particles, and the particle size was slightly increased (Fig. 1b). During the dispersion polymerization, DVB copolymerizes with St monomer to form the copolymer P(DVB-St). Participated P(DVB-St) nuclei move to the surface of growing particles and further develop into the cross-linked network [36]. In addition, the phase separation is closely associated with the density and distribution of the cross-linked network. Both the larger cross-linked density and more asymmetrical