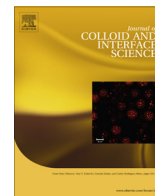




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Facile synthesis of core–shell/hollow anisotropic particles via control of cross-linking during one-pot dispersion polymerization

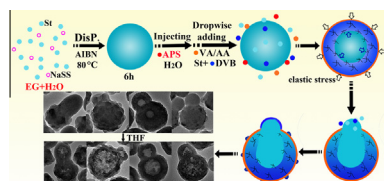


Yanan Liu, Yuhong Ma, Lianying Liu*, Wantai Yang*

Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

State Key Laboratory of Chemical Resource Engineering College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

Preparation of anisotropic particles based on seed phase separation involves multiple processes, and asymmetrical structures and surfaces cannot be produced when anisotropic shapes emerge. In conventional one-pot dispersion polymerization (Dis.P) using cross-linker, only spherical particles are prepared due to rapid and high cross-linking. Herein, monodisperse snowman-like particles with core-shell/hollow structures and partially rough surface were synthesized straightforward by a modified one-pot Dis.P, in which ethylene glycol and water (6/4, vol.) were used as medium, and ammonium persulfate (APS) aqueous solution, vinyl acetate (VA) and/or acrylic acid (AA), divinylbenzene (DVB) and styrene (St) were added at 6 h. The cross-linking of growing particles was confined to exterior (forming cross-linked shell), and gel contents were low, leading to phase separation. Asymmetrical morphologies, structures, sizes and surface roughness were flexibly tuned by varying amounts of APS, VA and/or AA, water and DVB, and DVB adding speed. At low APS contents or high DVB amounts, the inhomogeneous cross-linking of head enabled its phase to separate, producing elongated head. With addition of VA and AA, phase separations inside head and body were induced, generating hollow structure. Adding DVB very slowly, nonlinear growth of third compartment occurred, forming bowed head.

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1. Introduction

In recent years there have been rapid developments in preparation and application of anisotropic particles with asymmetric geometry and structure owing to great interest aroused by their

* Corresponding author at: P.O. Box 37, Beijing University of Chemical Technology, No. 15 Beisanhuan East Road, Chaoyang District, Beijing 100029, PR China. Fax: +86 10 6441 6338.

E-mail addresses: lyliu@mail.buct.edu.cn (L. Liu), yangwt@mail.buct.edu.cn (W. Yang).

unique properties such as surface amphiphilicity, photocatalytic and magnetic properties, etc [1–6]. Simple and readily scalable approaches [7–12] for production of uniform and well-defined anisotropic particles become a major concern nowadays [1,4,5]. Among them, a prevalent method is based on phase separation induced by swelling spherical seed particles with monomers [13–18], emulsion drops [19], or water-miscible solvents [20] during seeded polymerizations [21–31]. The spherical seed particles may be cross-linked [18,23,26]. They are usually fabricated through seeded polymerizations in which linear polymer spherical seed

particles are uniformly and fully swollen at first with monomer and cross-linker, and then undergo polymerization. During polymerization, monomer and cross-linker are consumed quickly, and an interpenetrating network (IPN) of cross-linked and linear polymers is formed [13–15,20]. These hinder the linear seed particle phase separation [14]. Only by using the resultant, monodisperse cross-linked spherical particles with IPN structure as seeds, and by swelling, heating and polymerization, anisotropic particles are synthesized [13–15,22,23]. The relaxation of swollen and stretched cross-linking network leads to phase separation of seed particles [16,22]. The size of newly formed phase is tunable by changing monomer (or solvent)/seed particle weight ratio or seed particle cross-linking density, etc [13,17,19]. Unfortunately, this technique still has some limitations. For example, multiple steps, including synthesis and surface modification of seed particles, swelling and subsequent seeded polymerization, are required [22–26]. Separating and swelling of seed particles are time-consuming. Surface roughness cannot be varied continuously, and core-shell or hollow structures are not easily generated during the formation of anisotropic shapes [16,19,23,28]. Particles with asymmetrical shapes, rough surfaces and core-shell or hollow structures are thought to have great potentials for self-assembly and some novel applications [32,33]. Hence, how to prepare anisotropic polymer particles with core-shell or hollow structures in large quantities and in a simple, direct and highly controlled manner still remains to be explored.

Dispersion polymerization (Dis.P) is an attractive method for large-scale preparation of micron-sized monodisperse polymeric spheres. To produce stable, highly cross-linked and monodisperse microspheres for applications, Winnik et al. [34–36] developed a two-stage dispersion polymerization (2-Dis.P) technique, in which a cross-linker such as divinylbenzene (DVB) was added after the end of nucleation stage. The growing particles remain swollen by monomer and oligomers during particle growth stage. The cross-linking and swelling of growing particles, as well as morphology, structure and stability of final particles, depend on the content of cross-linker inside growing particles. When a high content of cross-linker is added at a low conversion (e.g., <10%), the cross-linker is allowed to diffuse into the growing particles in well-swollen state. The content of cross-linker inside growing particles is high, producing rapid and high cross-linking. Meanwhile, the swelling of growing particles is reduced rapidly, limiting further diffusion of cross-linker, and hence leading to particle coagulation or instability. When a cross-linker is added at a high conversion (e.g., >80%), its diffusion is difficult due to low swelling ability and high interior viscosity of growing particles. The cross-linker content is low in interior, but high in exterior or in partial region of growing particles, producing spherical, only shell cross-linked [37–39] or partial region highly cross-linked [33] particles. This spatially non-uniform cross-linking across particles tends to localize contraction forces and induce phase separation of growing particles, providing a possible alternative method for direct fabrication of anisotropic particles. However, with rapid, high cross-linking and monomer's consumption, swelling ability of growing particle is excessively reduced, and migration of high molecular weight polymers are difficult. These are against the phase separation of growing particles, giving rise to only spherical particles. Therefore, to generate anisotropic particles, a proper control of the cross-linking and swelling of growing particles is required.

In this article, we present a facile and straightforward preparation of snowman-like polystyrene (PSt) particles with asymmetrical core-shell or hollow structure and rough surface through a modified one-pot Dis.P. As shown in Scheme 1, to suppress the cross-linking and retain proper swelling capacity of growing particles, a mixture of polar solvents (ethylene glycol-EG and water, 6/4 vol., solubility parameter $\delta_{\text{mix}} = 36.5(\text{J}/\text{cm}^3)^{1/2}$, calculated by

$\delta_{\text{mix}} = \delta_{\text{EG}}\phi_{\text{EG}} + \delta_{\text{H}_2\text{O}}\phi_{\text{H}_2\text{O}}$) is used as reaction medium, and reagents (ammonium persulfate-APS aqueous solution, monomers of vinyl acetate-VA and/or acrylic acid-AA, DVB and styrene-St) are added after polymerization had run for 6 h (conversion of initial St: 82%, SI). The high viscosity inside growing particles at 6 h, contraction of growing particles in a highly polar medium, and hydrophilic surface of growing particles can limit the diffusion of DVB, and thus mitigate the cross-linking inside growing particles. Furthermore, St added along with DVB can act as a monomer and swelling agent to alleviate cross-linking and improve swelling ability of growing particles. When the growing particles are properly cross-linked, and still are sufficiently swollen, phase separation occurs (monomers and low molecular weight polymers are extruded from the growing particles to release viscoelastic stress created on network), and snowman-like particles are produced. The detailed formation process of anisotropic particles has been reported recently [40]. In this work, the influences of reaction factors on formation and manipulation of anisotropic particles are investigated. In comparison with the multiple-step seeded polymerizations [12,16,18], the one-pot Dis.P for preparation of anisotropic particles has several inherent advantages: (1) the process is simple, straightforward and thus efficient. (2) Core-shell or hollow structures can be formed as anisotropic shapes are produced. (3) Upon phase separation, cross-linking can be preferentially transferred to the newly formed, uncross-linked domain. This facilitates the stable growth of particles even when high contents of cross-linker are added. (4) Asymmetrical morphologies, structures, sizes and surface roughness can be controlled flexibly by varying reaction factors such as content of APS, amount and adding speed of DVB, etc.

2. Experimental section

2.1. Materials

Styrene (St, 98%, Tianjin Yongda Chemical Reagent Co., Ltd), vinyl acetate (VA) and acrylic acid (AA) (99.5%, Tianjin Fuchen Chemical Reagents Factory) were distilled under reduced pressure before use. Sodium *p*-styrene sulfonate (NaSS, 99.9%, Alfa Aesar), divinylbenzene (DVB, 55%, mixture of isomers, Alfa Aesar), Azobis(isobutyronitrile) (AIBN, 99.9%, Sinopharm Chemical Reagent Co., Ltd.), and ammonium persulfate (APS, 98%, Alfa Aesar) were used without further purification. Ethylene glycol (EG), methanol (MeOH) and tetrahydrofuran (THF) from Beijing Chemical Reagents Co., Ltd. were used as received.

2.2. Preparation of anisotropic particles

One-pot Dis.P with delayed addition of DVB was adopted. Typically, St (2.5 ml), AIBN (0.0453 g), NaSS (0.0453 g), EG (15 ml) and deionized water (10 ml) were added to a 100 ml three-neck round-bottom flask equipped with a reflux condenser and a mechanical stirrer. The mixture was stirred at a speed of 200 rpm and 80 °C for a while to get a homogeneous solution and start reaction. After 30–40 min, the solution gradually became turbid and opalescent. When the reaction had run for 6 h, APS (0.2–0.8% in 5 ml of water, or 0.02 g APS in 2.5–12.5 ml of water) aqueous solution was injected. After that, VA (0–49.4%, based on weight of initial St), AA (0–12%, based on weight of initial St), DVB and St (DVB/St = 1/4 wt., DVB = 8–32%, based on weight of initial St) were added at a speed of 4 drops/min, unless otherwise indicated. The reaction was allowed to proceed for another 3 h (total reaction time was 9 h). The final particles were collected by centrifugation (10,000 rpm, 15 min) and washed with MeOH for three cycles, and then dried at 40 °C overnight in a vacuum oven.

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