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Preparation of poly(*N*-vinylcarbazole) (PVK) nanoparticles by emulsion polymerization and PVK hollow particles

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ABSTRACT

PVK nanoparticles were obtained by oil-in-water emulsion polymerization of *N*-vinylcarbazole (VCz). VCz is a white crystalline material with a melting point of 65 °C, which is an unsuitable monomer for conventional emulsion polymerization because of its crystallinity. However, we could successfully synthesize PVK nanoparticles by emulsion polymerization from VCz solution with organic solvent. And then, we found that the concentration of VCz influenced the particle size. PVK hollow particles were also obtained by etching of PMMA core from PMMA/PVK core–shell particles, and the size of a hollow particle was enlarged by two times compared with a core–shell particle due to the swelling process. PVK nanoparticles were probed by UV–vis absorption and fluorescence spectrometers, and hollow particles were characterized by FT-IR spectra. Both of them were confirmed by TEM, and the light-scattering instrument.

1. Introduction

Recently, organic nanostructured materials have been attracting considerable attention for a variety of applications in the fields of optics, cosmetics, electronics, and biomedicine [1–3]. In particular, the synthesis of conjugated polymer nanoparticles with a various size and morphologies has been developed by several polymerization techniques [4–7].

PVK is one of the semiconducting polymers for electroluminescent and photorefractive devices [8–10]. The chemical and thermal stabilities of PVK, combined with its excellent electrical properties, make it very useful in the electronic devices. The polymerization reactions of VCz can be performed in bulk, in solution, in suspension or in precipitation [8,11–12]. VCz monomer is polymerized by radical and cationic initiation both in the vinyl group and in the benzene ring because of its ability to stabilize electron-deficient centers by resonance involving the nonbonding electron pair on the nitrogen atom in the carbazole ring [11]. When the PVK polymerization proceeds through the vinyl group, a colorless photoconducting PVK is generally formed. The formation of the conducting PVK with dark green color, in which the polymer chain is formed exclusively by bonds between benzene rings, is possible [13–15].

Here, we report the fabrication of PVK nanoparticles by conventional emulsion polymerization of VCz. Emulsion polymerization is a well known polymerization method for producing dispersions with a well defined structure of the polymer particles. It is a free-radical-initiated chain polymerization in which a monomer or mixture of monomers is polymerized in the presence of an aqueous solution of surfactant to form a product [16]. However, VCz is an unsuitable monomer for conventional emulsion polymerization because of its crystallinity at room temperature. Therefore, we prepared VCz micelles in the water through dropping VCz solution obtained by dissolving the VCz in an organic solvent. And we investigated the effects of monomer concentration and initiators on the morphology and size of particles.

We also report the preparation of PVK hollow particles. PMMA core enclosed by cross-linked PVK shell was fabricated and then etched the PMMA core using the organic solvent. Polymer latex particles with a various structure have been developed. The hollow particles, i.e. polymer particles having voids, have more attention particularly in cosmetics, paints, coatings, and paper industries [17,18]. Several fabrication methods of hollow particles have been developed. Hollow particles can be produced by osmotic swelling method, water-in-oil-in-water (W/O/W) emulsion polymerization and the encapsulation of a non-solvent hydrocarbon using the phase separation technique [19–21]. Recently, the formation of hollow particles from core–shell system with core particles as template has been reported extensively [22–26]. Polymer hollow particles can be obtained using template materials such as polymer or inorganic particles.

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2. Experimental

2.1. Materials

N-Vinylcarbazole (VCz, 98%, Aldrich) was purified by recrystallization from absolute methanol, dried in vacuum at 30 °C. Potassium persulfate (KPS, 99+%, Aldrich), 2,2′-azobis(2-amidinopropane)dihydrochloride (V-50, 97%, Aldrich), 2,2′-azobisisobutyronitrile (AIBN, 98%, TCI) and sodium dodecyl sulfate (SDS, 95%, TCI) was used as received without purification. Methyl methacrylate (MMA, 99%, Aldrich) was purified by vacuum distillation. Divinylbenzene (DVB, 80%, Aldrich) of cross-liking agent was purified by neutral alumina column in order to remove the inhibitor. Water (18.2 MΩ cm) was purified with Rios and Milli-Q system (Millipore).

2.2. Preparation of nanoparticles by emulsion polymerization

Three-neck round double jacket flask was charged with 0.1 g of SDS and 250 g of water. The aqueous solution of surfactant was mechanically stirred over 3 h at room temperature. VCz (10–30 wt% of toluene) dissolved in 1 ml of toluene was added dropwise to the reactor. And then, the resultant monomer emulsion was subjected to mechanical agitation at 700 rpm for 1 h. The reaction was then initiated by the addition of initiator (1 wt% of monomer). The polymerization temperature was kept constant at 70 °C throughout the reaction (reaction time = 24 h) under nitrogen atmosphere. After predetermined time, the reaction mixture was cooled. And then, dialysis was carried out for 1–2 days in order to remove the surfactant and initiator. The polymer nanoparticles were separated from the dispersion medium by centrifuging and dried in vacuum over night.

2.3. Preparation of hollow particles

Three-neck round flask was charged with 0.1 g of SDS and 40 g of DI water. The aqueous solution of surfactant was mechanically stirred over 3 h at room temperature. 0.1 g of MMA was added dropwise to the reactor. MMA monomer emulsion was subjected to mechanical agitation at 700 rpm for 1 h. The reaction was then initiated by the addition of AIBN (1 wt% of monomer). The polymerization temperature was kept constant at 70 °C throughout the reaction (reaction time = 4 h) under nitrogen atmosphere. After predetermined time, the reaction mixture was cooled to room temperature and continuously stirred. And, 0.1 g of VCz and 0.05 g of DVB were added to the reactor after the reaction temperature was kept at 70 °C. The reaction was then initiated by the addition of AIBN (1 wt% of monomer) and the polymerization proceeded for 12 h. To prepare PVK hollow particles, methylene chloride as the organic solvent was used to dissolve the PMMA core. The solution was moved to a separation funnel, and then ethanol was added to remove the surfactants. PVK hollow particles were precipitated after 1 day, and the upper solution containing surfactants and PMMA was discarded. The products were dried at room temperature.

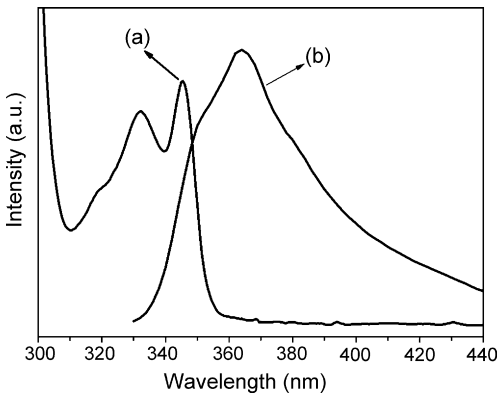

Fig. 2. UV–vis absorption (a) and fluorescence (b) spectra of PVK nanoparticles. The fluorescence spectrum is measured by excitation at 315 nm.

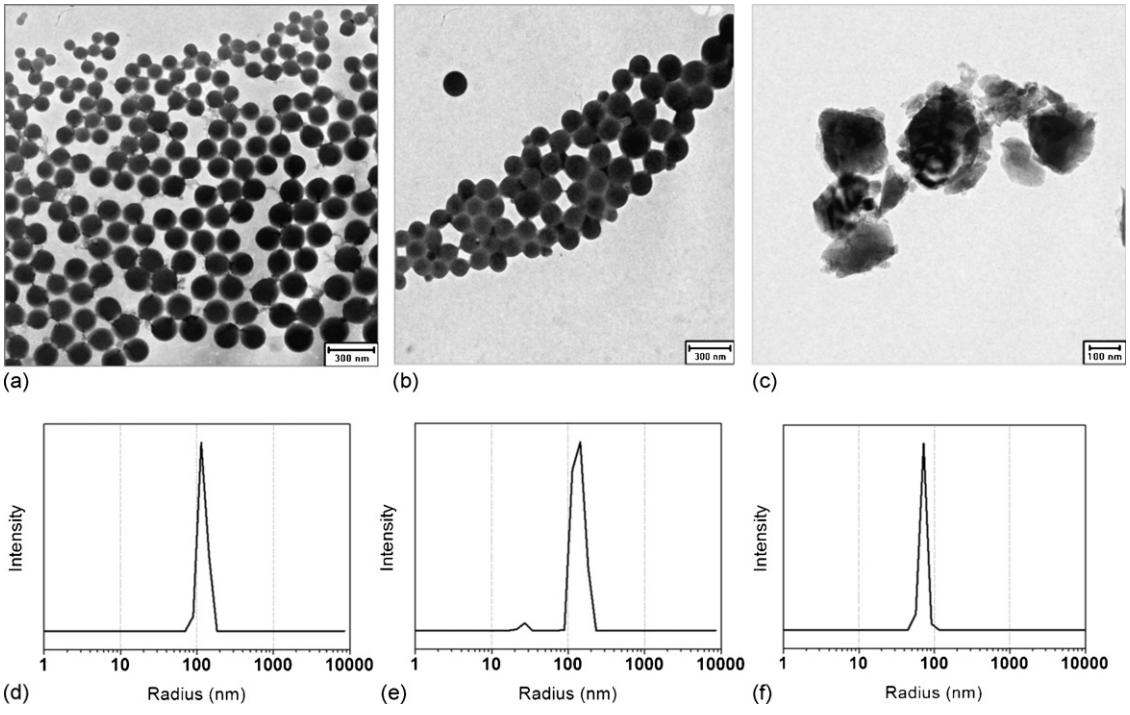

Fig. 1. TEM images (a–c) and the particle size distribution (d–f) of PVK nanoparticles with V-50 initiator under different concentration of VCz in toluene. (a and d) 10 wt%, (b and e) 20 wt%, (c and f) 30 wt%.