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Dispersion polymerization of *N*-vinylcarbazole using siloxane-based and fluorine-based surfactants in compressed liquid dimethyl ether

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Abstract

Spherical poly(*N*-vinylcarbazole) (PVK) was synthesized by dispersion polymerization of *N*-vinylcarbazole (NVCA) in compressed liquid dimethyl ether (DME) using siloxane-based (PDMS-*g*-pyrrolidone carboxylic acid) (Monasil PCA™) and fluorine-based (poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate)) (poly(HDFDMA)) polymers as surfactants and 2,2′-azobisisobutyronitrile (AIBN) as the initiator. Spherical and relatively uniform PVK particles can be produced even at 20 bar.

Keywords: Compressed liquid DME; PVK; Dispersion polymerization

1. Introduction

Supercritical carbon dioxide ($scCO_2$) has been used as the solvent medium for dispersion polymerization by DeSimone and others [1–17]. Application of $scCO_2$ as a dispersion polymerization medium has been limited because of its low solubility for high molecular weight or polar monomeric compounds. We suggest that dimethyl ether (DME) can be used successfully as a solvent for dispersion polymerization of *N*-vinylcarbazole (NVCA). DME provides an environmentally benign, non-toxic and chemically stable alternative to the aqueous or organic solvents conventionally employed by the industry [18–21]. However, care must be taken because DME is flammable.

Spherical polymeric micro-particles are of interest in many industrial applications, such as cosmetic ingredients, light-scattering agents, and electro-photographic toner. Various heterogeneous polymerization methods have been proposed and developed for the synthesis of these spherical polymeric particles [22]. The dispersion polymerization technique has many advantages for the production of spherical, uniform polymeric particles from 0.1 μm to 10 μm in diameter [23,24].

Poly(*N*-vinylcarbazole) (PVK) is a transparent thermoplastic and photo-conductive material with good thermal and chemical stabilities, and a high refractive index [25]. PVK was used originally as a dielectric capacitor, since it has very good electrical resistance over a range of temperatures and frequencies. The major application of spherical PVK today is in electrostatic dry copying (xerography) machines, as a consequence of its photoconductivity [23].

In this study, we performed free radical dispersion polymerization to synthesize spherical PVK particles by using compressed liquid DME as a polymerization medium at relatively low pressure compared with conventional dispersion polymerization using $scCO_2$. We investigated the effects of reaction temperature, siloxane-based and fluorine-based polymer surfactants, and the amount of polymer surfactants on the morphology, size and molecular weight of PVK particles.

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2. Experimental

2.1. Materials

DME with purity of 99.99% was purchased from LG Chem. NVCA (min. 98%) was purchased from Aldrich. 2,2′-Azobisisobutyronitrile (AIBN) (min. 98%) was purchased from Junsei Chemical and purified by recrystallization from methanol. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl methacrylate (HDFDMA) (min. 97%) and PDMS-*g*-pyrrolidone carboxylic acid (Monasil PCA™) were purchased from Aldrich and from Uniquema, respectively. Poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) (poly(HDFDMA)) was prepared by solution polymerization in $scCO_2$ at 70 °C and 300 bar [26]. The molecular structures of Monasil PCA™ and poly(HDFDMA) are illustrated in Fig. 1.

2.2. Polymerization apparatus and procedure

Dispersion polymerization of PVK was carried out in a 30 mL SUS 316 reactor and we observed the inner phase change via the observation window. Pressure was measured by a Bourdon tube pressure gauge (WIKA, type 213.53.063, accuracy class 1.0). Temperature was measured by a K (CA) type thermocouple and indicator (Hanyoung Electronics Inc. model DX-7) (accuracy 0.05 K).

After the polymerization step, DME was vented through two glass traps. To prevent discharge of unreacted monomer to atmosphere during separation of DME, the glass traps were filled with methanol and kept cold in an ice-water bath. A PTFE-coated magnetic stirring bar was used for agitation of the reaction mixture.

The reactor was charged with 2.00 g of NVCA, AIBN (1–3 wt% relative to the total monomer) and poly(HDFDMA) or Monasil PCA™ as the surfactants (2.5–20.0 wt% relative to the total monomer), and the system was purged with DME. The reactor was put into the ice-water bath, cooled to below 10 °C, and then filled with DME using a small high-pressure bomb. The reactor was heated to 60 °C or 70 °C, followed by the final pressurization to 20 bar. The mixture at the beginning of the reaction was in a homogenous phase, because NVCA, AIBN and surfactant are miscible with DME. But after 1 h, the solution inside the reactor became hazy and eventually developed into a white polymer. Polymerization was conducted for 24 h at $T = 60$ °C or 70 °C, $P = 20$ bar, with stirring. After polymerization was complete, the reactor was cooled to below 10 °C. Vapor/liquid phase separation occurred, and then DME was vented from the vapor phase. The polymer particles were washed with methanol to remove any unreacted monomer. The resulting polymer was dried in vacuo at room temperature.

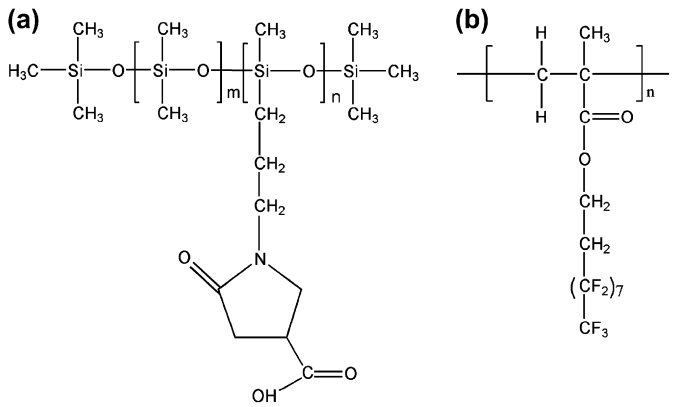

Fig. 1. Molecular structures for (a) Monasil PCA™ and (b) poly(HDFDMA).

2.3. Polymer characterization

The particle size and morphology of PVK were characterized by FE-SEM (Jeol 5410LV). The number-average particle size and the particle size distribution (PSD) were measured with an image analyzer (TDI Scope Eye™ ver 3.1) with SEM images. Number-average (D_n) and weight-average (D_w) particle diameters were calculated from the following equations [1,27].

$$D_n = \frac{\sum_{i=1}^{N} d_i}{N} \quad (1)$$

$$D_w = \frac{\sum_{i=1}^{N} d_i^4}{\sum_{i=1}^{N} d_i^3} \quad (2)$$

where d_i is the diameter of particle i, and N is the total number of particles measured in the SEM images. The PSD was determined from the polydispersity index (PDI):

$$\mathrm{PDI} = D_w/D_n$$

Gel permeation chromatography (GPC) (Waters, 600E controller) was used to measure the average molecular weight of PVK using tetrahydrofuran (THF) as the solvent at 35 °C. An RI detector (Waters, 410), three columns (Styragel® HT2, HT3, and HT4) and narrow standard poly(methyl methacrylate) (PMMA) were used.

3. Results and discussion

The polymerization of NVCA was carried out using poly(HDFDMA) and Monasil PCA™ as surfactants in compressed liquid DME in a 30 mL stainless steel reactor. The polymerization conditions and experimental results of PVK in compressed liquid DME with the two kinds of surfactants are summarized in Tables 1 and 2. Conventional dispersion polymerization in supercritical CO_2 yielded spherical particles at ~300 bar [2,7]. However, when DME was used as the dispersion polymerization medium, we could make spherical polymeric particles at pressures as low as 20 bar. The effect of the concentration of surfactant and reaction temperature on the particle size and morphology of PVK was investigated for each surfactant used.