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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.

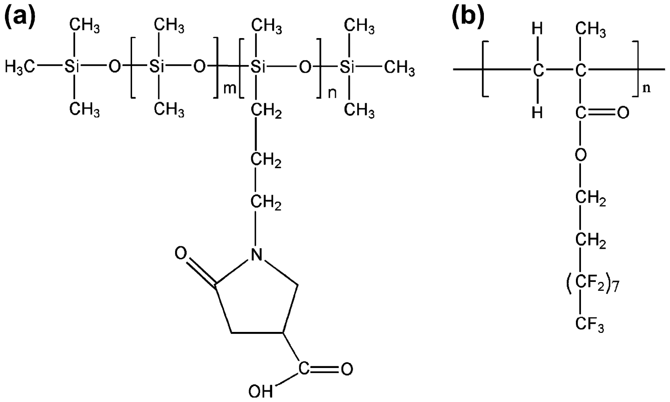

Fig. 1. Molecular structures for (a) Monasil PCA™ and (b) poly(HDFDMA).

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].

$$D_n = \frac{\sum_{i=1}^{N} d_i}{N} \tag{1}$$

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

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.

Table 1

Monasil PCA™ as surfactant for the polymerization of NVCA in compressed liquid DME[a]

Entry	Surfactant (wt% of monomer)		T (°C)	Particle size[b] (μm)	PSD[c]	M_w[d]
M1	Monasil PCA™	1.5	60 ± 0.5	0.79	1.01	114 000
M2		2.5		0.52	1.02	164 000
M3		5.0		0.38	1.01	100 000
M4		10.0		0.23	1.02	108 000
M5		15.0		0.20	1.02	113 000
M6		20.0		0.17	1.02	104 000
M7		1.8	70 ± 0.5	0.84	1.03	122 000
M8		2.5		0.52	1.03	136 000
M9		5.0		0.40	1.03	94 000
M10		10.0		0.23	1.01	92 000
M11		15.0		0.18	1.03	134 000

[a] Reaction condition: 1.0 wt% AIBN, 20 ± 5 bar and 24 h with stirring.
[b] Determined by FE-SEM.
[c] Particle size distribution.
[d] Determined by GPC.

Table 2

Poly(HDFDMA) as surfactant for the polymerization of NVCA in compressed liquid DME[a]

Entry	Surfactant (wt% of monomer)		T (°C)	Particle size[b] (μm)	PSD[c]	M_w[d]
H1	Poly(HDFDMA)	2.5	60 ± 0.5	1.62	1.03	190 000
H2		5.0		1.28	1.23	103 000
H3		10.0		1.42	1.02	138 000
H4		15.0		1.88	1.14	114 000
H5		2.5	70 ± 0.5	1.63	1.03	124 000
H6		5.0		1.11	1.03	118 000
H7		10.0		0.76	1.03	129 000
H8		15.0		0.69	1.04	107 000

[a] Reaction condition: 1.0 wt% AIBN, 20 ± 5 bar and 24 h with stirring.
[b] Determined by FE-SEM.
[c] Particle size distribution.
[d] Determined by GPC.

3.1. Dispersion polymerization of NVCA using Monasil PCA™

Data for the dispersion polymerization of NVCA in compressed liquid DME with Monasil PCA™ as a surfactant are summarized in Table 1.

The Monasil PCA™ for steric stabilization is effective in the dispersion polymerization. A role of the stabilizing molecule is to attach to the growing polymer particle surface by physical adsorption and inhibit the particles from agglomerating by steric stabilization. From the polymerization of NVCA in the presence of Monasil PCA™ in compressed liquid DME, submicron-sized and relatively narrow particle size distribution PVK particles were produced with good latex stability.

As shown in Table 1, PVK particles were polymerized with different amounts of surfactant (Monasil PCA™) at 60 °C (entry numbers M1−M6 in Table 1) and at 70 °C (entry numbers M7−M11 in Table 1). Fig. 2 shows PVK particles polymerized at 60 °C. When no Monasil PCA™ was added, i.e. in the case of precipitation polymerization, the resulting polymers were highly agglomerated. We could obtain very fine particles even at surfactant concentration of 2.5 wt%. The average size of the particles decreased from 0.84 μm to 0.17 μm, when the concentration of Monasil PCA™ was increased from 1.5 wt% to 20 wt% (to monomer). In the presence of a large amount of surfactant, it is believed that the oligomeric PVK particles could quickly adsorb the surfactant before agglomeration with other particles. As a result, there was an increase in the number of stable nuclei with higher surfactant content and correspondingly, smaller particles were made [1,3]. Fig. 3 shows that the average particle size decreased nearly exponentially with increasing concentration of Monasil PCA™. These results are in agreement with the findings reported by Dawkins and Taylor, who investigated that the diameter of the final polymer decreases with increasing surfactant concentration [28]. When the reaction temperature was 70 °C, the particle size, morphology and average molecular weight were very similar to the results obtained at 60 °C. Changing the temperature from 60 °C to 70 °C while maintaining the concentration of surfactant did not affect the particle size.

3.2. Dispersion polymerization of NVCA using poly(HDFDMA)

To investigate the effect of the surfactant type, NVCA was polymerized using a fluorine-based polymer surfactant, poly(HDFDMA), under the same reaction conditions ($T = 60$ °C or 70 °C and $P = 20$ bar). The experimental conditions and results are given in Table 2 (entry numbers H1−H8) and in Fig. 4 for different amounts of poly(HDFDMA) (2.5−15 wt%) at 70 °C. We observed the effects of changes to the concentration of surfactant and the reaction temperature. When the reaction temperature was 60 °C, as the concentration of the surfactant decreased, the resulting polymer particles became more highly aggregated. Although high yields as white solid were obtained in entries H1−H4, an expected stabilization of PVK was not obtained. A surfactant concentration of 10 wt% is needed to achieve good results for an NVCA polymerization using poly(HDFDMA) at 60 °C. However, when conducted at 70 °C (Fig. 4), we obtained uniform PVK particles in the whole range. As the concentration of the surfactant increased from 2.5 to 15 wt%, the average particle size decreased from 1.63 μm to 0.69 μm.

Generally, the polymer particles produced using poly(HDFDMA) as the surfactant were twice as large as those produced using Monasil PCA™ at the same concentration. Therefore, we could control the particle size of PVK by changing the amount and the type of surfactant. The PSD that results from using poly(HDFDMA) was less than 1.04 at 70 °C, and the PSD produced using poly(HDFDMA) was a little larger than those produced using Monasil PCA™.

GPC was used to obtain molecular weight information. In all cases, the average molecular weight was between 92 000 and 190 000. The average molecular weight of the polymer synthesized by dispersion polymerization using $scCO_2$ as the polymerization medium increased as the concentration of surfactant increased [29,30], but this was not the case when DME was the solvent.

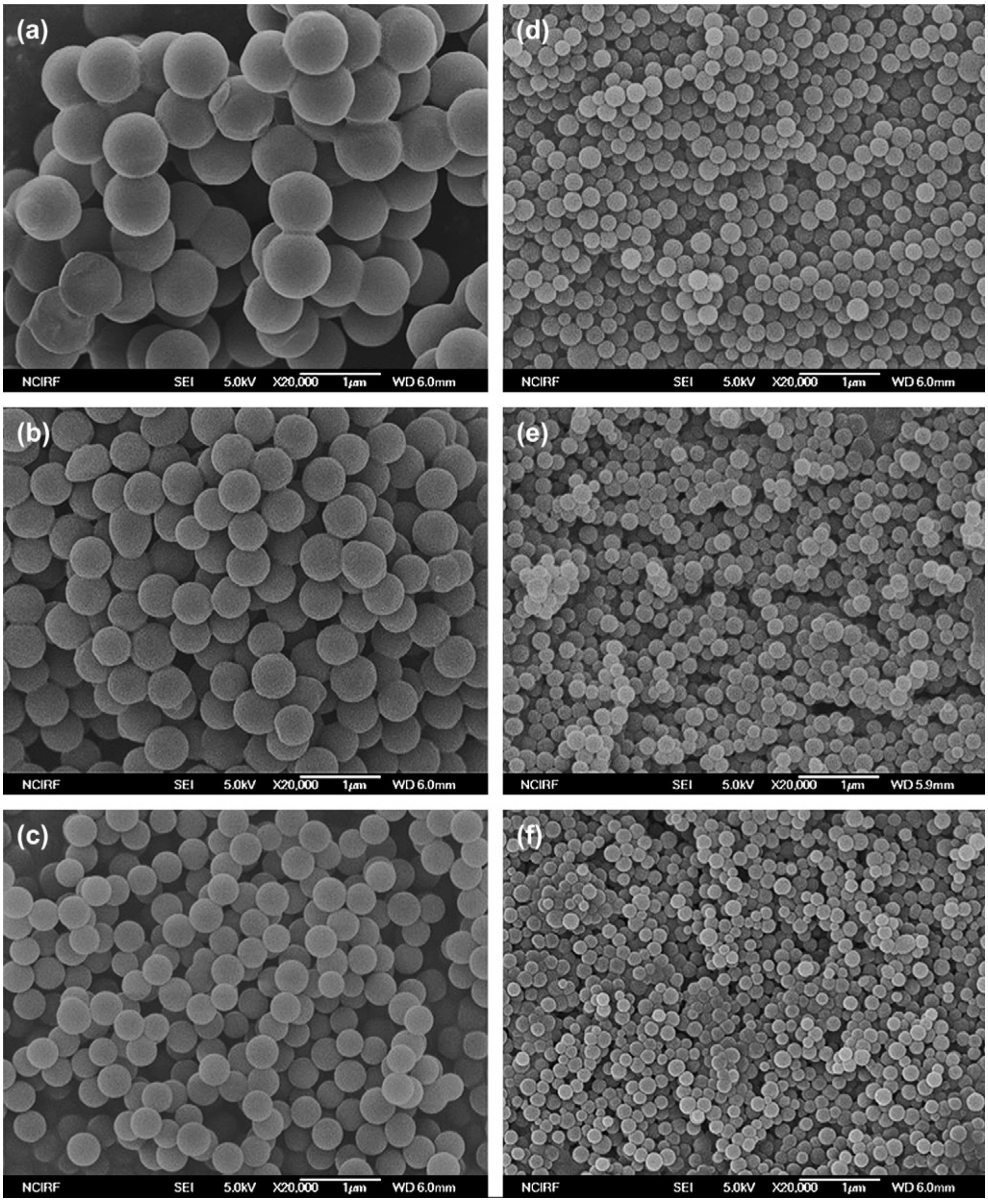

Fig. 2. SEM images of PVK particles polymerized with Monasil PCA™ (a) 1.5 wt%, (b) 2.5 wt%, (c) 5.0 wt%, (d) 10.0 wt%, (e) 15.0 wt%, (f) 20.0 wt% at 60 °C.

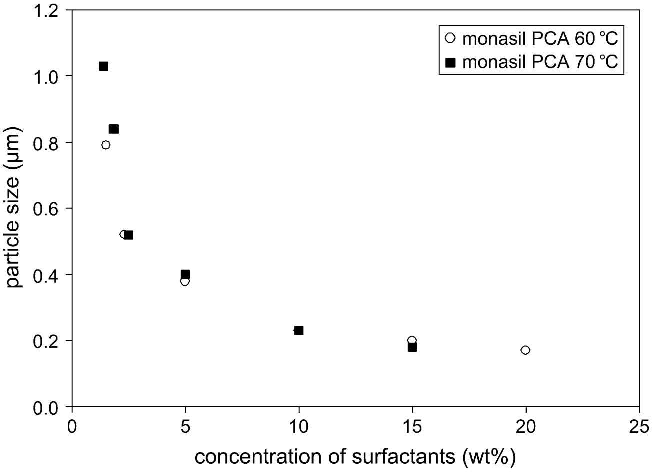

Fig. 3. Decrease in the size of PVK particles with increase in the concentration of Monasil PCA™.

4. Conclusions

We investigated dispersion polymerization using compressed liquid DME as the polymerization medium at a pressure of 20 bar. Spherical PVK particles were obtained successfully by dispersion polymerization using two kinds of surfactants: siloxane-based (Monasil PCA™) and fluorine-based (poly(HDFDMA)) polymer surfactants. In general, as the concentration of the surfactant increased, the average particle size of the polymer products decreased exponentially, except for the polymer obtained with poly(HDFDMA) surfactant at 60 °C. In the case of polymerization with Monasil PCA™ surfactant, no significant change was observed in the particle size or morphology for polymerization at different temperatures. When it was polymerized with poly(HDFDMA) surfactant at 70 °C, we obtained uniform particles that were about

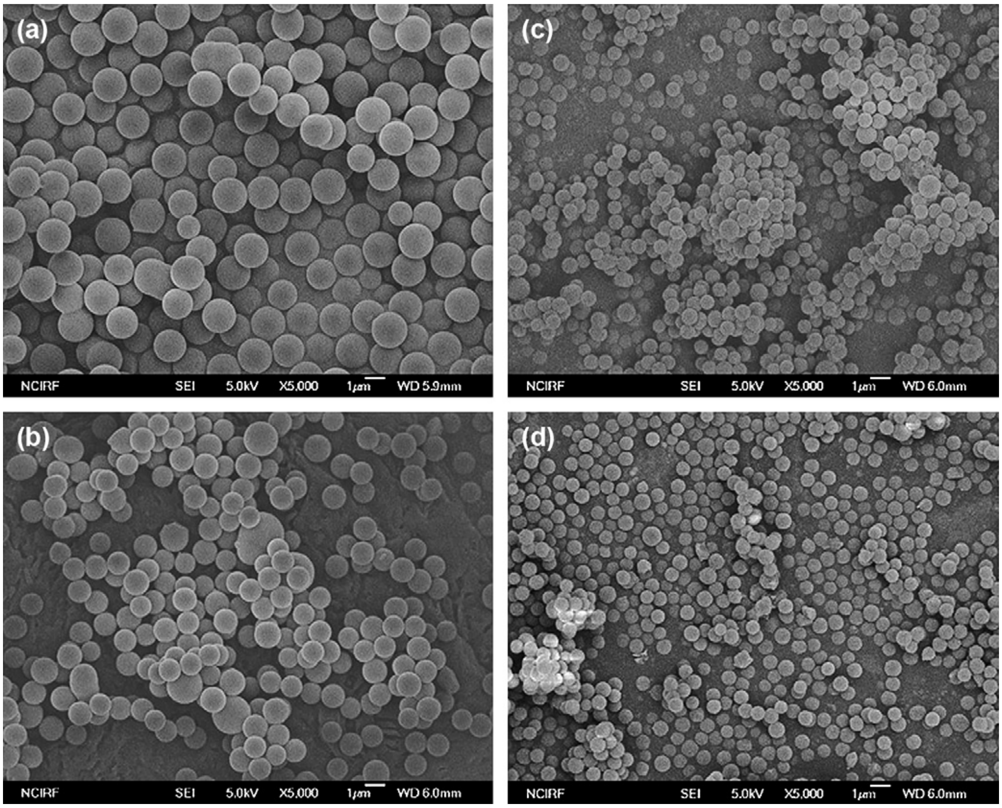

Fig. 4. SEM images of PVK particles polymerized with poly(HDFDMA) (a) 2.5 wt%, (b) 5.0 wt%, (c) 10.0 wt%, (d) 15.0 wt% at 70 °C.

twice as large in diameter as those produced with Monasil PCA™ at the same concentration.

In this study, fluorine-based and siloxane-based polymers were used as surfactant; however, in future it will be important to examine closely how the surfactants act in the polymerization formation.

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