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Dispersion polymerization of NVCA in compressed liquid dimethyl ether in the presence of PDMS-g-pyrrolidone carboxylic acid: Effects of initiators

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Abstract−Dispersion polymerization of N-vinylcarbazole (NVCA) was performed in compressed liquid dimethyl ether with PDMS-g-pyrrolidonecarboxylic acid (Monasil PCA^{TM}) as the surfactant and with 2,2'-azobis(2,4-Dimethylvaleronitrile) (V-65), 2,2-azobisisobutyronitrile (V-60) (AIBN) and dimethyl 2,2'-Azobis(isobutyrate) (V-601) as the initiators. The effects of polymerization temperature, initiator types and initiator concentration were investigated. Spherical poly(N-vinylcarbazole) (PVK) particles were produced, even at 40 °C, by the low-temperature initiator, 2,2'-azobis(2,4-Dimethylvaleronitrile) (V-65). Through low-temperature polymerization with V-65, we successfully obtained high molecular weight PVK.

Key words: V-65, V-601, AIBN, Dispersion Polymerization, PVK, DME, Monasil PCA

INTRODUCTION

Poly(N-vinylcarbazole) (PVK) is a promising polymer because it is a transparent thermoplastic and photo-conductive material with good thermal and chemical stability and a high refractive index [1], characteristics that are useful in charge-transfer complexes, electroluminescent devices, and photorefractive materials [2-4]. The major application of spherical PVK has been in electrostatic dry copying (xerography) machines due to its photoconductivity [5]. To be used for various applications related to food performance, the molecular weight of PVK must be controlled and increased [6].

Dimethyl ether (DME) is environmentally benign, non-toxic, and chemically stable [7,8]. It is physically similar to liquefied petroleum gas (LPG), which primarily contains propane and butane [9-11]. DME is used today as an aerosol propellant in the cosmetic industry to replace CFC propellants, as an assistant solvent, as a fuel additive, and as a liquefied petroleum gas substitute. It can also be used as an alternative refrigerant, since it is not harmful to the ozone layer and is easily degraded in the atmosphere. Recently, DME has been used successfully as a solvent for dispersion polymerization of NVCA [12]. As a wide range of polar monomers are soluble in DME and most of their polymers are insoluble in DME, the dispersion polymerization of various polar monomeric compounds is possible by using DME. Dispersion polymerization using DME has many advantages. DME is handled as a liquid and can be easily stored and transported because it is not a cryogenic liquid. Also, like CO_2, DME as a polymerization medium can be easily separated from the polymer product; therefore, the polymer is obtained as a dry, free-flowing powder by simply venting the DME. However, DME is flammable, so care must be exercised.

In our previous work [12], we conducted dispersion polymerization of 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 the surfactant and 2,2'-azobisisobutyronitrile (AIBN) as the initiator.

In this study, we used three kinds of initiators, such as azo nitrile-type initiators, 2,2'-azobis(2,4-Dimethylvaleronitrile) (V-65) and 2,2-azobisisobutyronitrile (V-60) (AIBN) and azo ester-type initiator, dimethyl 2,2'-Azobis(isobutyrate) (V-601). The differences in the decomposition rates of various initiators can be expressed in terms of the initiator half-life temperature defined as the time for the concentration of the initiator to decrease to one-half its original value. The half-life temperature of the three initiators is 51, 65, 66 °C, respectively. We focused on the effects of various initiators, initiator concentration and reaction temperature on the particle size, morphology, and molecular weight of the resulting polymer.

EXPERIMENTS

1. Materials

2,2'-azobis(2,4-Dimethylvaleronitrile) (V-65) and Dimethyl 2,2'-Azobis(isobutyrate) (V-601) were purchased from Wako Pure Chemical Industries, Ltd.. 2,2'-Azobisisobutyronitrile (AIBN) (min. 98%) was purchased from Junsei Chemical and purified by recrystallization from methanol. NVCA (min. 98%) was purchased from Aldrich and used without further purification. DME with a purity of 99.99% was purchased from LG Chem. PDMS-g-pyrrolidone carboxylic acid (Monasil PCA) was purchased from Uniquema. The molecular structures of the initiators, V-65, V-601 and AIBN, are illustrated in Fig. 1.

2. Polymerization Apparatus and Procedure

The polymerization apparatus is described in detail in our previous work [12]. Briefly, dispersion polymerization of NVCA was conducted in a 30-mL SUS 316 reactor, and we observed the inner phase change via the observation window. In a typical polymerization, 2.00 g of NVCA, the desired amount of initiator (wt% relative

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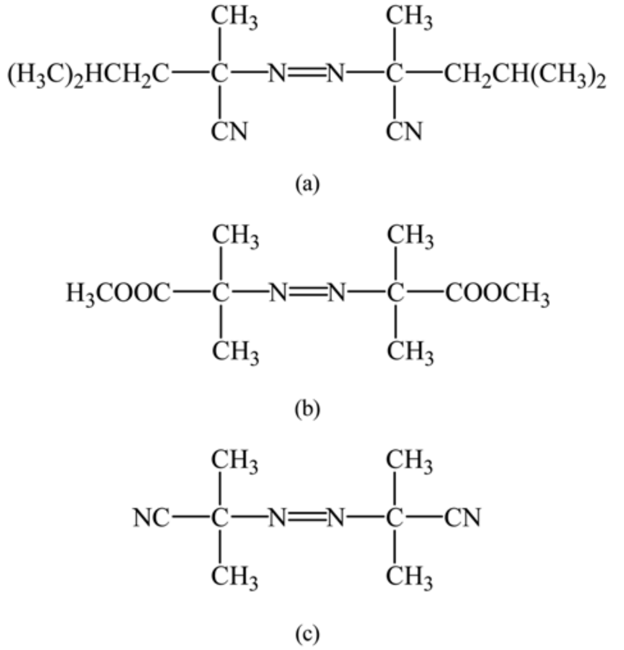

(a)

(b)

(c)

Fig. 1. Chemical structure of initiators: (a) V-65, (b) V-601, (c) AIBN.

to the total monomer) and Monasil PCA as the surfactant (wt% relative to the total monomer) were added to the reactor. The system was then purged with DME several times to remove oxygen. The reactor was placed in an ice-water bath, cooled to below 10 °C, and then filled with DME by using a small high-pressure bomb, so that when the reactor was heated to the desired temperature, the pressure was approximately 20 bar. 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). A PTFE-coated magnetic stirring bar was used to agitate the reaction mixture.

After 24 h from reaction started, the reactor was cooled to below 10 °C. The DME was then vented slowly through two glass traps. To prevent discharge of unreacted monomer into the atmosphere during separation of DME, the glass traps were filled with methanol and kept cold in an ice-water bath. The polymer particles were washed with methanol to remove any unreacted monomer. The resulting polymer was dried *in vacuo* at room temperature.

3. Polymer Characterization

The average 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 [13]:

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

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

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):

$$PDI = D_w/D_n$$

Gel permeation chromatography (GPC) (Waters, 600E controller) was used to measure the average molecular weight of PVK by 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.

RESULTS AND DISCUSSION

The yield of PVK was 90-94% for the dispersion polymerization of NVCA in compressed liquid DME, except that the AIBN and V-601 were used as initiators at 40 °C. When the polymerization was not stabilized well, the yields of PVK were below 90% and the polymer samples were highly agglomerated.

1. Dispersion Polymerization of NVCA in Presence of 2,2'-Azobis(2,4-dimethylvaleronitrile) (V-65) as the Initiator

As shown in Table 1, dispersion polymerizations were carried out at four temperatures between 40 and 70 °C with V-65 as the initiator in compressed liquid DME. Fig. 2 shows the scanning electron micrograph of PVK for each reaction temperature.

In all cases, Monasil PCA was used as the surfactant, and the

Table 1. Data for polymerizations of NVCA using V-65 in compressed liquid DME[a]

Entry	V-65 (wt% to the monomer)	Temperature (°C)	Yield[b] (%)	Particle size (mm)[c]	PSD[d]	M_w[e]	Particle morphology
1	1.0	40	90	0.21	1.04	255,000	Spherical
2		50	91	0.22	1.04	173,000	Spherical
3		60	94	0.24	1.03	110,000	Spherical
4		70	91	0.30	1.02	95,000	Spherical
5	2.0	70	92	0.31	1.04	89,000	Spherical
6	4.0		93	0.33	1.02	54,000	Spherical

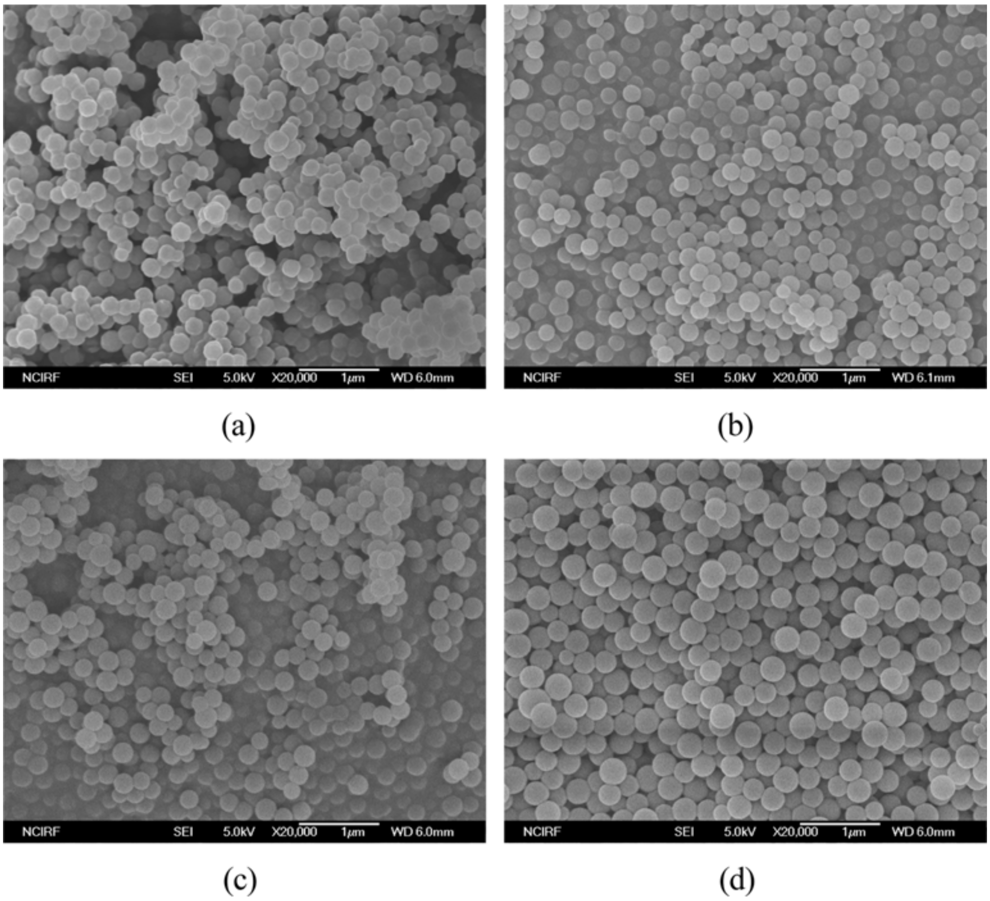
[a] Reaction conditions: 2.0 g of NVCA, 10.0 wt% Monasil PCA, 20±50 bar with stirring

[b] Yields were determined gravimetrically

[c] Determined by FE-SEM

[d] Particle size distribution

[e] Determined by GPC



(a) (b)

(c) (d)

Fig. 2. SEM images of PVK particles polymerized withV-65 at (a) 40 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C.

amounts of Monasil PCA as the surfactant and NVCA as the monomer were maintained at 0.2 g (10 wt% of the monomer) and 2 g, respectively.

Lyoo and co-workers found that the use of a low-temperature initiator, V-65, in the polymerization of vinyl acetate (VAc) [14] and NVCA [6] allowed them to lower the polymerization temperature to room temperature in organic solvents.

Fig. 3 presents the effects of reaction temperature on the M_w and the average particle size of PVK produced in compressed liquid DME. Very uniform, spherical particles were successfully obtained at temperatures as low as 40 °C (entry 1 in Table 1; Fig. 2(a)). The average particle size was slightly affected by the polymerization temperature. When the reaction temperature was increased from 40 to 70 °C, the average particle size of the polymer increased from 0.21 to 0.30 μm. These results are in agreement with the findings reported by Cao et al., who investigated the influence of initiator type. When they polymerized using V-65 as the initiator, larger polymer particles were obtained compared with AIBN. This is because the more active the initiator, the larger the particle size becomes and the narrower the size distribution tends to be. Therefore, in case of different temperature, V-65 becomes more active at higher temperature. Then the average particle size of the polymer increased.

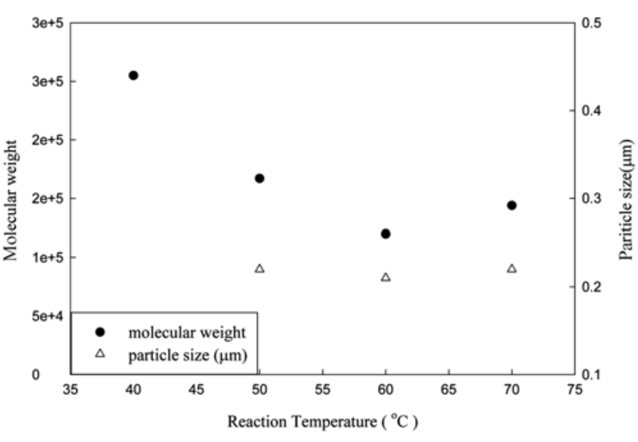


Fig. 3. Effect of polymerization temperature on the molecular weight and particle size of PVK with V-65.

Also, the molecular weight decreased from 255,000 to 95,000 as the polymerization temperature increased. These results indicate that the higher polymerization temperature promotes transfer reactions and decreases molecular weight.

Many factors affect the average particle size, such as the initiator concentration, the surfactant concentration, the surfactant type and so on. Fig. 4 shows the scanning electron micrograph of PVK obtained from reactions at each initiator concentration; we conducted dispersion polymerization at three different initiator concentrations (entries 4-6 in Table 1; Fig. 2(d); Fig. 4(a), (b)). Some researchers have reported that a change in the initiator concentration

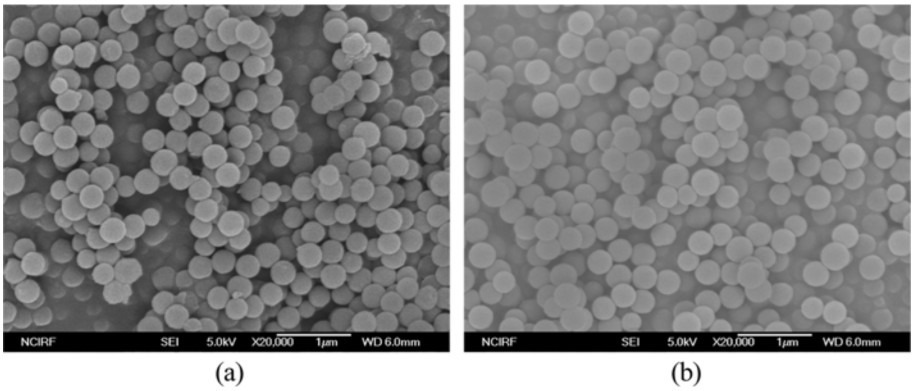

(a) (b)

Fig. 4. SEM images of PVK particles polymerized with V-65 at 70 °C (a) 2 wt%, (b) 4 wt%.

Table 2. Data for polymerizations of NVCA using V-601 in compressed liquid DME[a]

Entry	V-601 (wt% to the monomer)	Temperature (°C)	Yield[b] (%)	Particle size (mm)[c]	PSD[d]	M_w[e]	Particle morphology
7	1.0	40	81	-	-	255,000	Irregular
8		50	92	0.22	1.06	167,000	Spherical
9		60	90	0.21	1.06	120,000	Spherical
10		70	93	0.21	1.05	144,000	Spherical
11	2.0	70	92	0.46	1.08	50,000	Spherical
12	4.0		94	0.32	1.23	186,000	Spherical

[a] Reaction conditions: 2.0 g of NVCA, 10.0 wt% Monasil PCA, 20±50 bar with stirring

[b] Yields were determined gravimetrically

[c] Determined by FE-SEM

[d] Particle size distribution

[e] Determined by GPC

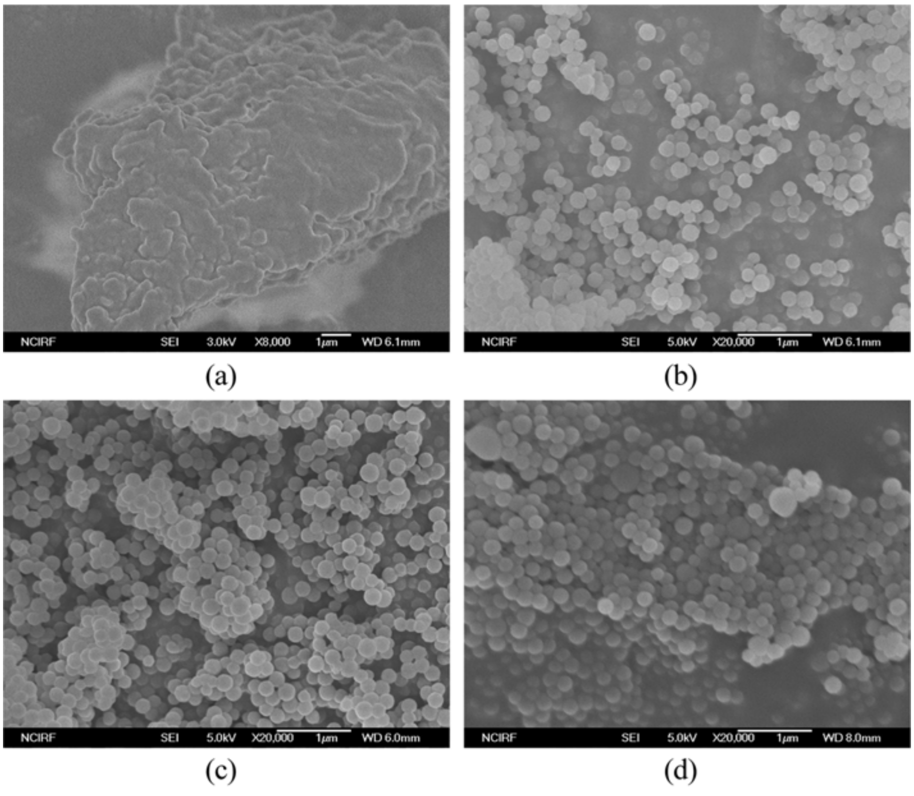

(a) (b) (c) (d)

Fig. 5. SEM images of PVK particles polymerized withV-601 at (a) 40 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C.

can influence PSD and the particle size in various ways [15]. The average particle size increased slightly from 0.30 to 0.33 μm and the average molecular weight decreased from 95,000 to 54,000 as the amount of V-65 increased from 1 to 4 wt% at 70 °C.

2. Dispersion Polymerization of NVCA in Presence of V-601 as the Initiator

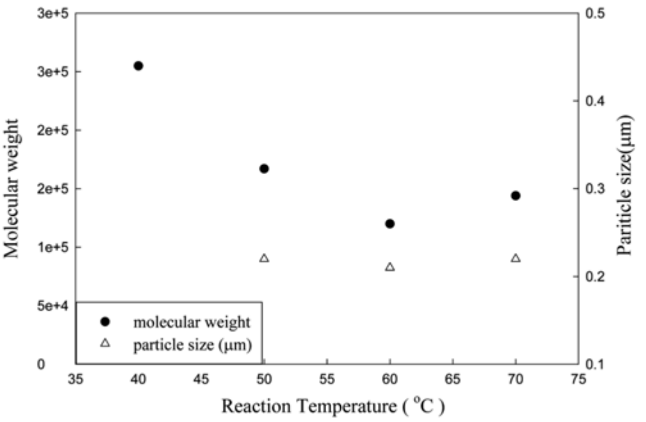
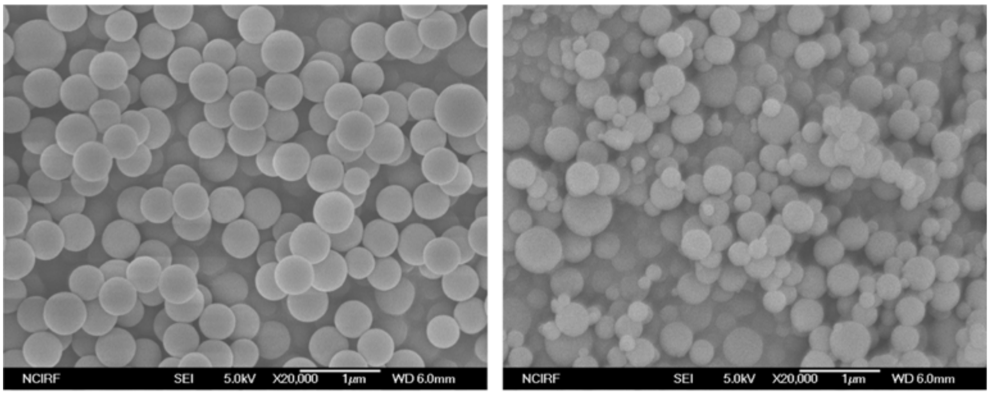


Fig. 6. Effect of the polymerization temperature on the molecular weight and particle size of PVK with V-601.

Table 2 summarizes data from the dispersion polymerization of NVCA in compressed liquid DME at several different polymerization temperatures with V-601 as the initiator. Fig. 5 presents the SEM images of PVK obtained by using V-601. At 40 °C, we could not obtain spherical PVK particles. When the polymerization temperature was higher than 40 °C, spherical polymeric particles were produced.

Fig. 6 shows plots of molecular weight vs. temperature and average particle size vs. temperature. Although spherical particles were not produced at 40 °C, we obtained the highest molecular weight among others. When the reaction temperatures were 50, 60 and 70 °C, the average particle size and morphology were very similar. The effects of initiator concentration on the average particle size and morphology produced at 70 °C using Monasil PCA as surfactant are presented in Fig. 5(d) and Fig. 7 (entries 10-12 in Table 2). With increasing the initiator concentration, the particle size increases and the PSD tend to broaden. The following changes are caused by an increase of initiator concentration: the number of free radicals and thus the concentration of the precipitated oligomeric chains increases. Obviously, the aggregation process is enhanced, resulting in larger particles. However, the larger particles capture fewer nuclei or oligoradicals from the continuous phase due to their lower total surface area. Therefore, the PSD will be significantly broadened when particle formation continues beyond a certain period. In the case of V-



(a) (b)

Fig. 7. SEM images of PVK particles polymerized with V-601 at 70 °C (a) 2 wt%, (b) 4 wt%.

Table 3. Data for polymerizations of NVCA using AIBN in compressed liquid DME[a]

Entry	AIBN (wt% to the monomer)	Temperature (°C)	Yield[b] (%)	Particle size (mm)[c]	PSD[d]	M_w[e]	Particle morphology
13	1.0	40	83	-	-	86,000	Irregular
14		50	92	0.24	1.06	224,000	Spherical
15	2.0	60	93	0.21	1.06	89,000	Spherical
16	3.0		91	0.17	1.06	104,000	Spherical
17	4.0		94	0.28	1.02	77,000	Spherical
18	2.0	70	91	0.34	1.06	61,000	Spherical
19	4.0		92	0.34	1.04	56,000	Spherical

[a] Reaction conditions: 2.0 g of NVCA, 10.0 wt% Monasil PCA, 20±50 bar with stirring.

[b] Yields were determined gravimetrically

[c] Determined by FE-SEM

[d] Particle size distribution

[e] Determined by GPC

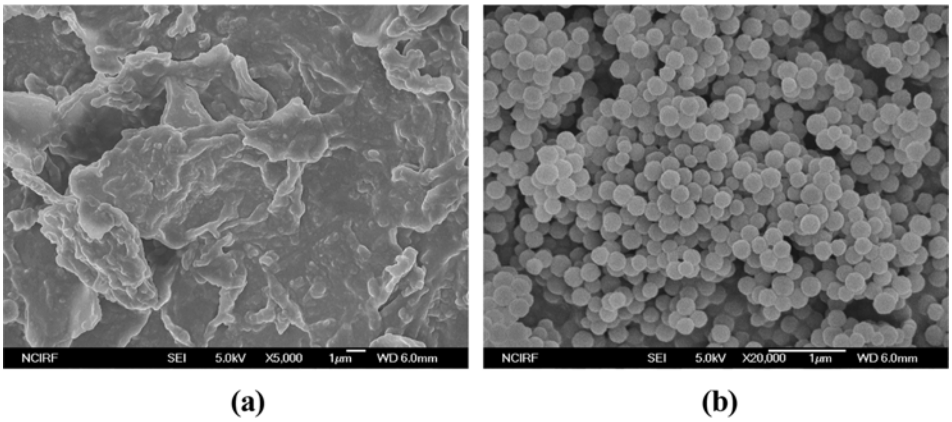


Fig. 8. SEM images of PVK particles polymerized with AIBN at (a) 40 °C, (b) 50 °C.

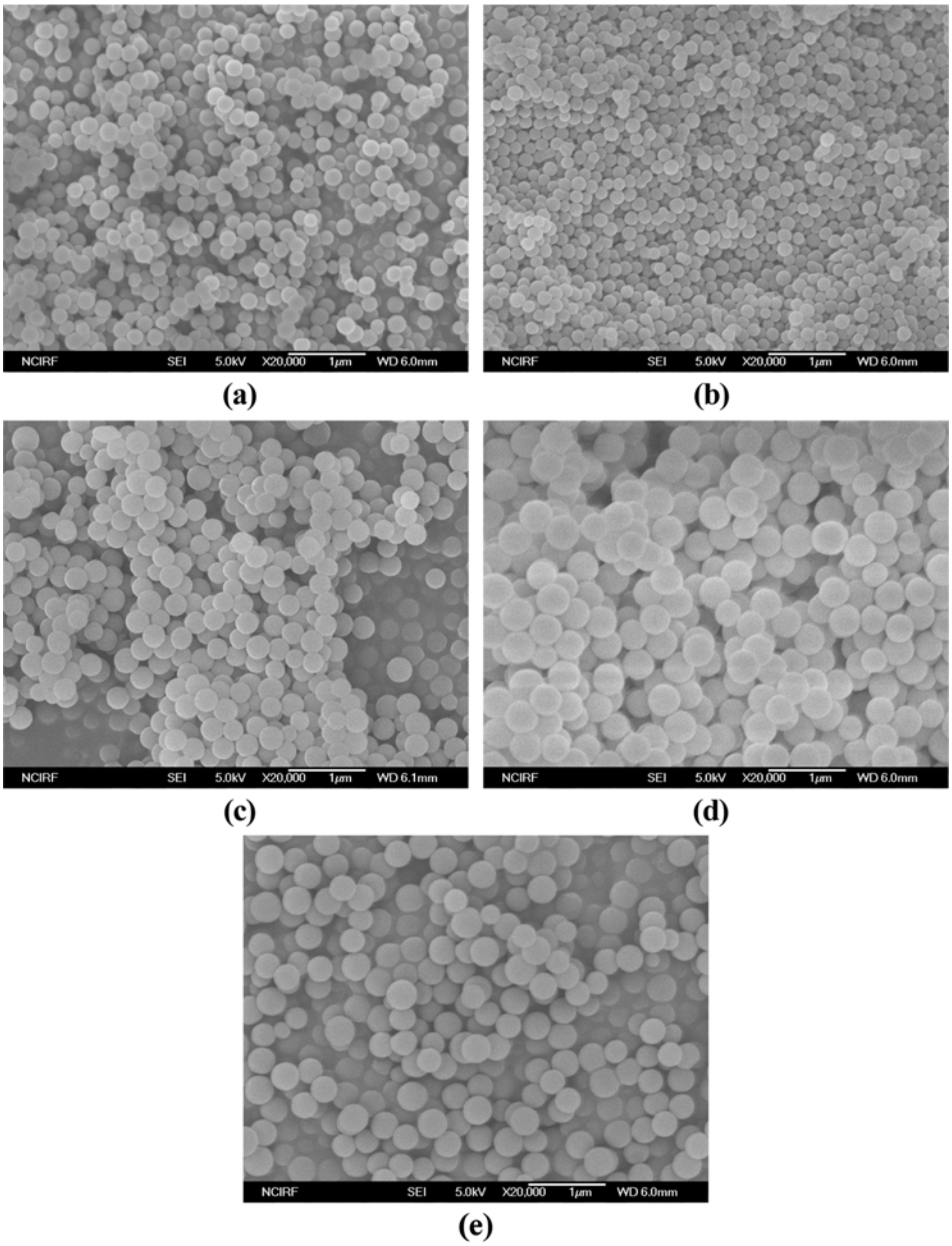


Fig. 9. SEM images of PVK particles polymerized with AIBN (a) 2 wt%, (b) 3 wt%, (c) 4 wt% at 60 °C; and (d) 2 wt%, (e) 4 wt% at 70 °C.

65, the average particle size slightly increased but did not affect the PSD, while increasing the concentration of V-65. However, as the concentration of V-601 increased from 1 to 4 wt%, not only the average particle size increased, but also PSD was broadened from 1.05 to 1.23.

3. Dispersion Polymerization of NVCA in Presence of AIBN as the Initiator

To observe the effects of AIBN on polymerization, NVCA was also polymerized by using AIBN in the presence of Monasil PCA as the surfactant. The experimental conditions and results are given in Table 3 and Figs. 8 and 9. We observed the effects of changing the reaction temperature and the AIBN concentration. The results from reaction temperatures of 60 and 70 °C with 1 wt% AIBN were described in our previous work [12]. As shown in Fig. 8 and in our previous work [12], spherical and uniform PVK products were synthesized at temperatures higher than 40 °C. The particle shape and size were very similar to those obtained by using V-601; however, the lowest molecular weight polymer was produced at 40 °C (entry 13 in Table 3; Fig. 8(a)). Increasing the reaction temperature decreased the molecular weight, except at 40 °C.

Fig. 9 presents the SEM images of PVK synthesized with different concentrations of AIBN at 60 (entries 15-17 in Table 3) and 70 °C (entries 18, 19 in Table 3). When the AIBN concentration increased, particle size increased at 60 and 70 °C, and the average molecular weight decreased at both 60 and 70 °C. As shown in Fig. 9, the polymer particles produced at 70 °C were generally larger than those produced at 60 °C.

CONCLUSION

We investigated dispersion polymerization in the presence of Monasil PCA in compressed liquid DME using three kinds of initiators: 2,2'-azobis(2,4-Dimethylvaleronitrile) (V-65), Dimethyl 2,2-azobisisobutyronitrile (AIBN) and 2,2'-Azobis(isobutyrate) (V-601). The effects of polymerization temperature, initiator type and initiator concentration on the particle shape and size and molecular weight were examined. In polymerization with V-601 and AIBN, highly aggregated polymers were obtained at 40 °C. But when PVK was polymerized with V-65, we obtained spherical and high molecular weight particles at 40 °C. The molecular weight decreased as the polymerization temperature increased. These results indicate that higher reaction temperatures promote transfer reactions and decrease molecular weight. Increases in initiator concentration also lead to decreases in the molecular weight.

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