

# Formation of Micron-Sized Cycloolefin Copolymer from Toluene Solution Using Compressed HFC-134a as Antisolvent

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**ABSTRACT:** A precipitation process employing 1,1,1,2-tetrafluoroethane (HFC-134a) as antisolvent was studied to see its feasibility for the separation of cycloolefin copolymer (COC) from toluene solution. The precipitation was carried out by spraying toluene solution containing 3 to 12 wt % of COC through a 0.4-mm nozzle into a compressed HFC-134a environment. More than 95% of COC could be precipitated under the conditions that both gas and liquid HFC-134a phases were present in the precipitator. The effects of temperature, pressure, COC concentration, HFC-134a flow rate, toluene solution flow rate, and liquid level in the precipitator on yield and morphology of the precipitated COC were systematically studied. Microspheres of COC with a narrow size distribution were exhibited for the COC concentration equal to or less than 5 wt %. The precipitation at these COC concentrations followed a nucleation and growth mechanism. Nucleation and solution breakup that affected morphology and size of the precipitated COC were allowed to occur in the gas space above the liquid. For the concentrations of 8, 10, and 12 wt %, fibers and films instead of microspheres were exhibited. The porosity of the precipitated COC was found to decrease with increasing the COC concentration, indicating that the precipitation was under a spinodal decomposition mechanism. The molecular weight and glass-transition temperature of the precipitated COC were found to be sufficiently close to those of the virgin chips, indicating that HFC-134a is an appropriate antisolvent to achieve separation of polymer from solution. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1657–1668, 2002; DOI 10.1002/app.10543

**Key words:** microstructure; morphology; separation techniques; yielding

## INTRODUCTION

Because cycloolefin copolymer (COC) possesses some special properties, such as high transpar-

ency, high glass-transition temperature, high heat distortion resistance, absence of chromophores, and low water adsorption, it has been used as an optical wave-guided polymer. Owing to a complicated synthesis process and a highly desired purity, a sophisticated separation process is needed to obtain COC with a desired morphology and size from solution after synthesis. Some antisolvents, such as acetone and ketone, are commonly used to

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precipitate COC,<sup>1,2</sup> but these antisolvents suffer from disadvantages that a significant amount of antisolvent is retained in the precipitated COC and a subsequent regeneration of antisolvent is required for cycling use. The technique of precipitation of a solid solute from an organic solvent with compressed antisolvent (PCA) has proved to be an efficient separation method.<sup>3–6</sup> It can recover antisolvent easily by simple reduction of pressure after precipitation. Besides, this method can result in different morphology and size of the precipitated COC by properly adjusting the operation conditions, such as temperature, pressure, solute concentration, and injection rate. In a PCA process the compressed fluid causes a volume expansion of liquid solution and thus lowers the solvent strength. As a result, precipitation of the dissolved solute occurs.

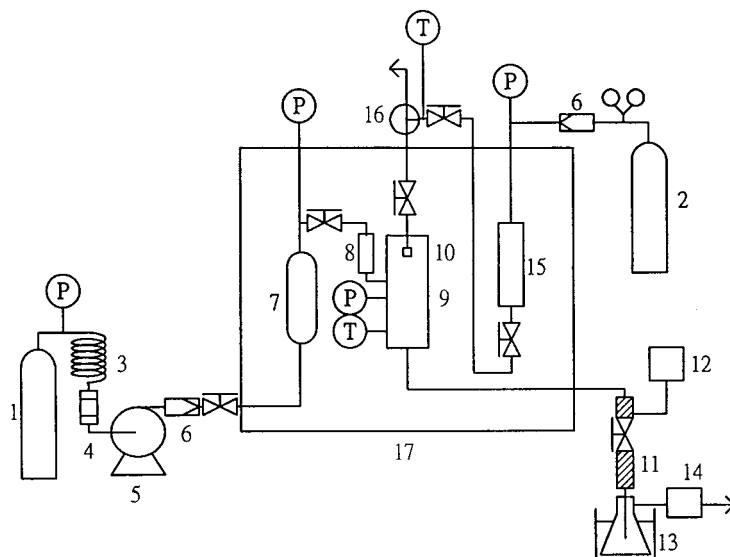
For separation of a polymer solution, addition of an antisolvent would lead to a phase split into a polymer-rich phase and a solvent-rich phase. The polymer would eventually precipitate from the polymer-rich phase by addition of more antisolvent.<sup>7–9</sup> As indicated by McHugh and Guckes,<sup>8</sup> the lower critical solution temperature of a polymer can be lowered by more than 100 K after introduction of the compressed carbon dioxide into the polymer solution. Under this circumstance, the PCA can be operated at much lower temperatures, at which less thermal degradation of polymer occurs.

In a continuous-mode PCA process, a polymer solution is generally sprayed into an antisolvent environment through an atomizer or a nozzle. Because of the formation of droplets of polymer solution, the mass transfer area between solution and antisolvent is much enhanced. An instant volume expansion of droplets by dissolution of antisolvent into solution thus results in micro-sized spheres, films, or fibers.<sup>10–14</sup> Dixon et al.<sup>10</sup> obtained polystyrene by spraying 1 wt % polystyrene in toluene solution into the compressed carbon dioxide through a 100  $\mu\text{m}$  nozzle at temperatures of 273–313 K and pressures of 45–225 bar. Micron-sized spherical polystyrene could be formed by a proper selection of temperature and carbon dioxide density. Unlike microspheres, hollow fibers and porous fibers of polystyrene were observed for the solutions containing 3.5–25.8 wt % of polystyrene,<sup>11</sup> which Dixon and Johnston<sup>11</sup> attributed to the precipitation under spinodal decomposition. Randolph et al.<sup>13</sup> obtained microspheres of poly(L-lactic acid) by spraying a dilute dichloromethane solution containing 0.6–1.0 wt

% of poly(L-lactic acid) into the compressed carbon dioxide at temperatures of 303 to 313 K and pressures of 55 to 97 bar. However, only fibers of the substituted polyamides could be formed when a DMSO or DMF solution containing 0.03–0.09 wt % of polyamides was sprayed into compressed carbon dioxide at temperatures of 296 to 313 K and the pressure of 103.4 bar.<sup>14</sup> Obviously, both the polymer structure and the polymer concentration in solution affect morphology and size of the precipitated polymer using the PCA method.

The operating pressures in all the above-mentioned studies were higher than 45 bar when carbon dioxide was used as antisolvent. Recently, Tan and Chang<sup>15</sup> observed that 1,1,1,2-tetrafluoroethane (HFC-134a) could expand toluene to a certain extent at much lower pressures compared to that of carbon dioxide. Using HFC-134a as antisolvent in the PCA method, polystyrene was found to precipitate from toluene solution at relatively lower pressures compared to using carbon dioxide.<sup>16</sup> The size and morphology of the precipitated polystyrene were observed to be dependent on temperature, pressure, and concentration of polystyrene in solution. Sarkari et al.<sup>17</sup> used CO<sub>2</sub>-philic refrigerants HFE-7100 and Vertrel as antisolvents to precipitate poly(L-lactic acid) at ambient conditions. They found that these two were effective antisolvents and the sizes of the precipitated poly(L-lactic acid) lay in a range between those using compressed carbon dioxide and the traditional organic compounds as antisolvents. Because HFE-7100 and Vertrel are liquids at ambient conditions, a drawback using this kind of antisolvents is that an additional separation from solution after precipitation is required. Nevertheless, their observation showed that fluorinated compounds may be a proper antisolvent used in a PCA process.

The objective of this study is to assess the applicability of a continuous PCA process for separation of COC from a toluene solution containing 3–12 wt % of COC using HFC-134a as antisolvent. The morphology and size of the precipitated COC were examined, and the properties including molecular weight ( $M_w$ ), molecular weight distribution ( $M_w/M_n$ ), and glass-transition temperature ( $T_g$ ) were measured and compared to those of the parent COC chips. The operation variables including temperature, pressure, COC concentration, flow rates of toluene solution and HFC-134a, and liquid HFC-134a level in the precipitator were varied to observe their effects on yield and morphology of the precipitated COC.



- |                            |                            |                               |
|----------------------------|----------------------------|-------------------------------|
| 1. HFC-134a cylinder       | 8. Dehumidifier            | 14. Wet gas meter             |
| 2. N <sub>2</sub> cylinder | 9. Precipitator            | 15. Jerguson gauge            |
| 3. Cooler                  | 10. Nozzle                 | 16. Three-way valve           |
| 4. Filter                  | 11. Heating tape           | 17. Constant temperature oven |
| 5. Pump                    | 12. Temperature controller | P: Pressure indicator         |
| 6. Check valve             | 13. Cold trap              | T: Temperature indicator      |
| 7. Surge tank              |                            |                               |

**Figure 1** Experimental apparatus for PCA using HFC-134a as antisolvent.

## EXPERIMENTAL

The experimental apparatus used for a continuous precipitation of COC from toluene solution using HFC-134a as antisolvent is shown in Figure 1. The precipitator was made of 316 stainless steel and had an inside diameter of 6.3 cm and a total volume of approximately 900 mL. It was equipped with two sapphire windows, through which precipitation of COC inside the precipitator could be observed. To trap the precipitated COC, a filter paper with a pore size of 0.45  $\mu\text{m}$  (HVHP04700, Millipore, Bedford, MA) sitting on a 100-mesh stainless steel sieve was placed at the bottom of the precipitator. The precipitator was placed in a constant-temperature oven, where the temperature could be maintained to within 0.2 K in a range of 253–333 K.

During the operation, HFC-134a (99.95% purity, Daikin Industries Ltd., Japan) was compressed by a minipump (396, Thermo Separation Products, Riviera Beach, FL) and was delivered to the top of the precipitator. The pressure inside the precipitator was indicated by a digital pres-

sure indicator (K054909, Asahi, Japan) whose minimum range was 0.07 bar. The flow rate of HFC-134a was determined by a wet gas meter (W-NK-1, Shinagawa) located downstream of the precipitator. A total of 30 g of solution containing 3–12 wt % COC was first loaded into a 70-mL container (13R-20; Jerguson Gauge, Upper Saddle River, NJ), from which the amount of solution flowed into the precipitator could be read by use of sight glasses. The COC–toluene solution was prepared by dissolving a known amount of COC ( $T_g = 403$  K,  $M_w = 1.04 \times 10^5$ , and  $M_w/M_n = 1.59$ ; Ticona, Frankfurt, Germany) in the HPLC-grade toluene (99.9% purity; Mallinckrodt Baker Inc., Paris, KY). The compressed nitrogen was used to pressurize the toluene solution. After the desired temperature and pressure in the precipitator were reached, the COC–toluene solution was allowed to enter the precipitator through a nozzle with a diameter of 0.4 mm and a length of 49.6 mm (TN-SS40; Spraying System, Wheaton, IL). The flow rate of the toluene solution was adjusted with a metering valve (SS-21RS2; Whitey, Highland Heights, OH). The solution drained from the

**Table I** Effect of Pressure on Yield and Morphology for the Operations at Temperature of 303 K, COC Concentration of 5 wt %, HFC-134a Flow Rate of 2000 mL/min, and Toluene Solution Flow Rate of 50 mL/min

| Pressure (bar)    | $\rho_{\text{HFC}}$ (g/cm <sup>3</sup> ) | Yield (wt %) | $M_w$ ( $\times 10^{-5}$ ) | $M_w/M_n$ | Macrostructure             | Morphology and Size   |
|-------------------|--|--------------|----------------------------|-----------|----------------------------|---|
| 9.65              | 1.189                                    | 98.2         | 1.04                       | 1.55      | Sl. flocc./agglom. powders | Microspheres, 1–5 $\mu\text{m}$ ; fibers, 20–30 $\mu\text{m}$ |
| 8.82              | 1.189                                    | 97.2         | 0.90                       | 1.63      | Sl. flocc./agglom. powders | Microspheres, 1.0–2.5 $\mu\text{m}$                           |
| 7.79 <sup>a</sup> | 0.037 (V)<br>1.188 (L)                   | 97.0         | 0.97                       | 1.48      | Sl. flocc./agglom. powders | Microspheres, 0.2–1.2 $\mu\text{m}$                           |
| 7.10              | 0.033                                    | 94.3         | 1.03                       | 1.57      | Fine powders and bulks     | Microspheres, 0.3–1.5 $\mu\text{m}$ ; rodlike structure       |
| 6.48              | 0.031                                    | 89.3         | 1.03                       | 1.59      | Fine powders and gel-like  | Microspheres, 0.4–1.0 $\mu\text{m}$ ; rodlike structure       |
| 5.79              | 0.026                                    | 72.4         | 0.96                       | 1.52      | Gel-like                   | Smooth film   |

<sup>a</sup>The liquid HFC-134a level was in the middle of the precipitator.

precipitator was collected in a cold trap, where the temperature was maintained at 263 K. During the spray of the toluene solution, the pressure was observed to vary within  $\pm 0.2$  bar.

After finishing the spray of the toluene solution, the compressed HFC-134a continuously flowed through the precipitator for 1 h to remove toluene adhering to the precipitated COC trapped on the filter paper. After this extraction process, the pressure in the precipitator was reduced to atmosphere and the COC on the filter paper was collected. A known amount of toluene was thus used to flush the precipitator to collect the residual COC deposited on the wall of the precipitator. Cycloolefin copolymers in the drainage solution and in the flushing toluene solution were precipitated by adding three times the volume of acetone (99.97% purity, Tedia Company, Inc., Fairfield, OH) to the solutions. All the collected precipitated COCs were heated in a vacuum at 353 K for 8 h before analysis. The collected COCs from the filter paper and from the drainage and flushing solutions were weighed to check the overall mass balance.

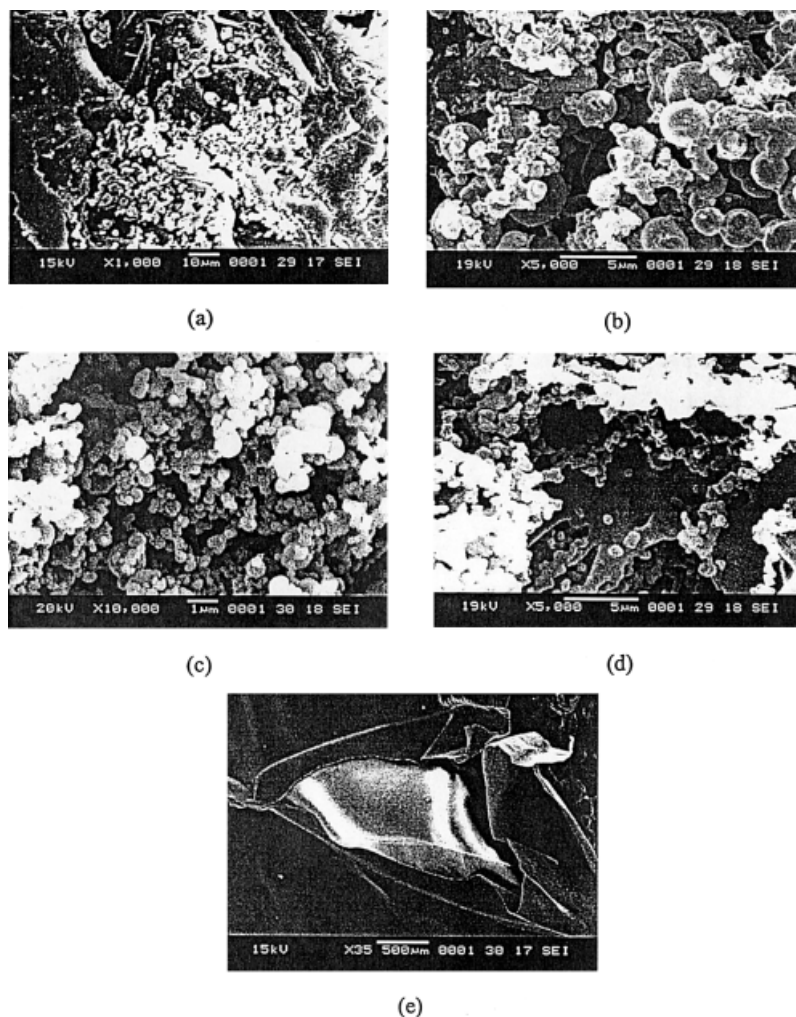
The molecular weights and the glass-transition temperatures of the collected COC were determined by a gel-permeation chromatograph (LC-9A, Shimadzu, Japan) using THF as the mobile phase and a differential scanning calorimeter (DSC-7 Perkin Elmer Cetus Instruments, Norwalk, CT), respectively. Scanning electron microscopy (JSM-5000 JEOL, Peabody, MA) was used to examine the morphology for the collected COC.

## RESULTS AND DISCUSSION

In each experiment, the overall mass of COC collected from the filter paper, the drainage solution, and the flushing solution was observed to be sufficiently close to the amount charged to the precipitator. The difference was always less than 5.0%. The reproducibility test was also performed at various temperatures, pressures, and flow rates of HFC-134a and toluene solution. The difference in the amount of COC collected from the precipitator was found to be less than 5.0%, and the morphology and size of the precipitated COC in macrostructure and microstructure were observed to be almost the same.

### Effects of Pressure and Temperature

For the polystyrene–toluene system, Tan and Lin<sup>16</sup> observed that almost all the dissolved polystyrene could be precipitated when the precipitator was filled with both gas and liquid HFC-134a or only liquid HFC-134a, but not for the operation in which only gaseous HFC-134 was present in the precipitator. For the present COC–toluene system, not only high yields were observed at conditions during which the precipitator was filled with only liquid phase or both gas and liquid phases of HFC-134a, but also a significant amount of COC was precipitated when the precipitator was filled with only gaseous HFC-134a, as shown in Table I. In this study, yield is defined as the ratio of the precipitated COC to the amount



**Figure 2** SEM of the precipitated COC by spraying a 5 wt % COC solution into HFC-134a at a temperature of 303 K, toluene solution flow rate of 50 mL/min, HFC-134a flow rate of 2000 mL/min, and pressures of (a) 9.65 bar, (b) 8.82 bar, (c) 7.79 bar, (d) 6.48 bar, (e) 5.79 bar.

of COC fed to the precipitator. These results indicated that the interaction force between COC and toluene was weaker than that between polystyrene and toluene. As a result, precipitation of COC occurred at a pressure lower than that for the polystyrene–toluene system, that is, the extent of volume expansion required to make precipitation to occur was less.

Because supersaturation is generally low at low pressures resulting from less volume expansions, the yield of COC therefore decreased with a decrease in pressure, as indicated in Table I. When the pressure was equal to the vapor pressure of HFC-134a and the liquid HFC-134a level was maintained in the middle of the precipitator, only microspheres were formed, shown in Figure

2. The liquid level was denoted as the portion of the precipitator occupied by liquid HFC-134a. At this operating condition, precipitation was visualized only when the solution contacted with liquid HFC-134a, indicating that nucleation was dominant in the space above liquid HFC-134a. When the precipitator was full of liquid HFC-134a, Figure 2 shows that only microspheres were formed at 8.82 bar, but fibers in addition to microspheres were also formed at 9.65 bar. Because the solution hit liquid HFC-134a once it left from the nozzle, both nucleation and growth happened instantly. More growth and coalescence might happen at higher pressures because of more COC precipitated, which thus resulted in a shape other than a microsphere. It should be mentioned that a

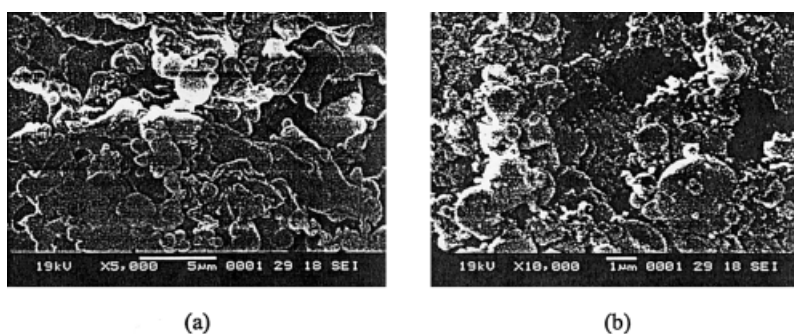
**Table II** Effect of Temperature on Yield and Morphology for the Operations at COC Concentration of 5 wt %, HFC-134a Flow Rate of 2000 mL/min, Toluene Solution Flow Rate of 50 mL/min, and liquid HFC-134a Level in the Middle of the Precipitator

| Temperature (K) | Pressure (bar) | $\rho_{\text{HFC}}$ (g/cm <sup>3</sup> ) | Yield (wt %) | $M_w$ ( $\times 10^{-5}$ ) | $M_w/M_n$ | Macrostructure             | Morphology and Size                               |
|-----------------|----------------|--|--------------|----------------------------|-----------|----------------------------|---|
| 303             | 7.79           | 0.037 (V)<br>1.188 (L)                   | 97.0         | 0.97                       | 1.48      | Sl. flocc./agglom. powders | Microspheres, 0.2–1.2 $\mu\text{m}$               |
| 293             | 5.79           | 0.028 (V)<br>1.226 (L)                   | 97.8         | 0.98                       | 1.51      | Sl. flocc./agglom. powders | Microspheres and flakelike, 0.4–3.0 $\mu\text{m}$ |
| 283             | 4.41           | 0.020 (V)<br>1.262 (L)                   | 97.4         | 0.97                       | 1.67      | Fine powders               | Microspheres and embryos, 0.1–2.5 $\mu\text{m}$   |

certain portion of the precipitated COC was found to adhere to the nozzle because of a rapid vitrification of COC. This is not desired, especially for a long-time operation. When the pressures were below 7.79 bar (i.e., under gas phase operation) shapes other than a sphere of the precipitated COC were also exhibited, shown in Figure 2. These results indicated that supersaturation was not extensive enough to generate more nuclei at low pressures. Under this condition, significant growth in the solution on the collected filter caused different shapes. Because of yield higher than 95%, no precipitated COC adhered to the nozzle, and formation of only microspheres, the operation that both vapor and liquid HFC-134a were present in the precipitator, was therefore suggested to separate COC from toluene solution.

When both liquid and gas HFC-134a were present in the precipitator and the liquid level was maintained in the middle of the precipitator, Table II shows that almost the same yield was obtained at all the studied temperatures. From the existing volume expansion data for the toluene–HFC-134a system,<sup>15</sup> it can be seen that the

volume expansions were all greater than 4.5 and increased with increasing temperature for the operating conditions shown in Table II. The former indicated that a volume expansion of 4.5 was sufficient to cause almost a complete precipitation. The latter, however, resulted in different morphology and size of the precipitated COC, as shown in Figures 2 and 3. A larger volume expansion would, in general, result in a larger supersaturation. Therefore, more nuclei were generated at the condition of 303 K and 7.79 bar compared to that at the other two operating conditions, given that the largest volume expansion happened at this condition. Under these circumstances, microspheres with a uniform size distribution were exhibited at 303 K and 7.79 bar. Although the morphology and size were different at these operating conditions, the visual appearance and the bulk density looked similar. A narrow size distribution of macroscale particles can result in a high bulk density that is usually required for subsequent delivery and processing. This requirement seemed to be satisfied for the

**Figure 3** SEM of the precipitated COC by spraying a 5 wt % COC solution into HFC-134a at a toluene solution flow rate of 50 mL/min, HFC-134a flow rate of 2000 mL/min, and temperatures and pressures of (a) 293 K, 5.79 bar, (b) 283 K, 4.41 bar.

**Table III** Effect of COC Concentration on Yield and Morphology for the Operations at Temperature of 303 K, Pressure of 7.79 bar, HFC-134a Flow Rate of 3000 mL/min, Toluene Solution Flow Rate of 50 mL/min, and Liquid HFC-134a Level in the Middle of the Precipitator

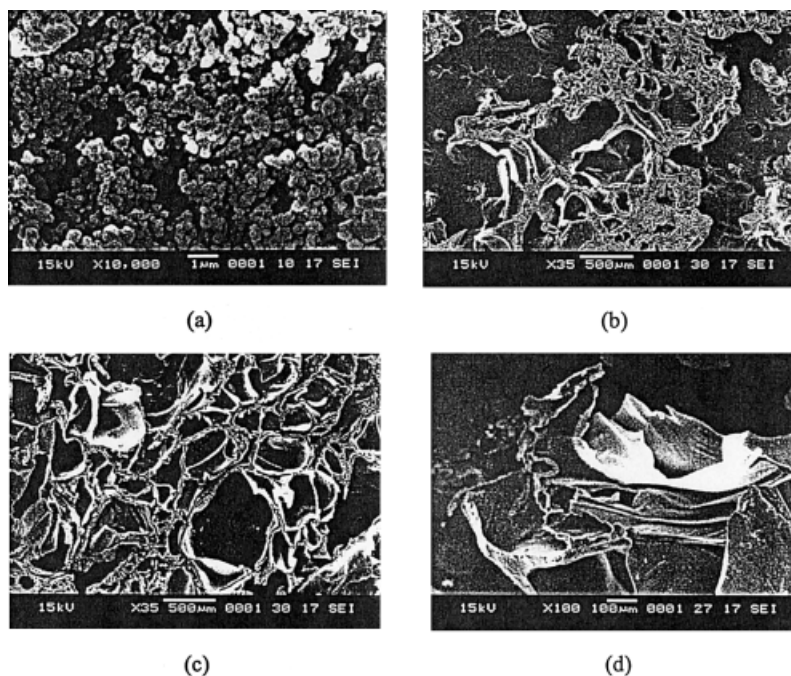
| $C_{\text{COC}}$<br>(wt %) | $\rho_{\text{HFC}}$<br>(g/cm <sup>3</sup> ) | Yield<br>(wt %) | $M_w$<br>( $\times 10^{-5}$ ) | $M_w/M_n$ | Macrostructure                | Morphology and Size                   |
|----------------------------|---|-----------------|-------------------------------|-----------|-------------------------------|---------------------------------------|
| 3                          | 0.037 (V)<br>1.188 (L)                      | 94.9            | 0.92                          | 1.63      | Fine powders                  | Microspheres, 0.2–2.0 $\mu\text{m}$   |
| 5                          | 0.037 (V)<br>1.188 (L)                      | 97.9            | 0.95                          | 1.59      | Sl. flocc./agglom.<br>powders | Microspheres, 1.0–4.0 $\mu\text{m}$   |
| 8                          | 0.037 (V)<br>1.188 (L)                      | 98.1            | 0.96                          | 1.55      | Airy bulks                    | Porous fibers, $\sim 100 \mu\text{m}$ |
| 10                         | 0.037 (V)<br>1.188 (L)                      | 97.9            | 0.93                          | 1.55      | Airy bulks                    | Broken film                           |
| 12                         | 0.037 (V)<br>1.188 (L)                      | 95.1            | 0.98                          | 1.68      | Sticky bulks<br>and gel-like  | Smooth film                           |

operation in which both gas and liquid HFC-134a were present in the precipitator.

#### Effect of COC Concentration

Although yield higher than 95% could be obtained at all the studied COC concentrations, the morphology and size of the precipitated COC were exhibited differently, as shown in Table III and

Figures 2 and 4. Microspheres of COC could be formed only at the COC concentrations of 3 and 5 wt %. The same results were also observed for the toluene–polystyrene system.<sup>16</sup> Because of formation of microspheres, the precipitation was believed to follow a nucleation and growth mechanism. When the COC concentration was equal to or greater than 8 wt %, the precipitated COC exhibited a continuously interpenetrating struc-



**Figure 4** SEM of the precipitated COC by spraying the COC solutions with concentrations of (a) 3 wt %, (b) 8 wt %, (c) 10 wt %, (d) 12 wt %, into HFC-134a at 303 K, 7.79 bar, toluene solution flow rate of 50 mL/min, and HFC-134a flow rate of 3000 mL/min.

**Table IV** Effect of HFC-134a Flow Rate on Yield and Morphology for the Operations at Temperature of 303 K, Pressure of 7.79 bar, COC Concentration of 5 wt %, Toluene Solution Flow Rate of 50 mL/min, and Liquid HFC-134a Level in the Middle of the Precipitator

| $Q_{\text{HFC}}$<br>(mL/min) | $\rho_{\text{HFC}}$<br>(g/cm <sup>3</sup> ) | Yield<br>(wt %) | Macrostructure             | Morphology and Size  |
|------------------------------|---|-----------------|----------------------------|--|
| 1000                         | 0.037 (V)<br>1.188 (L)                      | 96.6            | Agglomerated powders       | Entangled porous fibers, 10–30 $\mu\text{m}$                           |
| 2000                         | 0.037 (V)<br>1.188 (L)                      | 97.0            | Sl. flocc./agglom. powders | Microspheres, 0.2–1.2 $\mu\text{m}$                                    |
| 3000                         | 0.037 (V)<br>1.188 (L)                      | 97.9            | Sl. flocc./agglom. powders | Microspheres, 1.0–4.0 $\mu\text{m}$                                    |
| 4000                         | 0.037 (V)<br>1.188 (L)                      | 99.0            | Sl. flocc./agglom. powders | Fibers, 0.4–1.0 $\mu\text{m}$ ; microspheres,<br>0.1–1.0 $\mu\text{m}$ |
| 5000                         | 0.037 (V)<br>1.188 (L)                      | 97.1            | Sl. flocc./agglom. powders | Fibers, 0.4–2.0 $\mu\text{m}$ ; microspheres,<br>0.3–1.0 $\mu\text{m}$ |

ture in which voids were present, indicating the precipitation followed a spinodal decomposition mechanism. The major difference in morphology for the concentrations varying from 8 to 12 wt % was the distribution of voids. Dixon et al.<sup>12</sup> also observed this difference for the precipitated polystyrene from toluene using CO<sub>2</sub> as antisolvent and provided an explanation as well. Because the operating temperatures were at least 100 K below the glass-transition temperature, COC vitrified rapidly at the skin of the polymer-rich phase. Under these circumstances, little time was available for growth of solvent voids. As HFC-134a diffused through the glassy COC, the COC concentration decreased in the core. The solvent-rich droplets thus had time to grow and coalesce. This especially happened at restively low COC concentrations because the toluene concentration in the core was great enough to prevent vitrification of COC. Under these circumstances, large voids like holes in the precipitated COC were formed at the COC concentration of 8 wt %, as shown in Figure 4. When the COC concentration was raised to 10 wt %, the time available for growth and coalescence of the solvent-rich droplets decreased because of more vitrification that resulted from a higher COC concentration. As a consequence many local voids were formed and broken films composed of uniform pores were exhibited. When the COC concentration was further increased to 12 wt %, more and rapid vitrification caused the glassy skin to collapse instantaneously. Under these circumstances, smooth films with only few voids were exhibited. Obviously, the porosity of the precipitated COC decreased with increasing the COC concentra-

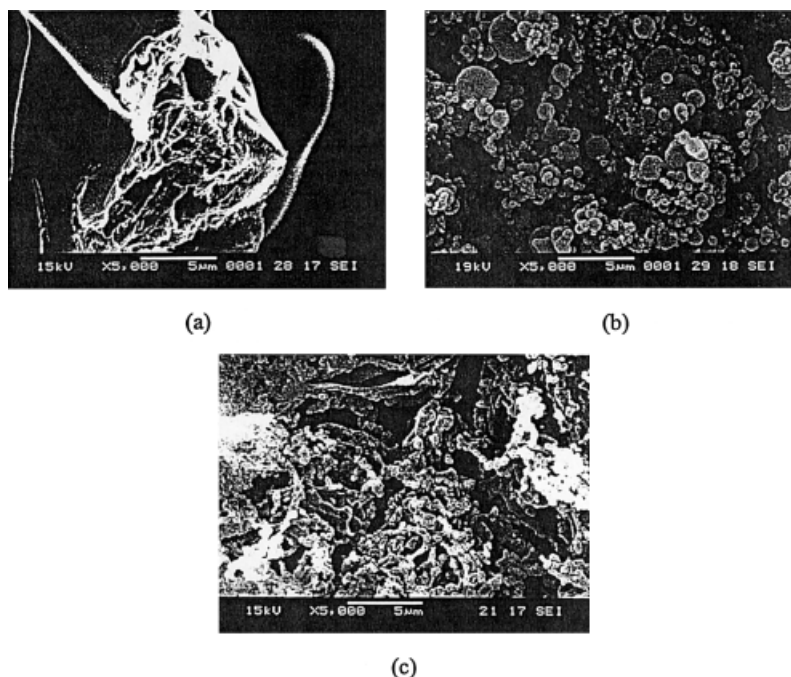
tions equal to or greater than 8 wt %, bulks instead of powders appeared macroscopically, indicating that the bulk density was low.

Besides the different precipitation mechanisms, the change in morphology with concentration was also influenced by the stabilization of the liquid jet. The measured viscosity of the 8 wt % solution was about twice that of the 5 wt % solution. Because the densities of these two solutions were not significantly different, the Reynolds number of the 8 wt % solution was about one-half that of the 5 wt % solution. A decrease in the Reynolds number thus reduced the possibility of jet breakup.<sup>18</sup> In addition, the entanglement between polymer chains in a high polymer concentration solution would obviously stabilize the liquid jet. These effects were more pronounced for the COC concentrations greater than 8 wt %. Under these circumstances, the spherical shape of the precipitated COC could not be formed.

#### Effects of HFC-134a Flow Rate and Toluene Solution Flow Rate

When the COC concentration was maintained at 5 wt %, Table IV shows that microspheres could not be formed at a flow rate of HFC-134a of 1000 mL/min. Although microspheres for the HFC-134a flow rates, varying from 2000 and 5000 mL/min, could all be formed, the sizes were slightly different and fiberlike precipitated COC was also exhibited at 4000 and 5000 mL/min, as shown in Figures 2 and 5. An increase in particle size with increasing antisolvent flow rate was also pointed out by Mawson et al.<sup>19</sup> when carbon dioxide was used as antisolvent. The dependency of morphol-





**Figure 5** SEM of the precipitated COC by spraying a 5 wt % COC solution into HFC-134a at 303 K, 7.79 bar, toluene solution flow rate of 50 mL/min, and HFC-134a flow rates of (a) 1000 mL/min, (b) 3000 mL/min, (c) 4000 mL/min.

ogy and size of the precipitated COC on HFC-134a flow rate might be explained in terms of the Reynolds and Weber numbers. The Weber number is defined as

$$N_{We} = \frac{\rho_{HFC} u^2 d}{\sigma}$$

where  $\rho_{HFC}$  is antisolvent density,  $u$  is the relatively linear velocity between antisolvent and solution,  $d$  is the jet diameter, and  $\sigma$  is the interfacial tension. An increase in HFC-134a flow rate would definitely result in a larger Reynolds number and more turbulences that favor the solution leaving from the tip of the nozzle to break up, thus enhancing mass transfer between solution droplets and HFC-134a. Under this situation small spheres would tend to form because of the presence of fine solution droplets. On the other hand, an increase in volumetric flow rate of HFC-134a would decrease  $u$ , given that the linear velocity of the toluene solution leaving a micron-sized nozzle was much greater than that of the HFC-134a stream. Consequently, the Weber number decreased. A decrease in Weber number would reduce the possibility for the solution breakup and thus would not favor the formation

of small-size precipitates. The opposite effects of the Reynolds and Weber numbers thus result in different morphology and size of the precipitates. Obviously, the Reynolds number played a more important role than that of the Weber number at a HFC-134a flow rate of 1000 mL/min, although the highest Weber number existed at this flow rate.

For the solution containing 5 wt % of COC and the HFC-134a flow rate of 2000 mL/min, Table V shows that microspheres were formed when the flow rate of the toluene solution was equal to or greater than 50 mL/min. These results indicate that a complete breakup of the solution jet occurred at these toluene flow rates. Under these circumstances, the morphology and size of the precipitates did not vary significantly. But when the COC concentration was increased to 8 or 10 wt %, a toluene solution flow rate of 100 mL/min was still not sufficient to break up the solution jet into fine droplets because of an increase in viscosity of the solution. Under this situation, microspheres could not be formed.

#### Effect of Liquid HFC-134a Level

When vapor and liquid HFC-134a coexisted in the precipitator and the solution contained 5 wt % of

**Table V Effect of Toluene Solution Flow Rate on Yield and Morphology for the Operations at Temperature of 303 K, Pressure of 7.79 bar, and Liquid HFC-134a Level in the Middle of the Precipitator**

| $C_{\text{COC}}$<br>(wt %)     | $Q_{\text{solution}}$<br>(mL/min) | $\rho_{\text{HFC}}$<br>(g/cm <sup>3</sup> ) | Yield<br>(wt %) | $M_w$<br>( $\times 10^{-5}$ ) | $M_w/M_n$ | Macrostructure                | Morphology and Size                     |
|--------------------------------|-----------------------------------|---|-----------------|-------------------------------|-----------|-------------------------------|---|
| $Q_{\text{HFC}} = 2000$ mL/min |                                   |   |                 |                               |           |                               |   |
| 5                              | 50                                | 0.037 (V)<br>1.188 (L)                      | 97.0            | 0.97                          | 1.48      | Sl. flocc./agglom.<br>powders | Microspheres, 0.2–1.2 $\mu\text{m}$     |
| 5                              | 100                               | 0.037 (V)<br>1.188 (L)                      | 96.2            | 0.96                          | 1.70      | Sl. flocc./agglom.<br>powders | Microspheres, 0.2–1.0 $\mu\text{m}$     |
| 5                              | 150                               | 0.037 (V)<br>1.188 (L)                      | 96.2            | 0.95                          | 1.59      | Sl. flocc./agglom.<br>powders | Microspheres, 0.1–1.0 $\mu\text{m}$     |
| $Q_{\text{HFC}} = 3000$ mL/min |                                   |   |                 |                               |           |                               |   |
| 8                              | 50                                | 0.037 (V)<br>1.188 (L)                      | 98.1            | 0.96                          | 1.55      | Airy bulks                    | Porous fibers, $\sim 100$ $\mu\text{m}$ |
| 8                              | 100                               | 0.037 (V)<br>1.188 (L)                      | 98.3            | 0.96                          | 1.73      | Bulks                         | Porous fibers, 10–20 $\mu\text{m}$      |
| 10                             | 50                                | 0.037 (V)<br>1.188 (L)                      | 97.9            | 0.93                          | 1.55      | Airy bulks                    | Broken film                             |
| 10                             | 100                               | 0.037 (V)<br>1.188 (L)                      | 98.4            | 1.00                          | 1.57      | Bulks                         | Porous fibers, 10–30 $\mu\text{m}$      |

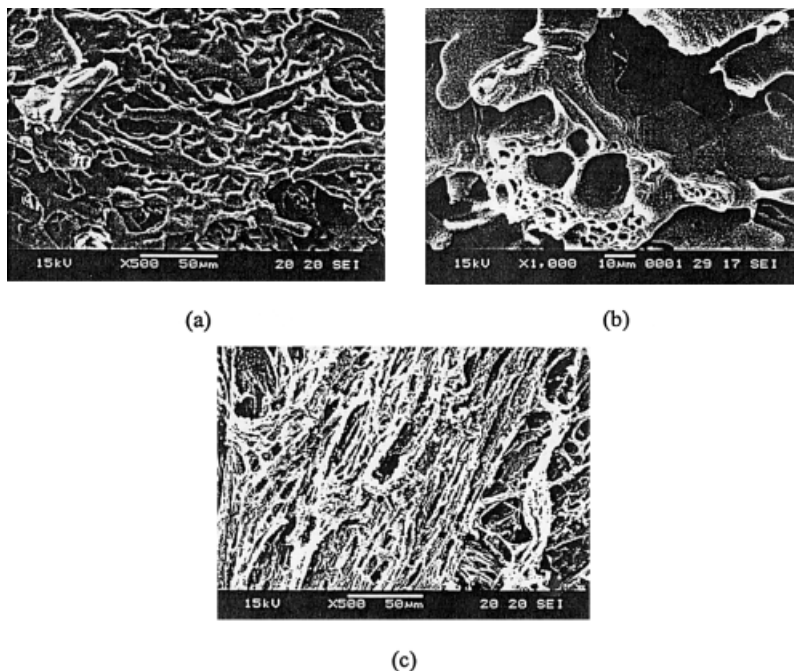
COC, the effect of liquid level on yield, morphology, and size of the precipitates is shown in Table VI. It can be seen that the yield increased when

the liquid level was lowered; although the difference was not significant. Although only microspheres were formed for the operations at any

**Table VI Effect of Liquid HFC-134a Level on Yield and Morphology for the Operations at Temperature of 303 K and Pressure of 7.79 bar**

| Liquid Level  | $\rho_{\text{HFC}}$<br>(g/cm <sup>3</sup> ) | Yield<br>(wt %) | Macrostructure             | Morphology and Size                              |
|---|---|-----------------|----------------------------|--|
| $C_{\text{COC}} = 5$ wt %, $Q_{\text{solution}} = 50$ mL/min, $Q_{\text{HFC}} = 2000$ mL/min  |   |                 |                            |  |
| 3/4   | 0.037 (V)<br>1.188 (L)                      | 95.5            | Sl. flocc./agglom. powders | Microspheres, 2–15 $\mu\text{m}$                 |
| 1/2   | 0.037 (V)<br>1.188 (L)                      | 97.0            | Sl. flocc./agglom. powders | Microspheres, 0.2–1.2 $\mu\text{m}$              |
| 1/4   | 0.037 (V)<br>1.188 (L)                      | 98.4            | Sl. flocc./agglom. powders | Microspheres, 0.2–1.2 $\mu\text{m}$              |
| $C_{\text{COC}} = 8$ wt %, $Q_{\text{solution}} = 100$ mL/min, $Q_{\text{HFC}} = 3000$ mL/min |   |                 |                            |  |
| 3/4   | 0.037 (V)<br>1.188 (L)                      | 95.9            | Sticky bulks               | Porous fibers, 10–200 $\mu\text{m}$              |
| 1/2   | 0.037 (V)<br>1.188 (L)                      | 98.3            | Bulks                      | Porous fibers, 10–20 $\mu\text{m}$               |
| 1/4   | 0.037 (V)<br>1.188 (L)                      | 99.1            | Bulks                      | Expanded fibers, <sup>a</sup> 4–20 $\mu\text{m}$ |
| 1/8   | 0.037 (V)<br>1.188 (L)                      | 98.3            | Bulks                      | Expanded fibers, <sup>a</sup> 1–5 $\mu\text{m}$  |

<sup>a</sup>Many microspheres adhered to the fibers.



**Figure 6** SEM of the precipitated COC by spraying an 8 wt % COC solution into HFC-134a at 303 K, 7.79 bar, toluene solution flow rate of 100 mL/min, HFC-134a flow rate of 3000 mL/min, and liquid HFC-134a levels of (a) 3/4, (b) 1/2, (c) 1/8.

liquid levels, the size exhibited for the liquid level at 3/4 was much larger than that for the liquid levels at 1/2 and 1/4. In each experiment, the precipitated COC was not visualized in the gas space and the precipitation occurred once the solution hit liquid HFC-134a. This visualization indicated no significant growth in the gas phase. Nucleation was thus believed to be dominant when the solution traveled through the gas space. When this space was short, the time was thus not sufficient to transfer HFC-134a into solution. Consequently, the nucleation rate was not comparable to that for the operation having a larger gas space. The gas space also allowed the solution to break up into fine droplets because of low surface tension and high inertial force possessed by gas HFC-134a and the sprayed solution, respectively. When the liquid level was kept at 3/4, the space was not large enough to generate sufficiently fine droplets when the solution passed through gas HFC-134a. The formation of larger droplets was not favorable to the transfer of HFC-134a into solution and to the generation of a high supersaturation. As a result, larger microspheres were formed and less yield was obtained compared to that of the operations with lower liquid levels.

A sufficient space needed to break up the solution jet to generate small-size precipitates was also evidenced for the COC concentration of 8.0 wt %. Figure 6 shows that microspheres could not be formed for the conditions with different liquid levels. These results indicated that the solution jet could not be completely broken up into fine droplets because of a high viscous solution. It can be seen from Figure 6 that slimmer fibers were formed when the liquid level was kept lower. Based on this observation, the solution jet was split more easily for an operation with a larger gas space.

The molecular weights and molecular weight distributions of the precipitated COC at all the operation conditions were measured by gel-permeation chromatography. The measured results shown in Tables I, II, III, and V indicate that they were sufficiently close to those of the parent COC chips, the differences of which were always less than 7.0%. In addition to molecular weight, the glass-transition temperature was also measured by a differential scanning calorimeter in this study. It was found that the  $T_g$  of all the precipitated COC was the same as that of the original. It thus concluded that the present technique using HFC-134a as an antisolvent would not alter

the physical and chemical properties of the precipitated COC.

## CONCLUSIONS

In a continuous spray of the COC–toluene solution into compressed HFC-134a, it was found that almost all the dissolved COC could be precipitated from the solution when the precipitator was filled with only liquid phase or both liquid and gas phases of HFC-134a. Because a certain portion of the precipitated COC was found to adhere to the nozzle when the precipitator was filled with only liquid HFC-134a, the operation in which gas and liquid HFC-134a coexisted in the precipitator was thus recommended. In this PCA process, the pressure required to achieve a yield higher than 95% was less than 10 bar at room temperature, and the recovery of HFC-134a after precipitation by a phase separation is simple. In addition, the physical and chemical properties of the precipitated COC were found to be sufficiently close to those of the original COC chips. These results indicate that HFC-134a is an appropriate antisolvent for separation COC from toluene.

The morphology of the precipitated COC was observed to be strongly dependent on the operating conditions. When the COC concentration was equal to or less than 5 wt %, micron-sized spheres with a uniform size distribution could be formed with proper combinations of temperature, pressure, HFC-134a flow rate, toluene solution flow rate, and liquid level in the precipitator. The precipitation at these concentrations was under a nucleation and growth mechanism. Nucleation was believed to occur mainly in the gas space above liquid HFC-134a. The gas space also allowed the solution to break up into fine droplets that affected the ultimate size of the precipitated COC. High bulk densities of the precipitated COC that are generally required for subsequent processing could be obtained, given that fine powders consisted of slightly agglomerated microspheres, were visualized. Fiber, film, and irregular shape instead of microsphere were observed for COC concentration in solution equal to or greater than 8 wt %. These outcomes resulted, in part, from a difficulty to break up a viscous solution jet. The precipitation at these concentrations followed a spinodal decomposition mechanism. The porosity

of the precipitated COC was found to decrease with increasing COC concentration. The effects of the operating variables such as temperature, pressure, polymer concentration in solution, and antisolvent flow rates on morphology and size of the precipitated COC using HFC-134a as antisolvent were similar to those for other polymer solutions using carbon dioxide as antisolvent; however, the pressure required was much lower using HFC-134a as antisolvent.

## REFERENCES

1. Weller, T.; Brekner, M.-J.; Osan, F. U.S. Pat. 5,498,677, 1996.
2. Brekner, M.-J.; Deckers, H.; Osan, F. U.S. Pat. 5,637,400, 1997.
3. Gallagher, P. M.; Coffey, M. P.; Krukoni, V. J.; Klasutis, N. in *Supercritical Fluid Science and Technology*, Johnston, K. P.; Penninger, J. M. L., Eds.; ACS Symposium Series 406; American Chemical Society: Washington, DC, 1989; pp 334–354.
4. Gallagher, P. M.; Coffey, M. P.; Krukoni, V. J.; Hillstrom, W. W. *J Supercrit Fluids* 1992, 5, 130.
5. Berends, E. M.; Bruinsma, O. S.; de Graauw, J.; van Rosmalen, G. M. *AIChE J* 1996, 42, 431.
6. Reverchon, E. *J Supercrit Fluids* 1999, 15, 1.
7. Seckner, A. J.; McClellan, A. K.; McHugh, M. A. *AIChE J* 1988, 34, 9.
8. McHugh, M. A.; Guckes, T. L. *Macromolecules* 1985, 18, 674.
9. Bungert, B.; Sadowski, G.; Arlt, W. *Ind Eng Chem Res* 1998, 37, 3208.
10. Dixon, D. J.; Johnston, K. P.; Bodmeier, R. A. *AIChE J* 1993, 39, 127.
11. Dixon, D. J.; Johnston, K. P. *J Appl Polym Sci* 1993, 50, 1929.
12. Dixon, D. J.; Luna-Bárcenas, G.; Johnston, K. P. *Polymer* 1994, 35, 3998.
13. Randolph, T. W.; Randolph, A. D.; Mebes, M.; Yeung, S. *Biotechnol Prog* 1993, 9, 429.
14. Yeo, S.-D.; Debenedetti, P. G.; Radosz, M.; Schmidt, H.-W. *Macromolecules* 1993, 26, 6207.
15. Tan, C.-S.; Chang, W.-W. *Ind Eng Chem Res* 1998, 37, 1821.
16. Tan, C.-S.; Lin, H.-Y. *Ind Eng Chem Res* 1999, 38, 3898.
17. Sarkari, M.; Darrat, I.; Knutson, B. L. *AIChE J* 2000, 46, 1850.
18. Lefebvre, A. H. *Atomization and Sprays*; Hemisphere: New York, 1989.
19. Mawson, S.; Kanakia, S.; Johnston, K. P. *J Appl Polym Sci* 1997, 64, 2105.