

# Synthesis and Rapid Expansion in Supercritical Carbon Dioxide through Porous Sintered Metal Plate of Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate)

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**ABSTRACT:** Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) [poly(TA-N)] was synthesized in dry benzene using AIBN as an initiator at 60°C. The effects of the monomer concentration ( $C_m$ ), initiator concentration ( $C_i$ ), and reaction time on the polymerization were investigated. The results of DSC and TGA showed that when the  $C_i$  remains constant, the higher the  $C_m$  value is, the better the thermal character for the product in the range of experiments. When the reaction was conducted for 30 h, polymerization is almost completed. The  $C_i$  should remain lower than 0.25 g/100 g monomer when the  $C_m$  is lower than 15 g/L. When the  $C_m$  is higher than 15 g/L, the  $C_i$  should be increased slightly. When the  $C_m$  remains constant, it was observed that an increase in the  $C_i$  increases the yield (mass of polymer after reaction/mass of monomer before reaction). On the other hand, the melting ( $T_m$ ) and decomposition ( $T_d$ ) temperatures of the reaction product decrease, except when the  $C_m$  reaches 20 g/L and the reaction time is 30 h. High purity

CO<sub>2</sub> was continuously pumped using a high pressure syringe pump. Rapid expansion of poly(TA-N) in supercritical CO<sub>2</sub> happened under control through a porous sintered metal plate. The poly(TA-N) morphology was analyzed with a scanning electron microscope. An amorphous polymer was formed at a preexpansion temperature of 45°C. Fibers were formed at temperatures of around 60–80°C. An increase of the temperature slightly increases the particle size. At 105°C, most of the particles are spheres and dendrites. The corresponding CO<sub>2</sub> flow rate upon expansion was 2.5–5.0 ± 0.3 L/min (STP) and the pressure drop was 2 MPa. At the higher CO<sub>2</sub> flow rate, the spheres and dendrites became smaller. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2763–2768, 2003

**Key words:** synthesis; poly(1,1,2,2-tetrahydroperfluorodecyl acrylate); rapid expansion; supercritical carbon dioxide; porous sintered metal plate

## INTRODUCTION

A fluid becomes supercritical when it is compressed and heated to conditions above its critical point, where it exhibits densities close to those of liquids and an increased solvent capacity for solutes with a low vapor pressure. In rapid expansion of a supercritical solution (RESS), the mechanical perturbation that occurs when a solution is expanded across a fine throttling device, such as a well-defined orifice, a nozzle, or a porous sintered metal plate, can lead to a rapid supersaturation and a characteristic time for the phase separation between 10<sup>-5</sup> and 10<sup>-7</sup> s.<sup>1</sup> Consequently, microstructural materials may be formed and quenched in the rapidly expanding solution.<sup>1–7</sup>

The majority of RESS studies of polymers have used organic solvents, such as C<sup>1</sup>–C<sup>5</sup> alkanes and alkenes, as well as chlorofluorocarbons. In supercritical fluid technology, great efforts are underway to attempt to replace these types of solvents with CO<sub>2</sub>.<sup>7–13</sup> Carbon

dioxide is nontoxic, nonflammable, and environmentally acceptable and has easily accessible critical conditions (i.e.,  $T_c = 304.2$  K,  $P_c = 7.38$  MPa). It has no dipole moment and a low cohesive energy density. Thus, CO<sub>2</sub> was used as the solvent for RESS in this research.

Unfortunately, most polymers are not typically soluble in pure supercritical carbon dioxide (SCCO<sub>2</sub>). To overcome this fact, supercritical fluid spray coating processes have employed organic liquid–CO<sub>2</sub> mixtures as solvents.<sup>14</sup> This substitution can reduce volatile organic compound emissions by up to 89% while producing coatings of similar or superior quality.<sup>15</sup> The expansion of SCCO<sub>2</sub> upon exiting the nozzle, referred to as decompressive atomization, creates a narrow and controllable distribution of paint droplet sizes that are spatially uniform across the spray pattern.<sup>16</sup>

The objective of this research is to synthesize a polymer, which is soluble in pure SCCO<sub>2</sub>, for use in coating applications by a solvent-free method. It is economically viable and will have implications for pollution prevention during polymer film formation throughout many related industries, for example, in

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submicron lithography, protective coating on chip modules, and dielectric layers. To achieve this goal, a significant polymer that is soluble in the pure supercritical solvent is essential. Only fluoropolymers and silicon polymers have been demonstrated to be soluble in pure SCCO<sub>2</sub> at the concentrations required for practical spraying operations.<sup>17</sup> In this study we synthesized a fluoropolymer, poly-(1,1,2,2-tetrahydroperfluorodecyl acrylate) [poly(TA-N)], and investigated the feasibility by the RESS method of using CO<sub>2</sub> as a solvent for producing submicron particles.

The preferred choice for a fine throttling device for RESS was an orifice or a nozzle, but it is difficult to process a superfine capillary, the diameter of which is only about 30  $\mu\text{m}$ . In this study a porous sintered metal plate was tried for the RESS process. This plate is easy to process and the diameter of the capillary can be even smaller than 0.5  $\mu\text{m}$ .

## EXPERIMENTAL

### Materials

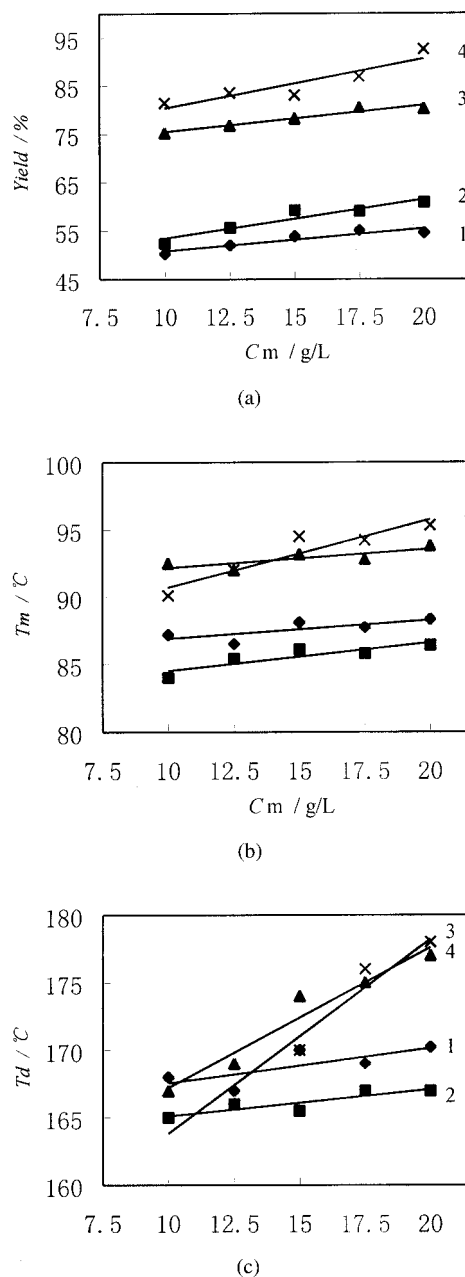
The TA-N monomer was kindly provided by DuPont. Benzene (certified grade, Fisher) was dried by a routine method. AIBN (99+%, Aldrich) was recrystallized twice from ethanol (absolute, Aldrich). Tetrahydrofuran (THF, certified grade, Fisher) and methanol (certified grade, Fisher) were used as the respective solvent and precipitant of poly(TA-N).

### Characterization

A Shimadzu TA-50 WSI thermal analyzer with a Shimadzu DSC 50 and TGA 50 modules was used to determine the thermal properties of the poly(TA-N) samples. The poly(TA-N) particles were analyzed with an ISI DSC 130 scanning electron microscope. Samples were coated on wafers with a thickness of approximately 15 nm.

### Synthesis

The TA-N monomer was polymerized in dry benzene using AIBN as initiator at 60°C. Polymerization was carried out under a nitrogen atmosphere in a three-necked flask containing a micromagnetic stir bar. The monomer and initiator concentrations for polymerization were varied from 10 to 20 g/L of solvent and 0.25 to 0.50 g/100 g of monomer, respectively. At the end of the polymerization, the reaction products were diluted with benzene, precipitated into a large excess of methanol, and washed several times with methanol. The filtered polymer was dried under a vacuum and then purified by successive reprecipitation from THF solutions into methanol.



**Figure 1** The effects of the monomer concentration on the (a) yield, (b)  $T_m$ , and (c)  $T_d$ : curve 1: 15-h reaction time,  $C_i = 0.25$  g/100 g monomer; curve 2: 15-h reaction time,  $C_i = 0.50$  g/100 g monomer; curve 3: 30-h reaction time,  $C_i = 0.25$  g/100 g monomer; curve 4: 30-h reaction time,  $C_i = 0.50$  g/100 g monomer.

## RESULTS AND DISCUSSION

### Effects of monomer concentration

Figure 1 shows the effects of the monomer concentration ( $C_m$ ) on the yield, temperature of melting ( $T_m$ ), and temperature of loss of 5% weight ( $T_d$ ) when the reaction time was 15 or 30 h, the initiator concentration ( $C_i$ ) remains 0.25 or 0.50 g/100 g of monomer, and the reaction temperature is 60°C. An increase of the  $C_m$

increases the yield. When the reaction was conducted for 15 h, the yield is 50–60%. After 30 h the reaction is almost completed. The DSC and TGA of the sample show that with the  $C_i$  remaining constant, the higher the  $C_m$  is the better the thermal character (in the range of experiments). When the reaction time is 15 h, the thermal character of sample 1 ( $C_i = 0.25$ ) is better than that of sample 2 ( $C_i = 0.50$ ), but the yield of sample 1 is lower than that of sample 2. When the reaction time is 30 h, the two curves ( $T_m$ - $C_m$ ) with different  $C_i$  cross over when their  $C_m$  is 15 g/L. This shows that the  $C_i$  should remain lower than 0.25 when the  $C_m$  is lower than 15 g/L. When the  $C_m$  is higher than 15 g/L, the  $C_i$  should be increased slightly. The trend of the  $T_d$ - $C_m$  curves is the same as that of the  $T_m$ - $C_m$  curves. Only the point of the cross is higher. With the intent to increase the thermal character and yield, the reaction time should remain 30 h.

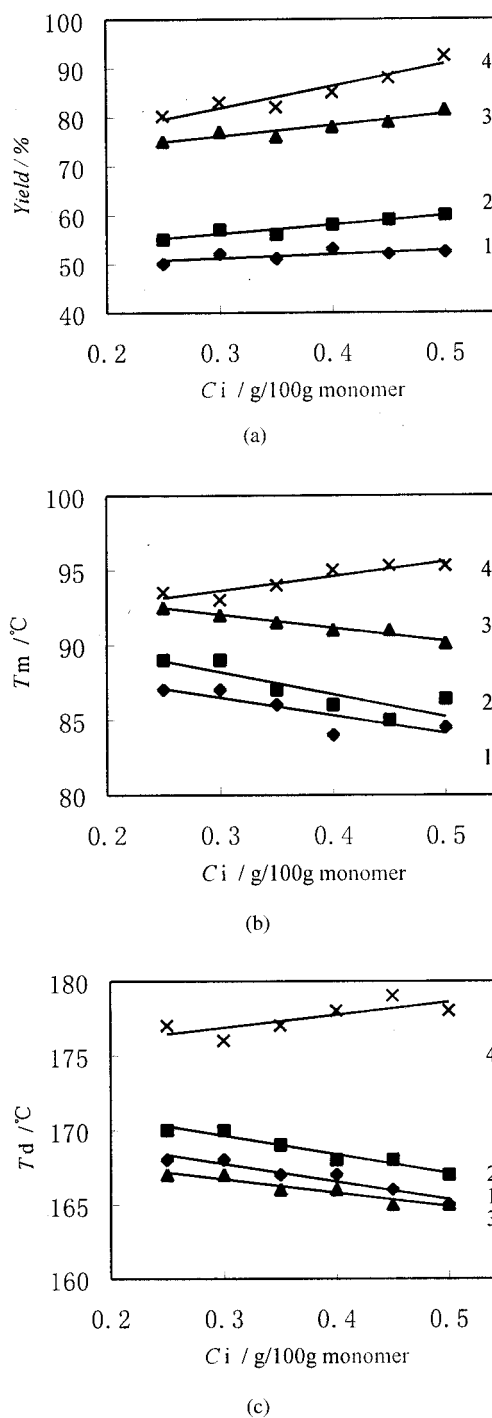
#### Effects of initiator concentration

In order to optimize the conditions for polymerization, the  $C_i$  values were varied from 0.25 to 0.50 g/100 g monomer. The yield and thermal characteristics were evaluated. Figure 2 shows the effects of the  $C_i$  on the yield and thermal characteristics when the  $C_m$  remains 10 or 20 g/L. The reaction temperature was 60°C, and the reaction time was 15 or 30 h. On the one hand, it was observed that an increase in the  $C_i$  increases the yield; on the other hand, the  $T_m$  and  $T_d$  of the samples decreases, except sample 4 when the reaction time is 30 h and the  $C_m$  is 20 g/L. This may be because the increase in the initiator facilitates the formation of more active centers, and the relative increment in active centers decreased the molecular weight and lowered the thermal property of the polymer. It is also observed from Figure 2 that the yield,  $T_m$ , and  $T_d$  when the  $C_m$  was 20 g/L were higher than those when the  $C_m$  was 10 g/L. However, the  $T_d$  of sample 3 (30-h reaction time) is lower than the  $T_d$  of sample 1 (15-h reaction time). It may be that the  $C_i$  is too high. Further, the longer reaction time led to the decrease of its  $T_d$ .

On the basis of the studies of the effects of  $C_m$ ,  $C_i$ , and reaction time on the polymerization reaction, when the  $C_i$  is 0.50 g/100 g monomer, the  $C_m$  is 20 g/L, the reaction time is 30 h, and the reaction temperature is 60°C. The reaction produced a higher yield, a higher  $T_m$ , and a higher  $T_d$  in the range of tests, so the polymerization technology was chosen for using in RESS.

#### Rapid expansion from SCCO<sub>2</sub>

The RESS design is summarized in Figure 3. High purity CO<sub>2</sub> (>99.95) was continuously pumped using a high pressure syringe pump (ISCO Inc.). The flow from the pump was split into one stream that passes



**Figure 2** The effects of the initiator concentration on the (a) yield, (b)  $T_m$ , and (c)  $T_d$ : curve 1: 15-h reaction time,  $C_m = 10$  g/L; curve 2: 15-h reaction time,  $C_m = 20$  g/L; curve 3: 30-h reaction time,  $C_m = 10$  g/L; curve 4: 30-h reaction time,  $C_m = 20$  g/L.

through a preheating coil and a polymer saturator column and a second steam that can be used to dilute the concentrated stream leaving the saturator. A porous, sintered stainless-steel frit nozzle was used as an expansion device.

Because poly(TA-N) is semicrystalline, 10 min is required for initial dissolution. The solution condition

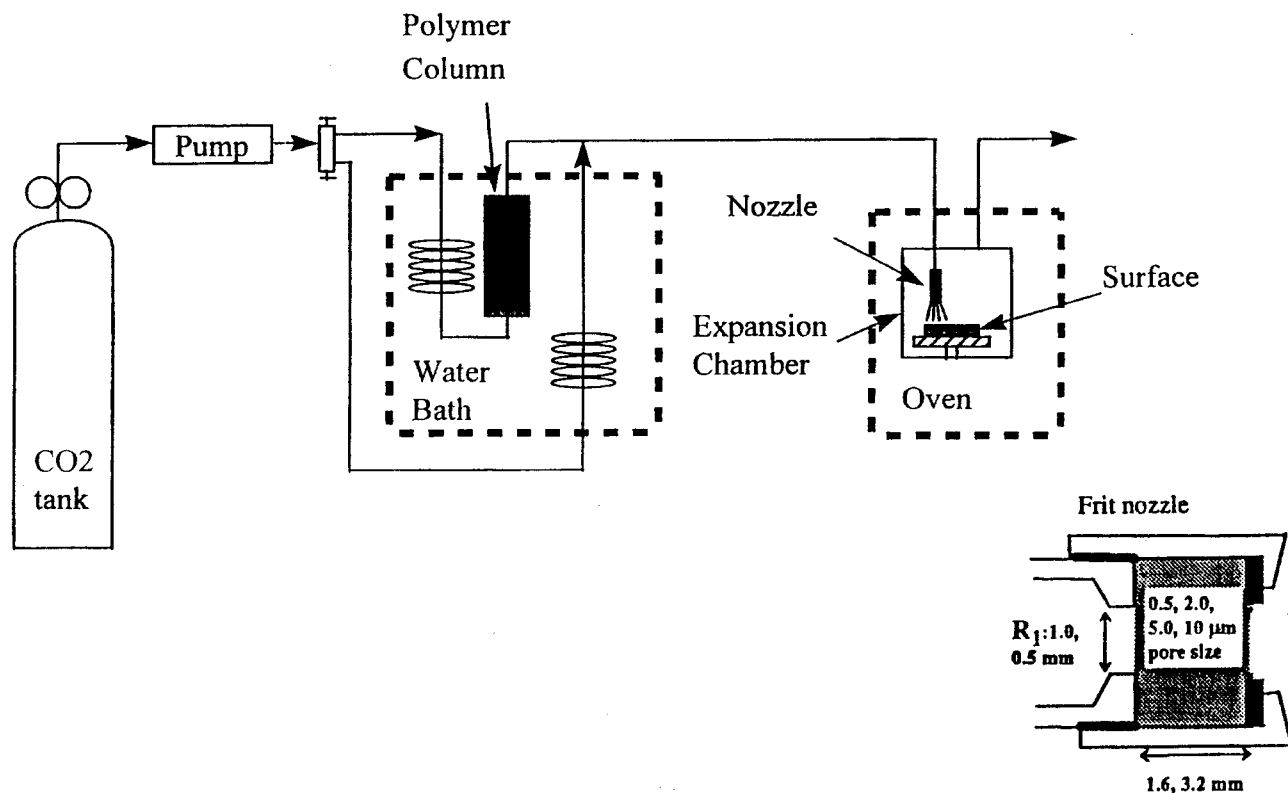


Figure 3 A schematic of the apparatus for the polymer coating experiments.

was maintained at 24°C and 20 MPa. The preexpansion temperature was varied from 45 to 105°C. The corresponding CO<sub>2</sub> flow rate upon expansion was from 2.5 to 5.0 ± 0.3 L/min (STP) and the pressure drop is 2 MPa. For different preexpansion temperatures and CO<sub>2</sub> flow rates, poly(TA-N) RESS sprays and the resulting morphology are presented in Table I. At 45°C an amorphous morphology was formed. At 60–80°C fibers are formed that range in size from 0.5 to 2.0 μm (see Fig. 4). Samples 1–4 reveal a profound change in morphology from fibers to spheres and dendrites. As shown in samples 2–4, at the higher CO<sub>2</sub> flow rate, the spheres and dendrites became smaller.

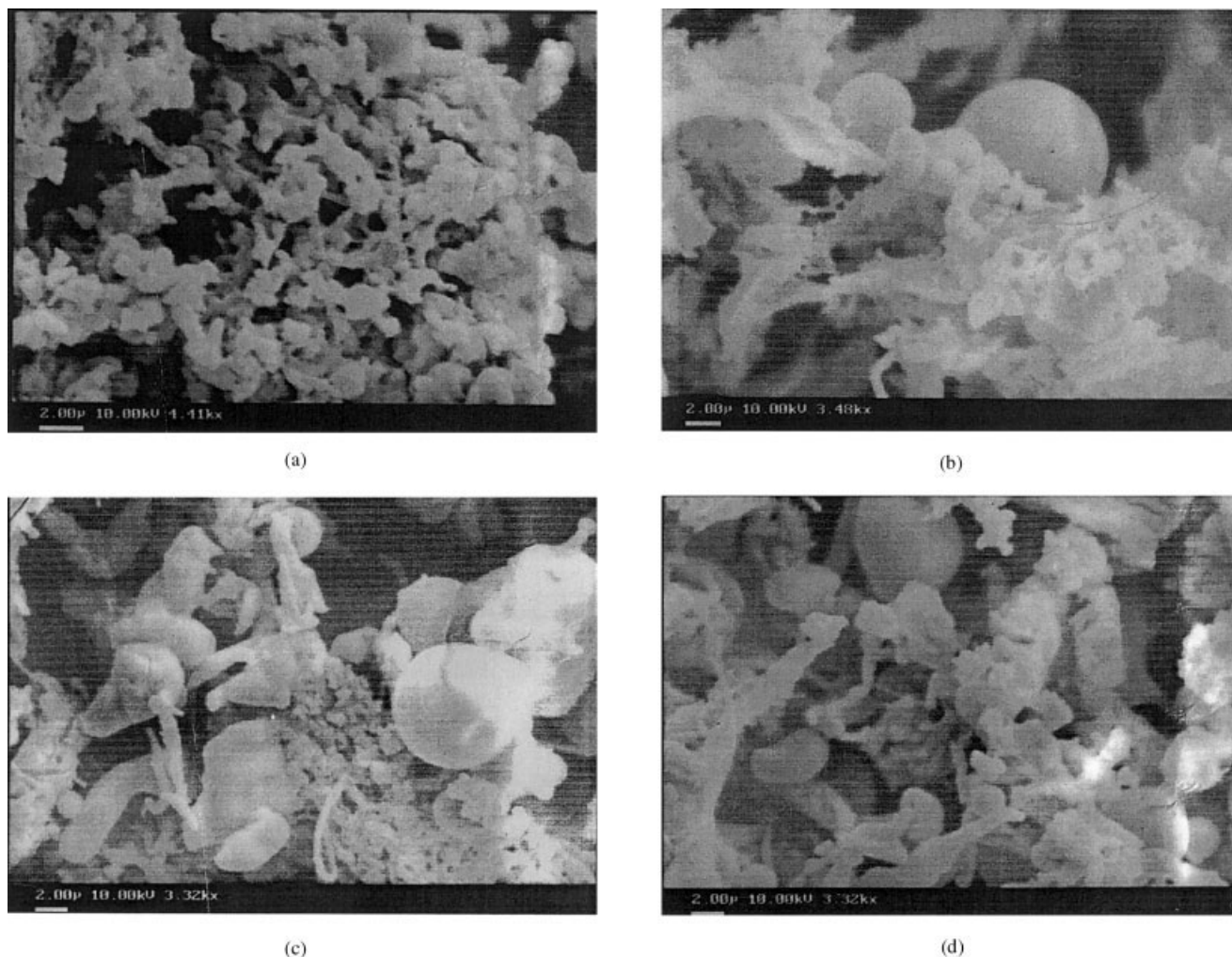
RESS has been simulated by classical nucleation theory and a surface energy model that has been developed by Liang and Rasmussen.<sup>18</sup> Lele and Shine<sup>19</sup>

offered a theoretical and conceptual framework for predicting whether fiber or particles are produced by RESS. Precipitation early in the capillary leads to fibers, because there is a long time (10 s) for growth of the polymer-rich donations, which are then sheared into fibers. The “long time” precipitation mode is likely when the solution entering the capillary is near the phase boundary or in a two-phase region. In contrast, fine particles are produced if the solution precipitates near the end of the capillary or in the free jet. This mode is likely when a homogeneous solution starts far from the phase boundary, because the time for growth is greatly diminished (10<sup>-6</sup> s). Thus, the characteristic time for particle growth and fiber formation depends upon the preexpansion temperature and flow rate of CO<sub>2</sub> in certain pressure drops.

TABLE I  
Poly(TA-N) RESS Sprays and Resulting Morphology

Sample	$T_{pre}$ (°C)	$D_{capillary}$ (μm)	Flow <sub>CO<sub>2</sub></sub> (L/min STP)	Morphology
	45	2	2.5 ± 0.3	Amorphous
	45	0.5	2.5 ± 0.3	Amorphous
1	60–80	0.5	2.5 ± 0.3	0.5–2.0 μm fibers
2	105	0.5	2.5 ± 0.3	2.0–6.0 μm spheres/dendrites
3	105	0.5	4.0 ± 0.3	1.5–5.0 μm spheres/dendrites
4	105	0.5	5.0 ± 0.3	1.0–4.0 μm spheres/dendrites

$P_{pre}$ , 20 MPa;  $\Delta P$ , 2 MPa;  $T_{dissolution}$ , 24°C.



**Figure 4** SEM micrographs of poly(TA-N) microparticles collected from the RESS: (a) sample 1: 60–80°C, CO<sub>2</sub> flow = 2.5 L/min STP; (b) sample 2: 105°C, CO<sub>2</sub> flow = 2.5 L/min STP; (c) sample 3: 105°C, CO<sub>2</sub> flow = 4.0 L/min STP; (d) sample 4: 105°C, CO<sub>2</sub> flow = 5.0 L/min STP.

### CONCLUSIONS

After 30 h the synthesis of poly(TA-N) can be completed in dry benzene using AIBN as an initiator at 60°C. When the reaction was conducted for 15 h, the yield was 50–60%. The DSC and TGA show that the higher the  $C_m$  is, the better the thermal character of the samples when the  $C_i$  remains constant (in the range of experiments). The  $C_i$  should remain lower than 0.25 g/100 g monomer when the  $C_m$  is lower than 15 g/L. When the  $C_m$  is higher than 15 g/L, the  $C_i$  should be increased slightly. An increase in the  $C_i$  increases the yield when the  $C_m$  remains constant in our range of experiments. However, the  $T_m$  and  $T_d$  decrease, except sample 4 when the reaction time is 30 h and the  $C_m$  is 20 g/L. When the  $C_i$  is 0.50 g/100 g monomer, the  $C_m$  is 20 g/L, the reaction time is 30 h, and the reaction temperature is 60°C, the reaction produced a higher yield, a higher  $T_m$ , and a higher  $T_d$  in the range of tests.

For the different preexpansion temperatures and CO<sub>2</sub> flow rates, the poly(TA-N) RESS morphologies

are different. At 45°C an amorphous product was formed. At 60–80°C fibers were formed, which ranged in size from 0.5 to 2.0 μm. A profound change in morphology from fibers to spheres and dendrites took place when the temperature increased. For the different CO<sub>2</sub> flow rates, the higher the CO<sub>2</sub> flow rate was, the smaller the spheres and dendrites were.

The RESS is an attractive process for the production of small, solvent-free powders of low vapor pressure solutes. These polymers will be able to be applied in coating applications in an organic solvent-free process that is economically viable, and they will have implications for pollution prevention during polymer film formation throughout many related industries.

### References

1. Lele, A. K.; Shine, A. D. *Ind Eng Chem Res* 1991, 33, 403.
2. Tom, J. W.; Debenedetti, P. G. *J Aerosol Sci* 1991, 22, 555.
3. Matson, D. W.; Fulton, J. L.; Petersen, R. C.; Smith, R. D. *Ind Eng Chem Res* 1987, 26, 2298.

4. Chang, C. J.; Randolph, A. D. *AIChE J* 1989, 35, 1876.
5. Ohgaki, K.; Kobayashi, H.; Katayama, T. *J Supercrit Fluids* 1990, 3, 103.
6. Lele, A. K.; Shine, A. D. *AIChE J* 1992, 38, 742.
7. Tom, J. W.; Debenedetti, P. G.; Jerome, R. *J Supercrit Fluids* 1994, 7, 9.
8. Goel, S. K.; Beckman, E. J. *Polym Eng Sci* 1994, 334, 1137.
9. Goel, S. K.; Beckman, E. J. *Polym Eng Sci* 1994, 334, 1148.
10. DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* 1992, 257, 9445.
11. Johnston, K. P. *Nature* 1994, 368, 187.
12. McFann, G. J.; Johnston, K. P.; Howdle, S. M. *AIChE J* 1994, 40, 543.
13. Hoefling, T. A.; Erick, R. M.; Backman, E. J. *J Phys Chem* 1991, 95, 7127.
14. Argyropoulos, J. N.; Nielsen, K. A.; Busby, D. C.; Lear, J. J. *Waterborne High Solids and Powder Coatings Symposium*, February 1994, p. 9.
15. Woods, R. J.; Busby, D. C. *Mater Perform* 1995, 34, 45.
16. Senser, D. W.; Colwell, J. C.; Smith, R. M. *Waterborne High Solids and Powder Coatings Symposium*, February 1995, p. 22.
17. Guan, Z.; DeSimone, J. M. *Macromolecules* 1994, 26, 5527.
18. Liang, M.; Rasmussen, D. H. *AIChE J*, to appear.
19. Lele, A. K.; Shine, A. D. *Ind Eng Chem Res* 1994, 33, 1476.