Colloid Polym Sci (2008) 286:975–981
DOI 10.1007/s00396-008-1857-3

ORIGINAL CONTRIBUTION

Synthesis of spherical particles by self-assembly of poly[2-(perfluorooctyl)ethyl acrylate-*co*-acrylic acid] in supercritical carbon dioxide

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Received: 9 January 2008 / Revised: 6 February 2008 / Accepted: 19 February 2008 / Published online: 10 April 2008

Abstract Spherical particles were prepared from poly[2-(perfluorooctyl)ethyl acrylateco-acrylic acid] random copolymers (P(POA-co-AA)) by self-assembly in supercritical carbon dioxide (scCO2). The P(POA-co-AA) copolymers with 9:1, 8:2, 7:3, and 6:4 molar ratios of the POA/AA unit completely dissolved in scCO2, however, the solubility was dependent on the POA/AA ratio. The copolymer with the higher AA content had a lower solubility. The scanning electron microscopy (SEM) observations revealed that the spherical particles were obtained in a heterogeneous state at pressures lower than the cloud point pressure. Dynamic light scattering and 1H NMR studies demonstrated that the copolymers formed random copolymer micelles consisting of the shells of the CO2-philic POA units and the cores of the CO2-phobic AA units and main chains. It was found that the formation of spherical particles could be optimized by the manipulation of the CO2 pressure and temperature for the different compositions of the copolymers.

Keywords Poly[2-(perfluorooctyl)ethyl acrylate-*co*-acrylic acid] · Self-assembly · Supercritical carbon dioxide · Cloud point pressure · Spherical particles · CO_2 density

Introduction

The importance of molecular self-assembly has been increasing in industry because it can control the molecular behavior on a nanoscale level. The self-assembly of molecules has produced many artificial architectures such as double [1] and triple helices [2], polyrotaxanes [3, 4], catenanes [5], a molecular shuttle [6], supramolecular cylinders [7], and spherical supermolecular dendrimers [7]. The self-assembly is also important in providing reversible and environmentally benign reactions without any direct chemical reactions. The self-assembly in supercritical carbon dioxide ($scCO_2$) has both the benefits combining its energy-saving reaction and its environmental benefits of being nontoxic, odorless, spontaneous, and volatile. The benefits also include the industrial utilities of being recyclable and having mild critical conditions (31.1 °C, 73.8 bar) [8]. While the self-assembly in $scCO_2$ has many industrial applications such as extraction of natural products [9, 10], dyeing fibers [11], and dry cleaning [12], it also has advantages in preparing microspheres. This is because the heterogeneous polymerizations in $scCO_2$ like emulsion polymerization [13] and dispersion polymerization [14] require a long time to produce microspheres and have the problem of unreacted monomers remaining in the microspheres. We already reported the synthesis of microspheres in $scCO_2$ by the indirect self-assembly of random copolymers containing amino groups via dicarboxylic acid [15, 16]. We found a novel and convenient method of preparing spherical particles by direct self-assembly of poly[2-(perfluorooctyl)ethyl acrylate-*co*-acrylic acid] random copolymers (P(POA-*co*-AA)) in $scCO_2$. Whereas some copolymers of alkyl acrylates with the fluorinated monomers were reported [17], there are a few publications on copolymers of acrylic acid with fluorinated vinyl compounds. These are random copolymers obtained by γ-ray irradiated radical copolymerization of acrylic acid with perfluoroalkyl acrylate [18] and graft copolymers of acrylic acid with poly(ethylene-tetrafluoroethylene) [19]. The direct

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self-assembly of the P(POA-*co*-AA) copolymer should promise a convenient and safe method to provide spherical particles containing no monomers unreacted. This paper describes the synthesis of spherical particles by the direct self-assembly of P(POA-*co*-AA) in $scCO_2$ and the control of the self-assembly by the pressure and temperature.

Experimental

Instrumentation

The ^{1}H NMR measurement was conducted using a Varian 300 FT NMR spectrometer. The size exclusion chromatography (SEC) was performed using a Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and a RI-8020 refractometer. Two polystyrene gel columns, Tosoh TSKgel GMH_{HR}-M, were used with hexafluoroisopropanol as the eluent at 40 °C. The scanning electron microscopy (SEM) measurements were made using a JEOL JSM-6300 electron microscope. The cloud point measurement was performed with a Nekken variable volume view cell (with a window made of tempered glass) equipped with an Eyela CCA-1110 cooler and a Nihon Seimitsu Kagaku NP-D-321 personal pump.

Materials

2-(Perfluorooctyl)ethyl acrylate (POA) was purchased from Daikin Chemical and was deinhibited by passage through an alumina column. *tert*-Butyl acrylate (TBA) was purified by distillation under reduced pressure over calcium hydride. Hexafluorobenzene to be used as a solvent for ^{1}H NMR measurements was also distilled over calcium hydride. Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Synthesis of P(POA-*co*-AA): General procedure

POA (4.60 g, 8.88 mmol), TBA (481 mg, 3.75 mmol), and AIBN (21 mg, 0.128 mmol) were placed in an ampoule. After the contents were degassed, the ampoule was sealed in vacuo. The polymerization was carried out at 50 °C for 2 h and was terminated by cooling with liquid nitrogen. The reaction mixture was dissolved in 40 ml of hexafluorobenzene and was poured into 1 l of methanol to precipitate a polymer. The polymer was collected and was dried in vacuo for several hours to obtain poly(POA-*co*-TBA) (4.44 g).

The P(POA-*co*-TBA) (2.00 g) was dissolved in hexafluoroisopropanol (60 ml). Concentrated hydrochloric acid (2 ml) was added to the copolymer solution at room temperature, and the solution was refluxed for 3 h. After the solution was cooled to room temperature, it was concentrated to one third of its original volume with an evaporator. The residual solution was poured into hexane (1 l) to precipitate a polymer. The polymer was purified by reprecipitation from hexafluorobenzene (5 ml) into hexane (500 ml). The resulting polymer was dried in vacuo for 5 h to obtain P(POA-*co*-AA) (1.76 g).

Cloud point measurement

The cloud point measurement was performed with a variable volume view cell [15]. P(POA-*co*-AA) (30 mg) was placed in the cell, then CO_2 liquefied with a cooler was added to it. The cloud point was defined as the point at which the contents of the cell turned opaque, indicating precipitation of the polymer from solution.

Preparation of spherical particles

P(POA-*co*-AA) (POA/AA = 7:3, 30 mg) was placed in the variable volume view cell, then liquid CO_2 was added to it. The solution was stirred at 3,620 psi and 45.0 °C for 10 min. The pressure of the homogeneous solution was reduced until the cloud point (3,059 psi) was reached by volume expansion. The pressure was further reduced to 2,759 psi, and the heterogeneous solution was sprayed into a plastic bag made of polyethylene to collect the polymer particles (29 mg).

SEM measurement of P(POA-*co*-AA) particles

The polymer particles were placed on a carbon adhesive tape and were subjected to SEM measurement after coated with Pt.

Light scattering measurement of P(POA-*co*-AA)

P(POA-*co*-AA) (24 mg) was dissolved in 3 ml of hexafluorobenzene. The solution was subjected to light scattering at θ=90 ° and 25 °C. The distribution of the hydrodynamic diameter of the copolymer was obtained by the Marquadt analysis [20].

Results and discussion

The P(POA-*co*-AA) random copolymers were obtained by the hydrolysis of P(POA-*co*-TBA) prepared by the radical polymerization (Fig. 1). The radical copolymerization of POA and TBA was performed in bulk at 50 °C by AIBN until the reaction mixtures solidified. The hydrolysis of P(POA-*co*-TBA) was carried out in hexafluoroisopropanol using concentrated hydrochloric acid under reflux for 3 h.

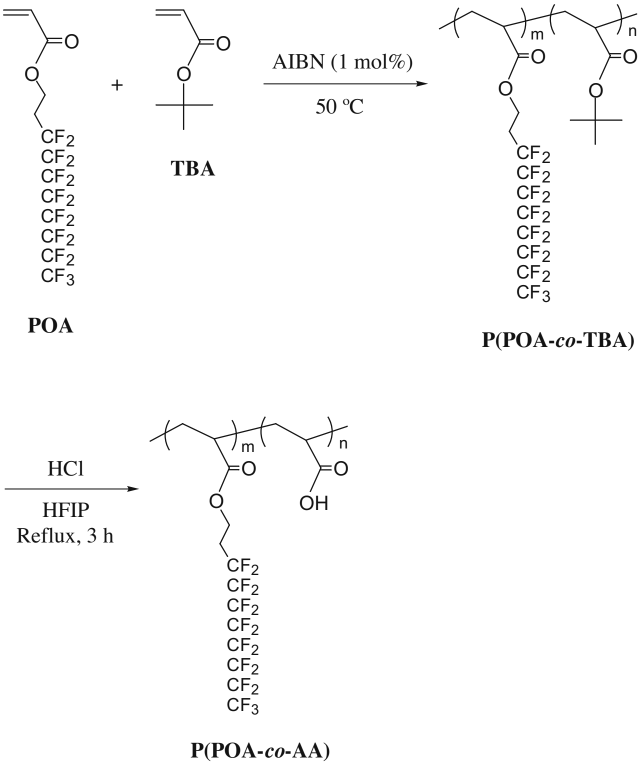
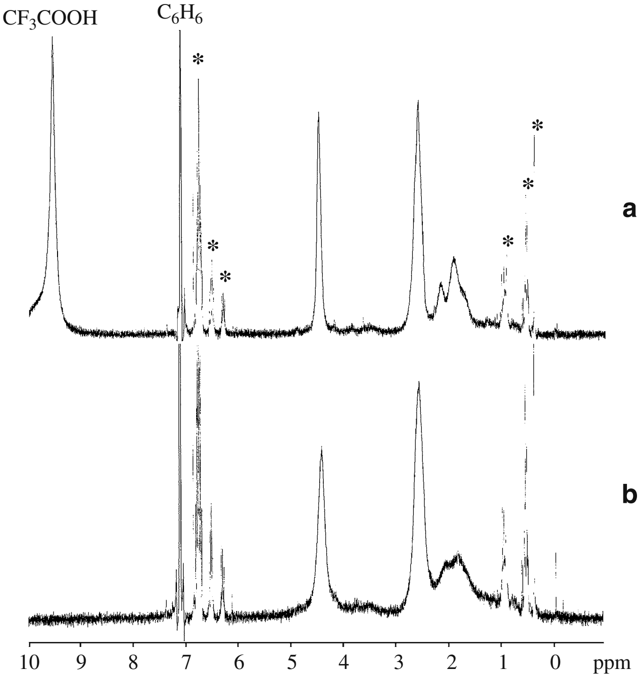


Fig. 1 Synthesis of the P(POA-*co*-AA) copolymers



* Impurities in C_6F_6

Fig. 2 ^{1}H NMR spectra of P(POA-*co*-AA) with a 7:3 POA/AA ratio in the presence (**a**) and absence (**b**) of CF_3COOH. Solvent: C_6F_6 including C_6D_6

Table 1 The P(POA-*co*-AA) random copolymers

Feed ratio POA	AA	Time (min)	Yield (%)	Mn[a]	Composition POA	AA
0.90	0.10	30	84	110,000	0.89	0.11
0.80	0.20	45	98	97,000	0.80	0.20
0.70	0.30	120	89	72,000	0.70	0.30
0.60	0.40	40	98	84,000	0.64	0.36

[a] Estimated by SEC based on poly(methyl methacrylate) standard

Figure 2 a shows the ^{1}H NMR spectrum of the P(POA-*co*-AA) copolymer. The ^{1}H NMR measurement was carried out in the presence of trifluoroacetic acid to avoid the aggregation of the copolymer. The proton signal at 4.36 ppm originated from the methylene attached to the oxygen in the POA unit. The signals at 2.55 ppm were attributed to methylene bonding to the perfluorooctyl chain. The signals at 2.15 and 1.88 ppm were based on the methyne and methylene in the main chain, respectively. The molar ratios of the POA unit to the AA were determined on the basis of the ratios of the signal intensity at 4.36 ppm to that at 1.2–2.9 ppm. The characterizations of the P(POA-*co*-AA) copolymers are listed in Table 1. The molecular weights of the copolymers were estimated by SEC based on poly(methyl methacrylate) standards. The molecular weight distributions could not be estimated due to the very broad distribution. The copolymers obtained should be random copolymers because the perfluoroalkyl acrylates copolymerize with a variety of monomers [21, 22] and the monomer reactivity is similar to alkyl acrylates such as ethyl acrylate [23], isobutyl acrylate [24], and methyl phenyl acrylate [25]. Actually, the radical copolymerization of POA with 2-(dimethylamino)ethyl acrylate produced random copolymers in our previous work [15].

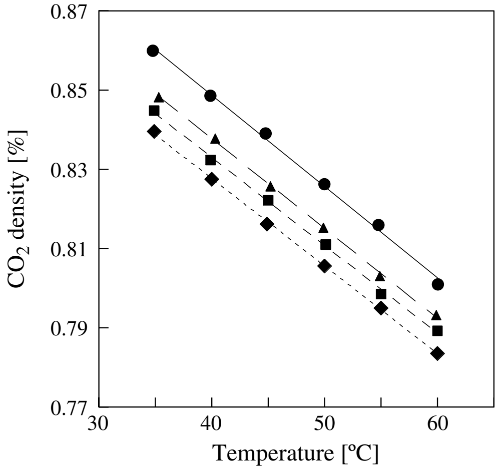


Fig. 3 Plots of the experimental cloud points of the copolymers with POA/AA of 6:4. (●), 7:3 (▲), 8:2 (■), and 9:1 (♦) at each temperature vs the CO_2 density

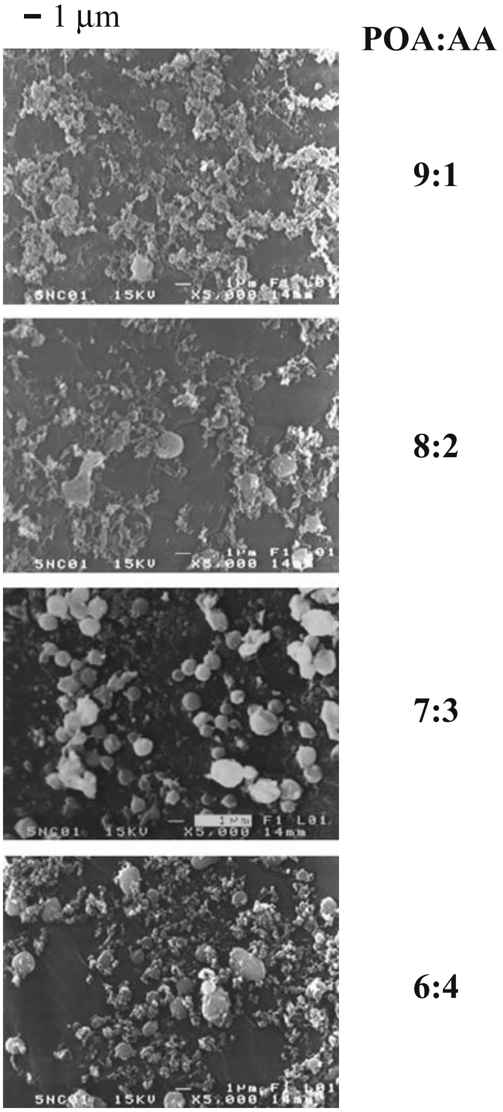


Fig. 4 SEM images of the polymer particles obtained from the copolymers in $scCO_2$ at 45 °C and the cloud point pressure −300 psi

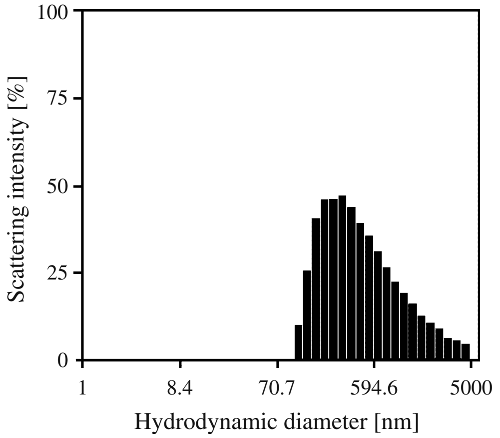


Fig. 5 Scattering intensity distribution of the hydrodynamic diameter of P(POA-*co*-AA) with a 7:3 POA:AA ratio in hexafluorobenzene at 25 °C and θ = 90°. [copolymer] = 8.00 g/l

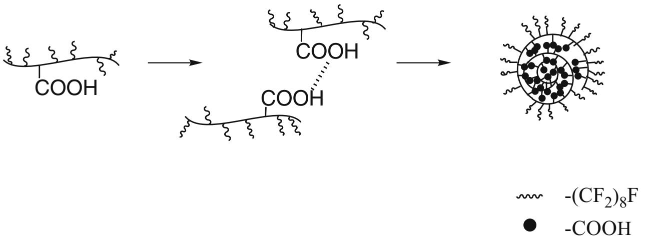


Fig. 6 A schematic of the formation of the spherical particles

The P(POA-*co*-AA) copolymers completely dissolved in $scCO_2$. It was found that the solubility of the copolymers was dependent on the POA/AA ratio. To explore the solubility behaviors in $scCO_2$, the cloud points of the copolymers were determined. Figure 3 shows the CO_2 density at the cloud points plotted versus temperature. The CO_2 density at the cloud points decreased as the temperature increased, indicating that the solubility of the copolymers increased with the increasing temperature. And further, the copolymer with a higher AA ratio had a lower solubility, suggesting that the hydrogen bonding based on the AA units prevented the copolymer from dissolving in $scCO_2$.

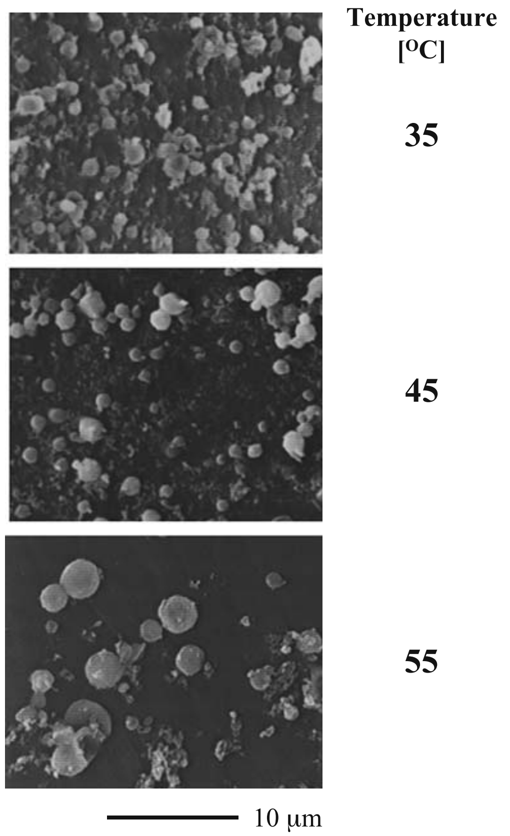


Fig. 7 SEM images of the polymer particles obtained at 35, 45, and 55 °C at the cloud point pressure −300 psi

SEM observations revealed that the P(POA-*co*-AA) copolymers self-assembled into spherical particles in $scCO_2$. Figure 4 shows the SEM images of the particles obtained from the copolymer solution at 45 °C in a heterogeneous state at a pressure lower than the cloud point pressure. The images included spherical particles independent of the POA/AA ratio. However, the proportion of the spherical particles was different among the various ratios. The copolymers with the 9:1 and 8:2 ratios contained some spherical particles of several micrometers in diameter and a lot of small particles with nonspecific forms. These copolymers had too low an AA content to aggregate into spherical forms. The copolymer with the 6:4 ratio also contained both the spherical particles and the small particles. However, the small particles also had a spherical shape with several hundreds of nanometer diameters. It is likely that the intramolecular aggregation is preferable for the 6:4 sample due to a large contribution of the hydrogen bonding based on the higher AA content. The copolymer with the 7:3 ratio produced the largest amount of spherical particles among the copolymers. Based on the SEM image of the 7:3 sample, the size of the spherical particles was estimated to be 0.82 μm on average, and the size distribution was 1.20 [26].

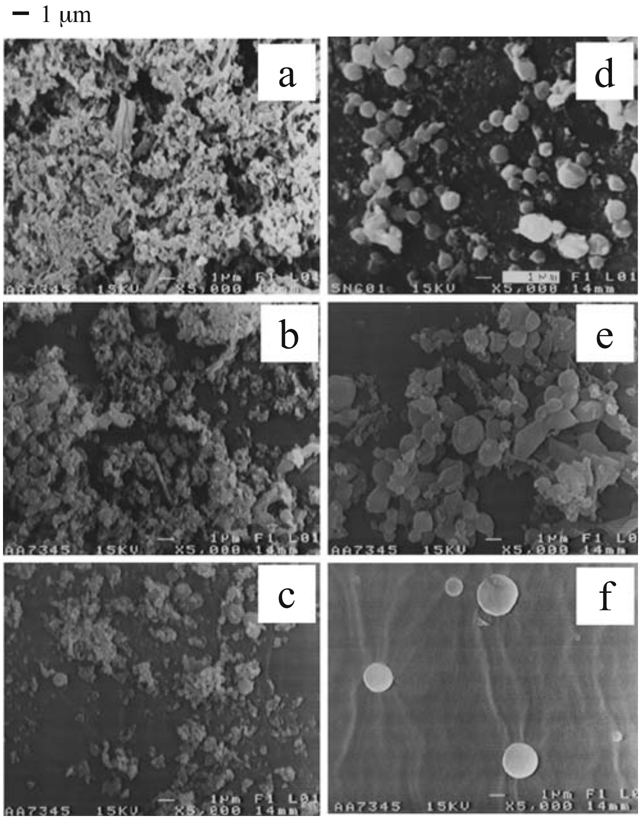


Fig. 8 SEM images of the polymer particles obtained at the cloud point pressure + 200 (**a**), ±0 (**b**), −100 (**c**), −300 (**d**), −900 (**e**), and −1500 psi (**f**)

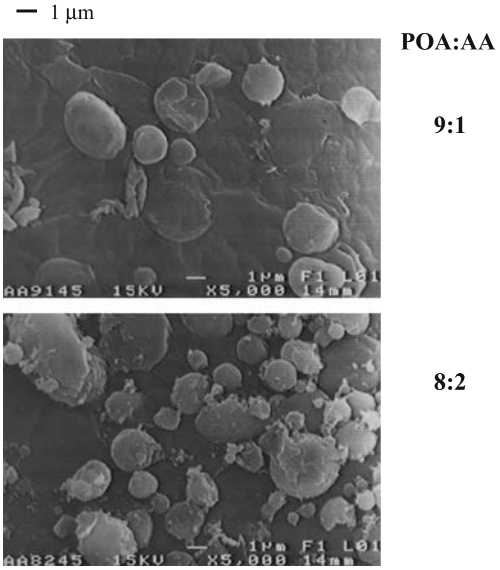


Fig. 9 SEM images of the polymer particles obtained from the copolymers with 9:1 and 8:2 POA/AA ratios at 45 °C and the cloud point pressure −1,500 psi

These SEM images are for the polymer particles obtained by spraying the heterogeneous solutions into the atmosphere based on the assumption that the shapes of the particles formed in $scCO_2$ are maintained in this atmosphere at ambient temperature by rapidly releasing the CO_2 pressure. To explore the shapes of the particles in solution, the light scattering measurements of the copolymer were

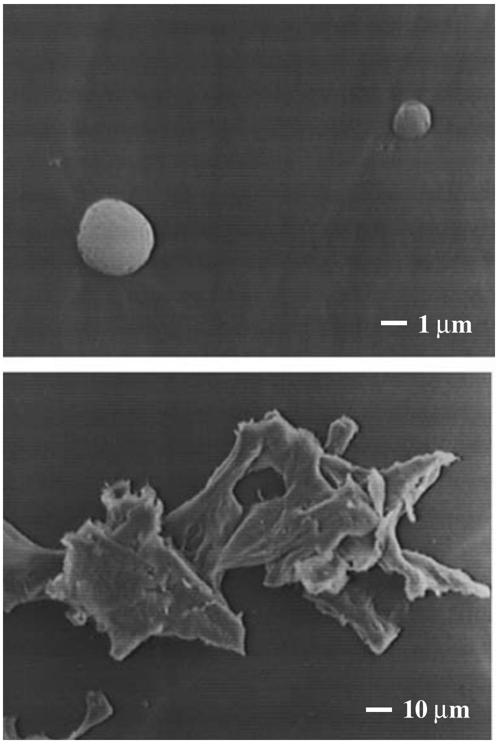


Fig. 10 SEM images of the polymer particles obtained from the copolymer with a 6:4 POA/AA ratio at 45 °C and the cloud point pressure −1,500 psi

performed in hexafluorobenzene. Hexafluorobenzene is similar to $scCO_2$ in having low polarity and the ability to dissolve fluoropolymers. Figure 5 shows the scattering intensity distribution of the hydrodynamic diameter of the particles formed by the copolymer with the 7:3 ratio in hexafluorobenzene. The intensity distribution was obtained by a Marquadt analysis of the dynamic light scattering results. The hydrodynamic diameter of the particles was estimated to be 0.60 μm based on the Marquadt analysis. Compared with the particle size based on the SEM image, the copolymer formed smaller particles in hexafluorobenzene. This can be accounted for by the fact that the AA units more tightly formed the particle cores in hexafluorobenzene than in $scCO_2$ because of the lower affinity of hexafluorobenzene to the AA units and also that the particles swelled when rapidly sprayed into the atmosphere.

The ^1H NMR analysis confirmed that the particles consisted of the POA unit shells and the AA unit cores. The signals based on the methyne and methylene in the main chain were broadened in the absence of trifluoroacetic acid, as compared to those in its presence (Fig. 2b). This broadening of the signals indicates that the insoluble AA units and main chains were shielded from the magnetic field. Consequently, it is expected that the copolymers formed random copolymer micelles consisting of the shells of the CO_2-philic perfluorooctyl groups and the cores of the CO_2-phobic AA units and main chains when the copolymers were placed in $scCO_2$ as well as in hexafluorobenzene (Fig. 6).

The shapes of the polymer particles were dependent on temperature based on the formation by hydrogen bonding. Figure 7 shows the SEM images of the polymer particles obtained at three different temperatures in the heterogeneous state. The particles were not completely spherical at 35 °C. The copolymer could not completely take a spherical shape because of the low mobility of the copolymer at this low temperature. On the other hand, the copolymer produced large spherical particles of several micrometers at 55 °C, along with small particles with hundreds of nanometer diameters. It was considered that an increase in the mobility of the copolymer at the high temperature promoted both the intermolecular aggregation and the intramolecular association.

The self-assembly of the copolymers into spherical particles was controlled by the CO_2 pressure. Figure 8 shows the SEM images of the polymer particles produced under the different pressures. The particles produced at a pressure higher than the cloud point pressure had nonspecific forms. Spherical particles were hardly observed in the image. The particles prepared at the cloud point pressure included a small amount of spherical parts; however, most of the particles were still nonspecific. When the pressure was reduced to 100 psi lower than the cloud point pressure, the copolymer somewhat aggregated into spherical particles. At a pressure 300 psi lower than the cloud point, most of the particles had spherical shapes. However, it was observed that the spherical particles partly combined at the cloud point pressure minus 900 psi. Completely spherical and larger-sized particles were produced at the cloud point minus 1,500 psi. It was found that more stable spherical particles were produced at the lower pressure and that the self-assembly of the copolymer was controlled through varying the solvent quality manipulated by the CO_2 pressure.

The copolymers with the 9:1 and 8:2 ratios were found to produce nearly spherical particles at the pressure 1,500 psi lower than the cloud point pressure, although a few spherical particles were obtained at the cloud point pressure minus 300 psi (Fig. 9). The hydrogen bonding interaction among the AA units increased with the decreasing pressure, thus the self-assembly of the copolymers into spherical particles was promoted. At the pressure 1,500 psi lower than the cloud point, the copolymer with the 6:4 ratio formed not only spherical particles but also a small amount of nonspecific aggregates of dozens or hundreds of micrometers (Fig. 10). Too strong hydrogen bonding at a very low pressure should have caused a partial second aggregation of the spherical particles into large nonspecific particles. It was deduced that the formation of spherical particles could be optimized by the manipulation of the CO_2 pressure for the different compositions of the copolymers.

Conclusion

The synthesis of spherical particles was attained by the self-assembly of P(POA-*co*-AA) random copolymers in $scCO_2$. The copolymers formed spherical particles in a heterogeneous state at pressures lower than the cloud point pressure. The formation of spherical particles was also dependent on the temperature. The dynamic light scattering and ^1H NMR studies demonstrated that the copolymers formed random copolymer micelles consisting of the shells of the CO_2-philic POA units and the cores of the CO_2-phobic AA units and main chains. This is the first attempt at demonstrating that the formation of spherical particles could be optimized through varying the solvent quality by the manipulation of the CO_2 pressure and temperature for the different copolymer compositions.

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