Effect of cosolvents on the precipitation polymerization of acrylic acid in supercritical carbon dioxide

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Abstract

The precipitation polymerization of acrylic acid (AA) in supercritical (SC) carbon dioxide with acetic acid and ethanol as the cosolvent were studied at 335 K in the range 12–17 MPa; $2,2'$-azobis(isobutyronitrile) AIBN was used as the initiator. Analysis by viscosity measurement and differential scanning calorimetry (DSC) indicates that the cosolvents have a pronounced effect on the product molecular weight and glass transition temperature (T_g). Scanning electron microscopy (SEM) shows that the products are microparticles, and their sizes are affected by the structure and concentration of the cosolvents. A UV/Vis spectroscopic method was used to study the initiation rate of AIBN. The molecular weights of the products are closely related to the decomposition rate. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon dioxide provides an environmentally benign alternative to the organic solvents traditionally employed in the polymer industry because it is inexpensive, non-toxic, and non-flammable, and it has easily accessible critical temperature and critical pressure [1]. In addition, supercritical (SC) CO_2 behaves very much like a hydrocarbon solvent with respect to its capability to dissolve small molecules, and thus many monomers exhibit high solubility in SC CO_2 [2]. DeSimone and others have shown that SC CO_2 is a versatile solvent for both homogeneous [3–6] and heterogeneous [7–13] polymerizations. Among these polymerizations, DeSimone et al. have reported the successful precipitation polymerization of acrylic acid in supercritical carbon dioxide [11].

Supercritical fluids (SCFs) are highly compressible, and the density (and therefore solvent properties such as viscosity and dielectric constant) can be tuned by varying the pressure or temperature of the system. The solubility of solutes can be altered by adding cosolvents to the system [14–24]. Cosolvents can adjust the equilibrium constants of different reactions [17,22], improve the selectivity of reaction [23] and increase the rate of reaction [16]. In this work, we investigated the effect of acetic acid and ethanol as the

cosolvents, respectively, on the polymerization of acrylic acid in SC CO_2.

2. Experimental section

Materials. The purity of CO_2 was 99.995% and was obtained from Beijing Analytical Instrument Factory. $2,2'$-Azobis(isobutyronitrile) (AIBN) was supplied by Beijing Chemical Factory and was recrystallized twice from methanol. Acrylic acid (97%) was obtained from the Beijing Chemical Agent Factory and was purified by vacuum distillation. Acetic acid and ethanol were A.R. grade, produced by Beijing Chemical Factory.

Apparatus. High-pressure reactions were carried out in a 10-ml stainless steel reactor equipped with two quartz windows, for observation of the phase behavior. Liquid CO_2 was delivered to the reactor with an SFC 8000 pump. The pressure in the reactor was measured using a pressure gauge consisting of a transducer (IC Sensors Co.Model 93) and an indicator, which can be accurate to ±0.05 MPa, in the pressure range of 0–20 MPa. The temperature of the reactor was measured with a platinum resistance thermometer (model XMT, produced by Beijing Chaoyang Automatic Instrument Factory). A magnetic stirrer was used for mixing.

Polymerization. In a typical reaction, the reactor was purged with CO_2 for about 15 min, and then charged with AIBN (0.020 g) and the desired amount of cosolvent. Liquid

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carbon dioxide was then added until a homogeneous solution occupied approximately half the cell volume. Temperature was gradually increased to the desired reaction temperature of 335 K. Deoxygenated acrylic acid was charged into the reactor and more CO_2 was added until the desired pressure was reached. Reactions were allowed to proceed for 4 h with stirring. At the end of the reaction, the reactor was cooled and the CO_2 was slowly vented from the cell. The product was collected as fluffy, white, free flowing powder. The product was dried to remove traces of the cosolvent, and the yield was determined gravimetrically.

Characterization. Viscosity measurements were used to get the average molecular weight. IR (PE 683) spectra confirmed that the products were polyacrylic acid. Scanning electron micrograph (SEM) (Hitachi, Model S-530) and differential scanning calorimetry (DSC) (PE 7 series) were used to observe the polymer morphologies and the glass transition temperature (T_g).

3. Results and discussion

The precipitation polymerizations were conducted at 335 K in the pressure range of 12–17 MPa. It is worthwhile to point out that the reaction system of CO_2, initiator, cosolvent, and monomer was a single phase at the experimental conditions, which could be seen clearly through the windows of the reactor, i.e. the polymerization began as a homogeneous phase. Experiments also showed that all the AIBN in the system can be dissolved in CO_2 and the CO_2-cosolvent mixtures at the experimental temperatures and pressures. The onset of polymerization was observed. The color changed from yellow to orange (it is due to the Tyndall effect, i.e. the growing particle was large enough to scatter the visible light [25]). Within minutes white particles of solid precipitate could be observed settling on the windows and wall of the cell. The cell was filled with precipitated polymer after the polymerization process. Upon venting the carbon dioxide, the polymer was collected, and the yields were more than 90%. The products were readily dissolved in water. Molecular weight and T_g of the products are listed in Tables 1–3.

Effect of monomer concentration on molecular weight. Precipitation polymerizations were carried out at 13.5 and

Table 1
Effect of monomer concentration on the precipitation polymerization of acrylic acid (AA) in pure supercritical CO_2. Reaction conditions: [AIBN] $= 1.2 \times 10^{-2}$ M; 4 h reaction time; $T = 335$ K

Sample	AA concentration (mol/L)	P (MPa)	$\langle M\eta \rangle \times 10^{-5}$ [a]	T_g (K)
1	0.75	13.5	3.596	400.0
2	0.75	17.0	3.986	400.0
3	1.5	13.5	6.085	402.1
4	1.5	17.0	6.100	402.3

[a] Average molecular weight was determined by viscosity measurement.

Table 2
Effect of pressure on the precipitation polymerization in SC CO_2. Reaction conditions: concentration of monomer $= 1.5$ mol/L; [AIBN] $= 1.2 \times 10^{-2}$ M; 4 h reaction time; $T = 335$ K. Cc, concentration of acetic acid

Sample	Solvent	Pressure (MPa)	$\langle M\eta \rangle \times 10^{-5}$ [a]	T_g (K)
1	Pure CO_2	11.5	6.110	402.5
2	Pure CO_2	13.5	6.085	402.1
3	Pure CO_2	17.0	6.100	402.3
4	Cc $= 0.14$ mol/L	11.5	3.875	402.7
5	Cc $= 0.14$ mol/L	13.5	2.596	402.1
6	Cc $= 0.14$ mol/L	17.0	2.314	398.9

[a] Average molecular weight was determined by viscosity measurement.

17.0 MPa, with monomer concentrations of 0.75 and 1.50 mol/L. Table 1 summarizes the glass transition temperature and average molecular weight of the products. The results in Table 1 indicate that average molecular weights increase with the concentration of monomer. This can be explained qualitatively on the basis of the following equations [26].

$$R_p = -d[M]/dt = K_p[M\cdot][M] \tag{1}$$

$$R_t = -d[M\cdot]/dt = 2K_t[M\cdot]^2 \tag{2}$$

$$V = R_p/R_t = K_p[M]/2K_t[M\cdot] = K_p[M]/2(fK_dK_t[I]^{1/2}) \tag{3}$$

where R_p, R_t, and V are propagation rate, termination rate, and chain length, respectively. $[M\cdot]$, $[M]$, and $[I]$ stand for, respectively, radical, monomer, and initiator concentrations. K_p and K_t are the propagation and termination rate constants, and f denotes initiator efficiency, K_d is the decomposition rate constant of the initiator. Eq. (3) shows that increasing the concentration of monomer $[M]$ is expected to increase the molecular weight for a radical polymerization. The glass transition temperatures of the products polymerized at the higher monomer concentration are higher than those polymerized at the lower monomer concentration. This is related to the average molecular weight.

Effect of pressure on the molecular weight. A primary

Table 3
Effect of cosolvents on the precipitation polymerization in SC CO_2 at 13.5 MPa. Reaction conditions: concentration of monomer $= 1.5$ mol/L; [AIBN] $= 1.2 \times 10^{-2}$ M; 4 h reaction time; $T = 335$ K. Cc, cosolvent concentration (mol/L)

Sample	Cosolvent	Cc	$\langle M\eta \rangle \times 10^{-5}$ [a]	T_g (K)
1	Acetic acid	0	6.085	402.1
2	Acetic acid	0.14	2.596	402.1
3	Acetic acid	0.27	4.415	402.5
4	Acetic acid	0.41	5.236	403.3
5	Ethanol	0	6.085	402.1
6	Ethanol	0.14	2.704	402.2
7	Ethanol	0.27	2.607	401.4
8	Ethanol	0.41	2.144	397.8

[a] Average molecular weight was determined by viscosity measurement.

Table 4
Decomposition rates of AIBN in CO_2–acetic acid–propionic acid (PA) and in CO_2–ethanol–PA mixtures at 335 K and 1.35 MPa. Cc, cosolvent concentration (mol/L)

Sample	Fluids	Cc	r (s^{-1})
1	CO_2	0	5.81×10^{-6}
2	CO_2–acetic acid–PA	0.14	7.92×10^{-6}
3	CO_2–acetic acid–PA	0.27	6.08×10^{-6}
4	CO_2–acetic acid–PA	0.41	5.55×10^{-6}
5	CO_2–ethanol–PA	0.14	1.18×10^{-6}
6	CO_2–ethanol–PA	0.27	1.97×10^{-6}
7	CO_2–ethanol –PA	0.41	3.02×10^{-6}

advantage of employing supercritical CO_2 lies in the ability to tune solvent density and the dielectric constant by changing pressure. Pressure effect was studied using two different solvents: pure SC CO_2 system (samples 1–3) and SC CO_2–acetic acid systems (samples 4–6) in which the concentration of acetic acid was 0.14 mol/L. The experimental results at 11.5, 13.5, and 17.0 MPa are listed in Table 2. Table 2 shows that the reaction pressure has no effect on the molecular weight and T_g of the products polymerized in pure SC CO_2, which agrees with that reported in the literature [11]. However, in the SC CO_2–acetic acid mixture system (samples 4–6), the average molecular

Fig. 1. Scanning electron micrographs of poly(acrylic acid) prepared by precipitation polymerization in pure SC CO_2 (335 K, 17.0 MPa) at different monomer concentrations (top, 0.75 mol/L; bottom, 1.5 mol/L).

weight and T_g decrease considerably with the reaction pressure. Therefore, the average molecular weight of the product can be altered by pressure in the systems containing a cosolvent. One of the reasons may be that the dielectric constant of a CO_2–polar cosolvent mixture is more sensitive to pressure [27].

Effect of cosolvent concentration on molecular weight. Table 3 shows the average molecular weights and T_g of the products polymerized in SC CO_2, with acetic acid and ethanol as the cosolvents at 13.5 MPa. The cosolvent concentrations are 0.14, 0.27, and 0.41 mol/L, respectively. The average molecular weight and the T_g decrease with the increase of cosolvent concentration when ethanol is used as cosolvent. However, the average molecular weight and T_g increases with the increase of the cosolvent concentration in the cosolvent concentration range 0.14–0.41 mol/L when acetic acid is used as cosolvent. The T_g of the products polymerized in the presence of the cosolvents is higher than that polymerized in pure CO_2 provided that the molecular weights were the same.

Eq. (3) indicates that the molecular weight of the product is inversely proportional to the radical concentration $[M \cdot]$. i.e. the higher the radical concentrations, the lower the molecular weights. $[M \cdot]$ increases with the decomposition rates of the initiator AIBN, and thus the molecular weight should decreases with an increase of the decomposition rate. Therefore, study of the decomposition rate of AIBN is helpful to understand the effect of the cosolvents on molecular weight. In this work, utilizing the UV/Vis spectroscopic method reported by Guan et al. [5], we determined the decomposition rates of AIBN under the same conditions of the polymerization system. The only difference was that propionic acid was used to replace the acrylic acid. This was done to avoid the polymerization of acrylic acid during the experiments. We believe that propionic acid and acrylic acid have a similar effect on the decomposition rate of AIBN. The experimental results are listed in Table 4.

As discussed above, the higher the decomposition rate of the initiator for the same system, the lower the molecular weight of the products. The decomposition rate of AIBN in SC CO_2–acetic acid–propionic acid mixture decrease with the increase of acetic acid concentration, as shown in Table 4. This explains why the molecular weight of the product increases with the concentration of acetic acid in Table 3. The decomposition rates of AIBN in SC CO_2–ethanol– propionic acid increases with the concentration of ethanol and explains why the molecular weight decreases with ethanol concentration. For the systems containing different cosolvents, there is no apparent relation between the decomposition rate and molecular weight. Therefore, the decomposition rate of the initiator is only one of the main factors to affect the molecular weight. Other factors, such as molecular interactions, need to be investigated further.

Morphology of the products. SEM was used to study the morphology of the products. Some typical results are shown in Figs. 1–3. From Fig. 1 it can be seen that the primary
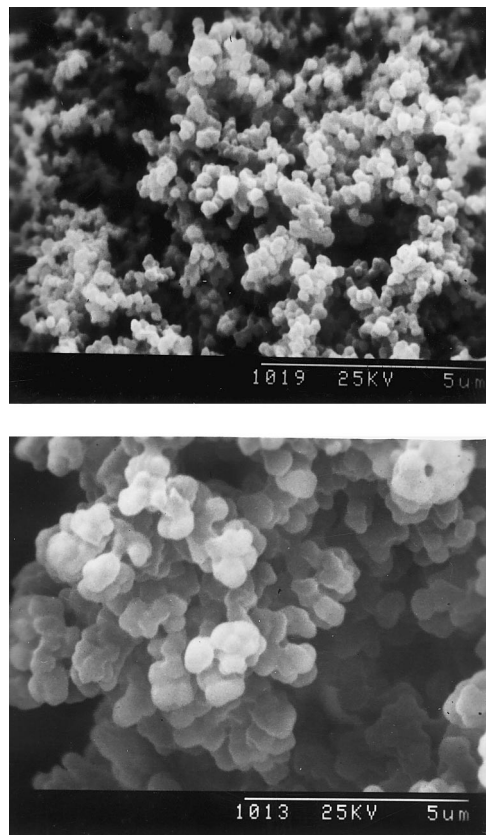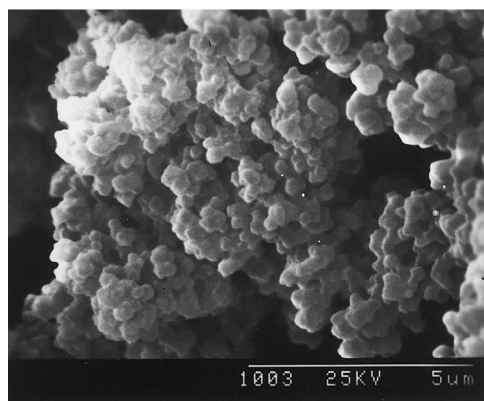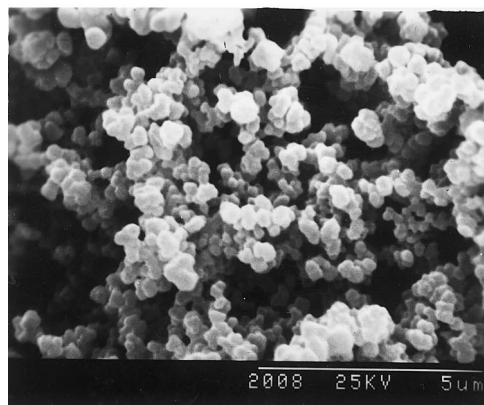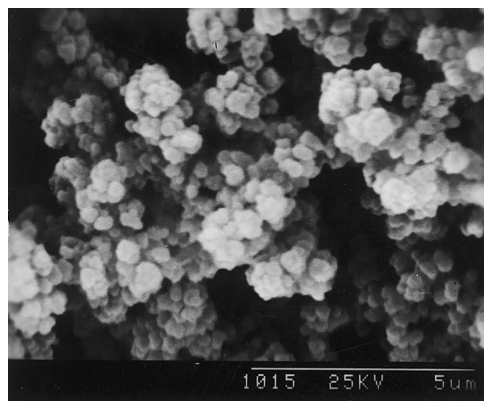
Fig. 2. Scanning electron micrographs of poly(acrylic acid) prepared by precipitation polymerization in SC CO_2 at 335 K and 13.5 MPa (the monomer concentration:1.5 mol/L) with different concentration of acetic acid (top, $Cc = 0$; middle, $Cc = 0.27$ mol/L; bottom, $Cc = 0.41$ mol/L; Cc, concentration of acetic acid).

Fig. 3. Scanning electron micrographs of poly(acrylic acid) prepared by precipitation polymerization in SC CO_2 at 13.5 MPa (the monomer concentration:1.5 mol/L) with different concentration of ethanol (top, $Cc = 0.14$ mol/L; middle, $Cc = 0.27$ mol/L; bottom, $Cc = 0.41$ mol/L; Cc, concentration of ethanol).

particle size of the product polymerized in pure SC CO_2 is about 200 nm (monomer concentration = 0.75 mol/L), which is similar to that reported by Desimone et al. [11] And the particle size increases with the concentration of monomer. Figs. 2 and 3 show the effect of cosolvent concentration on morphology of the products. The effect of acetic acid on the particle size is not considerable. However, the particle size increases significantly with ethanol concentration when ethanol is the cosolvent. The particle size is about
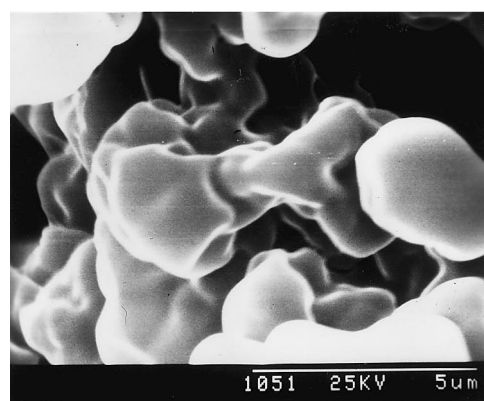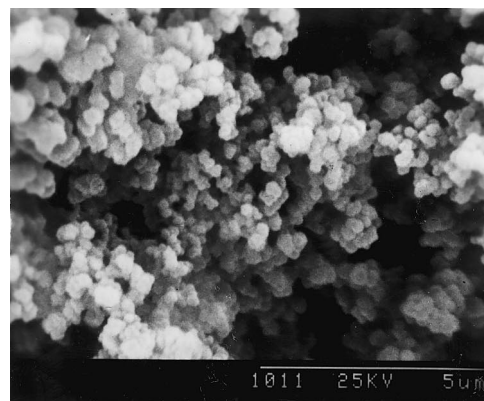
4 μm when ethanol concentration is 0.41 mol/L, which is much large than the particle size of 100 nm reported by Desimone et al. [11], who conducted the polymerization in pure SC CO_2. It is concluded that different cosolvents have different effects on the morphology of the product in SC CO_2. The mechanism requires further investigation. From Figs. 2 and 3, it can be observed that the degree of coalescence among the particles increases with the concentration of the cosolvents.

4. Conclusions

Precipitation polymerization of acrylic acid in SC CO_2 with and without acetic acid or ethanol cosolvents has been carried out at 335 K.

In SC CO_2, the average molecular weight, glass transition temperature and particles size increase with the concentration of monomer.

The effect of pressure on the molecular weight of the product polymerized in pure SC CO_2 is very limited. However, the molecular weight of the products polymerized in SC CO_2–acetic acid mixture decreases with pressure.

The average molecule weight of the products decreases with increasing cosolvent concentration when ethanol is used as the cosolvent. However, the average molecular weight increases with the increase of the cosolvent concentration in the cosolvent concentration range 0.14–0.41 mol/L, when acetic acid is used as cosolvent.

The particle size of the products increases with the concentration of ethanol in SC CO_2–ethanol mixture, but is not affected considerably by the concentration of acetic acid in SC CO_2–acetic acid mixture.

The different cosolvents affect the decomposition rate of the initiator considerably, which affects the molecular weight of the products.

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