Precipitation Polymerization of Acrylic Acid in Compressed Carbon Dioxide–Cosolvent Systems

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ABSTRACT: Precipitation polymerizations of acrylic acid (AA) in compressed carbon dioxide (65 bar) with different cosolvents, acetic acid, ethanol, and tetrahydrofuran, were studied. Analyses by viscosity measurement and differential scanning calorimetry indicate that the cosolvents have a pronounced effect on the properties of the product. Scanning electron microscopy shows that the products progress from microparticles to bicontinuous networks to fibers with the change of cosolvents and reaction conditions. Measurement of the volume expansion (ΔV%) of the liquid phase containing different cosolvents indicates that the miscibility of compressed CO_2 with the liquid phase is dependent on the cosolvent. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1876–1880, 2003

Key words: polymerization; miscibility; differential scanning calorimetry (DSC)

INTRODUCTION

Supercritical carbon dioxide possesses many unique properties[1,2] that make it an increasing alternative to the synthesis chemistry and polymer industries.[3] Among its many advantages, the most important are its fluid properties[4] and its environmental advantages. When chemical reactions are conducted in supercritical CO_2, the reaction environment (solvent properties) can be manipulated by the temperature or pressure, the transport limitations on reaction rates can be eliminated, and the reaction and product separation can be integrated. In addition to the advantages in polymerization and separation process, the molecular weight of the polymerization product can be adjusted by varying the pressure.[5]

DeSimone and others have shown that supercritical CO_2 is indeed a promising solvent in polymerization from all kinds of successful homogeneous[6–9] and heterogeneous[10–16] polymerizations. Among these polymerizations, DeSimone et al. has reported the successful precipitation polymerization of acrylic acid in supercritical carbon dioxide.[14]

Compared with conventional liquid solvents, the density of supercritical fluid can be varied continuously from gaslike to liquidlike values; the density-dependent solvent properties, such as the dielectric constant and viscosity, are thus also varied from gaslike to liquidlike values by introducing modest changes in the pressure or temperature. This will cause corresponding changes in solute solvation. In addition, the solubility of solutes can be altered by addition of cosolvents to the system[1,17–26] and the interaction of cosolvent–solute becomes the basis to adjust the equilibrium constants of different reactions,[19,24] improve the selectivity of reaction,[25] and increase the rate of reaction.[18] In this work, to further investigate the effect of cosolvent, polymerizations in compressed CO_2 with acetic acid, ethanol, and tetrahydrofuran (THF) as cosolvents at a pressure of 65 bar were studied. When polymerizations proceeded in compressed CO_2, it can be conceived that CO_2 replaces a portion of the organic solvent. Thus it is important to study the miscibility of CO_2 with acrylic acid–cosolvent mixture systems and the miscibility can be reflected in the volume expansion of the liquid phase. Measurement of the volume expansion of the liquid phase has been studied widely in the gas–antisolvent (GAS) process. The technique of supercritical antisolvent (SAS) precipitation has been applied to the production of submicronic particles[27–29] and formation of microparticulate protein powder.[30] In our work, at the end of polymerization, the compressed CO_2 became the antisolvent for the polyacrylic acid and it affected the morphology of the products to some extent.

EXPERIMENTAL

Materials

CO_2 (purity 99.995%) was obtained from Beijing Analytical Instrument Factory. 2,2'-Azobis(isobutyroni-

trile) (AIBN) was supplied by Beijing Chemical Factory and was recrystallized twice from methanol. Acrylic acid (97%) was obtained from Beijing Chemical Agent Factory and was deinhibited and purified by vacuum distillation. Acetic acid, ethanol, and THF (Beijing Chemical Factory) were analytical reagent grade.

Equipment

High-pressure reactions were carried out in a 10-mL stainless steel reactor equipped with two quartz windows for observation of phase behavior. Liquid CO_2 was delivered to the reactor with an SFC 8000 pump (Beijing Satellite Manufacturing Factory, Beijing, China). The pressure in the reactor was measured by use of a pressure gauge consisting of a transducer (model 93; IC Sensors Co, Beijing Tianchen Automatic Instrument Factory, China) and an indicator, which can be accurate to ± 0.5 bar in the pressure range from 0 to 200 bar. The temperature of the reactor was measured with a platinum resistance thermometer (model XMT; Beijing Chaoyang Automatic Instrument Factory). A magnetic stirrer was used to mix the materials in the reactor.

Volume expansions were measured in a 33-mL stainless steel autoclave with two quartz windows to observe the gas–liquid surface. The autoclave was immersed in a water bath and its temperature was controlled with a temperature controller (Haake F3; Germany). A magnetic stirrer was used to mix the contents in the vessel.

Polymerization

A suitable amount of acrylic acid monomer, 0.020 g initiator (AIBN), and the desired amount of cosolvent were simultaneously added to the reactor. Then CO_2 was charged into the reactor and the stirrer in the cell was started until vapor–liquid equilibrium was reached at about 25°C and 50 bar. The temperature of the cell was then increased and maintained at 62°C. The pressure in the cell was then increased to 65 bar by charging CO_2 again. The reaction was allowed to last for 4 h.

Characterization

Viscosity measurement was used to get the average molecular weight. IR (PE 683; Perkin Elmer Cetus Instruments, Norwalk, CT) study confirmed that the products were polyacrylic acid. Scanning electron micrography (SEM, model S-530; Hitachi, Tokyo, Japan) was used to observe the polymer morphologies and differential scanning calorimetry (DSC, PE 7 series; Perkin Elmer) was used to obtain the glass-transition temperature (T_g).

TABLE I
Summary of Molecular Weights and Glass-Transition Temperatures of Acrylic Acid Precipitation Polymerization in Compressed CO_2 and Supercritical CO_2 with Different Cosolvents[a]

Sample	Cosolvent	Pressure (bar)	M_n $(\times 10^{-5})$[b]	T_g (°C)
1	Acetic acid	65	2.382	113.69
2	Acetic acid	135	5.236[c]	130.15
3	Ethanol	65	2.470	125.40
4	Ethanol	135	2.144[c]	124.63
5	THF	65	2.141	122.45
6	THF	135	1.649	125.72

[a] Reaction conditions: concentration of monomer = 1.5 mol/L; concentration of cosolvent = 0.41 mol/L; [AIBN] = 1.2×10^{-2} M; reaction time = 4 h; T = 62°C.
[b] Average molecular weights were determined by viscosity measurement.
[c] From author's previous work.[21]

RESULTS AND DISCUSSION

Polymerization

In the polymerization process, it can be observed that the dissolved CO_2 in the liquid phase causes the liquid to expand. Before polymerization there were two phases, a gas phase at the top and a liquid phase at the bottom that contained CO_2, AA monomer, initiator AIBN, and cosolvent. Within just a few minutes, the onset of polymerization could be observed, in which the liquid phase became increasingly more viscous and this lasted about 10 min. In addition the system in the reactor first became slightly opaque, then fully opaque, and finally translucent again. At the end of the polymerization, the liquid phase became a white mass. Product yield was determined gravimetrically and more than 85% conversion could be achieved. The properties of the products are given in Table I.

Precipitation polymerizations were carried out at the cosolvent concentration of 0.41 mol/L in compressed CO_2. Table I presents a summary of the average molecular weights and glass-transition temperatures of the products. To compare the effect of cosolvent on the polymerization product in supercritical and compressed CO_2, respectively, the properties of the product polymerized at 135 bar are also listed in Table I. Table I shows that when acetic acid was used as the cosolvent in the polymerization system, there was a difference between the product polymerized in supercritical and compressed CO_2. The average molecular weight and glass-transition temperature of the product polymerized in supercritical CO_2 are apparently higher than those polymerized in compressed CO_2. Contrary to the effect of acetic acid, when either THF or ethanol was used as the cosolvent, the average molecular weights obtained in supercritical CO_2 were lower than those in compressed CO_2. When polymerization proceeded in compressed CO_2, the monomer

mainly existed in the liquid phase. Thus the monomer concentration was higher than that of the supercritical CO_2 system, which was homogeneous in the reactor. The average molecular weight thus will be higher because of higher concentration of monomer. When THF and ethanol were used as cosolvents, the experimental results were in accordance with this outcome.

How does one explain the effect of acetic acid as the cosolvent? It is deduced that in supercritical CO_2, the influence of acetic acid on molecular weight is more effective than that of either THF or ethanol. Usually in a supercritical system a cosolvent affects the molecular weight of the product in two opposite ways. First, it can increase the polarity of the solvent, and results in stronger interaction between the reaction transition-state molecules and the solvent medium. More radical molecules transfer to solvent molecules, which is not favorable for increasing the molecular weight. Second, the solvation power of a solvent is increased by addition of the cosolvents. Thus the critical degree of polymerization at which the oligomeric radicals precipitate from the solution is increased, which results in an increase of molecular weight. The overall effect depends on which factor is dominant. For acetic acid as cosolvent, the average molecular weight decreased at the beginning and then increased with the cosolvent concentration above a fixed value.[21] For THF and ethanol as cosolvents in the supercritical polymerization, the first factor was always dominant.

Expansion of liquid phase with different cosolvents

In the compressed CO_2 polymerization, there was a mixture of monomer, initiator, cosolvent, and compressed CO_2 before the polymerization. Thus the miscibility of CO_2 in the monomer–cosolvent liquid phase is necessary for the cosolvent to exert its effect.
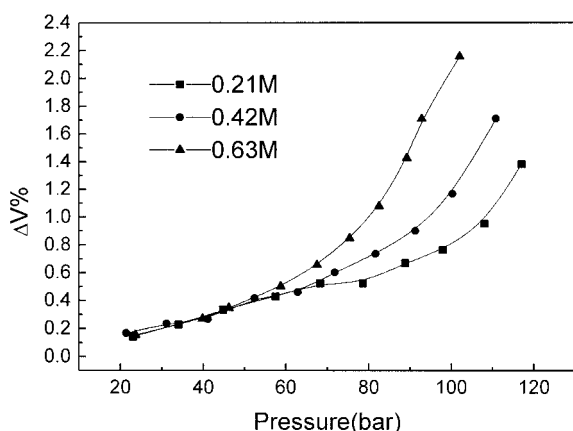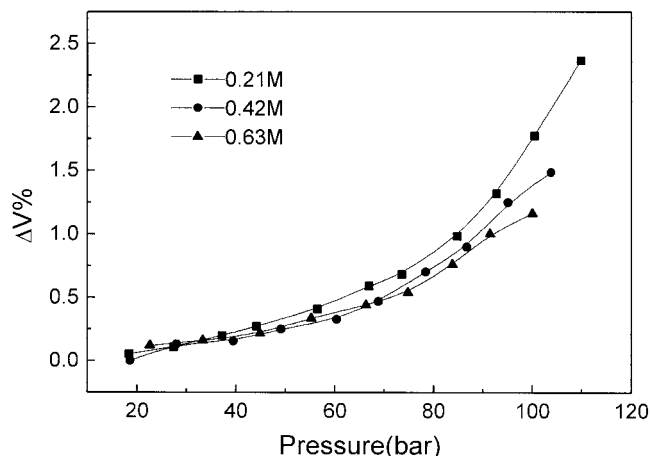

Figure 2 Volume expansion of acrylic acid-ethanol in CO_2 as a function of pressure at various ethanol concentrations.

The extent of miscibility is reflected in the volume expansion of the liquid phase. The volume expansion of the liquid phase ΔV (%) at a certain pressure P and temperature T is defined by

$$\Delta V \,(\%) = [V\,(P, T) - V\,(P°, T)]/V(P°, T)$$
$$\times 100\% \quad (1)$$

where $P°$ represents the atmospheric pressure.

Figures 1–3 show the volume expansion data of the liquid phase containing different concentrations of cosolvent. The difference of the three cosolvents can be observed from the figures. For the acetic acid–acrylic acid system, the volume expansion increases with increasing amounts of acetic acid. For the ethanol–acrylic acid system and the THF–acrylic acid system, the volume expansion decreases slightly with increasing concentrations of cosolvent. It is deduced that this is attributable to the hydrogen bonding of acrylic aid with the cosolvents acetic acid, ethanol, and THF.
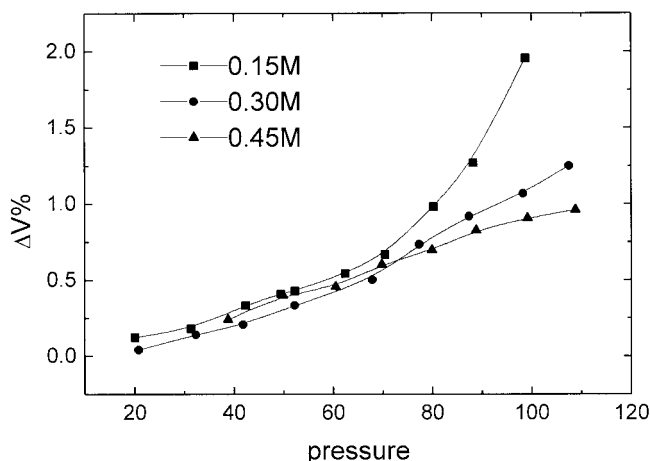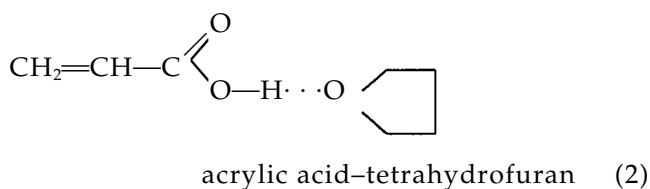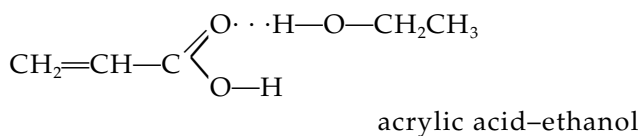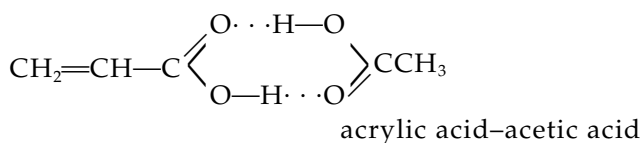

Figure 1 Volume expansion of acrylic acid-acetic acid in CO_2 as a function of pressure at various acetic acid concentrations.

Figure 3 Volume expansion of acrylic acid-THF in CO_2 as a function of pressure at various THF concentrations.

$$CH_2=CH-C\begin{array}{c}O\cdots H-O\\O-H\cdots O\end{array}CCH_3$$

acrylic acid–acetic acid

$$CH_2=CH-C\begin{array}{c}O\cdots H-O-CH_2CH_3\\O-H\end{array}$$

acrylic acid–ethanol

$$CH_2=CH-C\begin{array}{c}O\\O-H\cdots O\end{array}$$

acrylic acid–tetrahydrofuran   (2)

The difference stems from the ring dimer of the acrylic acid and acetic acid. Because of the structure of
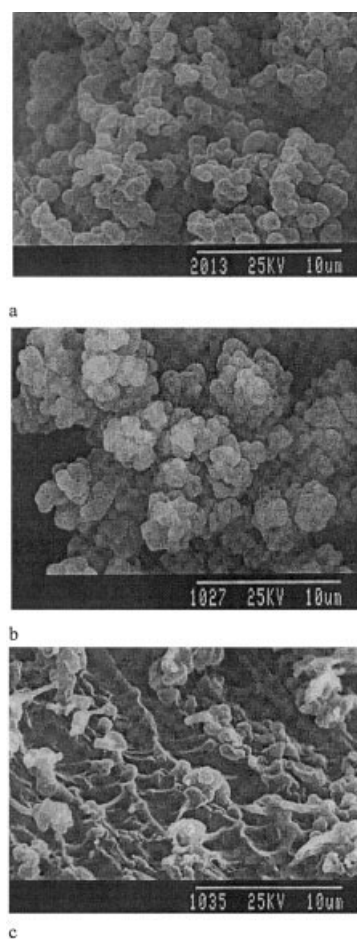

Figure 4 Scanning electron micrographs of poly(acrylic acid) prepared by precipitation polymerization in compressed CO_2 (62°C, 65 bar) with various cosolvents (monomer concentration = 1.5 mol/L; cosolvent concentration = 0.41 mol/L): (a) acetic acid; (b) ethanol; (c) THF.
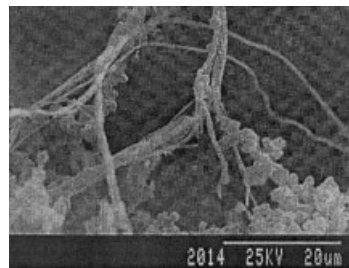

Figure 5 Scanning electron micrograph of the apparent flocculation when acetic acid is the cosolvent [Fig. 4(a)].

the ring dimer of the acrylic acid and acetic acid, more carbon dioxide molecules can be dissolved into the liquid phase. The mechanism needs to be studied further.

Morphology of products

The morphologies of the products prepared in compressed CO_2 with different cosolvents were studied. Figure 4 shows the experimental results. An apparent difference can be observed in the product morphologies when polymerization proceeded in compressed CO_2 with different cosolvents. When acetic acid was used as the cosolvent, the morphology of the product was in the form of microspheres and fibers were formed between the microspheres. Figure 5 shows the apparent flocculation of microspheres forming fibers. When ethanol was used as the cosolvent, clusters were formed among the microspheres. Figure 4(c) shows the surface morphology of the product prepared with THF as the cosolvent in compressed CO_2. It is in the form of a wave and microspheres can be formed on the wave crest; the cross section of the product is a cobweb structure, as shown in Figure 6. What contributes to the form of the products with different morphologies? At the end of polymerization, compressed CO_2 became the antisolvent to the products. Although there are numerous reports about preparing polymers with different morphologies using a supercritical antisolvent technique in the literature,[31–34] we are more inclined to believe that the kinds of morphologies of
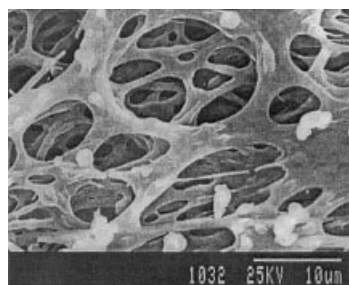

Figure 6 Scanning electron micrograph of the cross section of Figure 4(c).

our products are attributed to the period of nucleation and growth of the particles; that is, the different cosolvents (acetic acid, ethanol, and THF) can change the mass-transfer pathways through molecular interaction on the ternary diagram, as shown in the literature.[31]

CONCLUSIONS

Precipitation polymerizations of acrylic acid in compressed CO_2 with acetic acid, ethanol, and THF as cosolvents were carried out at 62°C. Considering that the polymerizations were in the liquid phase, the miscibility of compressed CO_2 with the acrylic acid monomer–cosolvent liquid phase was achieved through volume expansion. SEM studies indicate that different cosolvents have a pronounced effect on the morphologies of the polymerization products, and the products progress from microparticles to bicontinuous networks to fibers.

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