Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 47 (2006) 4276–4281

polymer

www.elsevier.com/locate/polymer

Cross-linking polymerization of acrylic acid in supercritical carbon dioxide

Tao Liu [a,1], Joseph M. DeSimone [a,b,2], George W. Roberts [a,*]

[a] Department of Chemical and Biomolecular Engineering, North Carolina State University, Campus Box 7905, Raleigh, NC 27695-7905, USA
[b] Venable and Kenan Laboratories, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, CB 3290, NC 27599-3290, USA

Received 18 October 2005; received in revised form 22 March 2006; accepted 28 March 2006
Available online 2 May 2006

Abstract

Cross-linking polymerization of acrylic acid in supercritical carbon dioxide ($scCO_2$) was studied in a batch reactor at 50 °C and 207 bar with either triallyl pentaerythritol ether or tetraallyl pentaerythritol ether as the cross-linker and with 2,2′-azobis(2,4-dimethyl-valeronitrile) as the free radical initiator. All polymers were white, dry, fine powders. Scanning electron microscopy showed that the morphology of the polymer particles was not affected by cross-linking. As the cross-linker concentration was increased, the polymer glass transition temperature first decreased, then increased. Water-soluble and water-insoluble polymers were synthesized by adjusting the cross-linker concentration. Viscosity measurements showed that the polymer thickening effect strongly depended on the degree of cross-linking. Finally, cross-linking polymerization of acrylic acid in $scCO_2$ was carried out in a continuous stirred tank reactor. The use of cross-linker decreased the monomer conversion in this system.

Keywords: Acrylic acid; Cross-linking polymerization; Supercritical carbon dioxide

1. Introduction

Acrylic acid polymers and copolymers are widely used as dispersants, thickeners, flocculants and superabsorbent polymers (SAPs). The most prevalent commercial process to make such polymers is solution polymerization of acrylic acid in water [1]. An energy-intensive drying process then is necessary to get dry polymer. Other processes, such as suspension polymerization, dispersion polymerization and precipitation polymerization, are carried out in organic media. The use of organic solvents and/or surfactants inevitably leads to chemical contamination of the polymer. For applications where extremely clean polymers are desired (e.g. food and pharmaceutical applications), costly purification processes are necessary. Although contamination can be reduced to very low levels, complete removal cannot be accomplished.

Acrylic acid is moderately soluble in supercritical carbon dioxide ($scCO_2$), while poly(acrylic acid) (PAA) is insoluble [2]. Therefore, the polymerization of acrylic acid in $scCO_2$ reflects a traditional precipitation polymerization: the chains that begin in the continuous phase eventually precipitate as solid polymer particles. This technique may provide an attractive alternative to the conventional methods in that: (1) carbon dioxide (CO_2) is environmentally benign; (2) the products are completely dry after depressurizing to remove the CO_2, and; (3) the final polymer is virtually free of contamination. Unreacted monomer and initiator are easily removed by extraction with $scCO_2$.

Polymerization of acrylic acid in liquid and supercritical CO_2 was first reported in a French patent [3] in 1968. The United States version of this patent [4] appeared in 1970. In 1986, a Canadian patent [5] issued to BASF Corporation described the synthesis in $scCO_2$ of water-soluble acrylic acid homopolymer. In 1988, a United States patent [6] issued to the same company demonstrated the synthesis of cross-linked, water-soluble PAA in $scCO_2$. In 1989, Goodrich also was granted a patent [7] for the synthesis of cross-linked, water-soluble PAA in $scCO_2$.

Although, the BASF and Goodrich patents define the operational conditions for the synthesis of water-soluble, cross-linked PAAs that are suitable as thickening agents, a systematic study on the effect of operating variables on polymer properties has not been reported. Recently, the continuous homopolymerization of acrylic acid in $scCO_2$ using a continuous stirred tank reactor (CSTR) has been reported [8,9]. The experimental data showed that the polymerization mainly took place in the polymer particles.

---

[*] Corresponding author. Tel.: +1 919 515 7328; fax: +1 919 513 3465.
E-mail addresses: tliu@unity.ncsu.edu (T. Liu), desimone@unc.edu (J.M. DeSimone), groberts@eos.ncsu.edu (G.W. Roberts).
[1] Tel.: +1 919 513 2834; fax: +1 919 513 1655.
[2] Tel.: +1 919 962 2166; fax: +1 919 962 5467.

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.03.103

Notation

APE2	diallyl pentaerythritol ether
APE3	triallyl pentaerythritol ether
[APE3]	APE3 concentration with respect to acrylic acid in batch polymerization (wt%)
APE4	tetraallyl pentaerythritol ether
[APE4]	APE4 concentration with respect to acrylic acid in batch polymerization (wt%)
$[\mathrm{APE4}]_{\mathrm{in}}$	inlet APE4 concentration with respect to acrylic acid in CSTR polymerization (wt%)
CSTR	continuous stirred tank reactor
Freon 113	1,1,2-trichloro-1,2,2-trifluoroethane
$[I]_0$	initial initiator concentration in batch polymerization (mol/L)
$[I]_{\mathrm{in}}$	inlet initiator concentration in CSTR polymerization (mol/L)
$[M]_0$	initial monomer concentration in batch polymerization (mol/L)
$[M]_{\mathrm{in}}$	inlet monomer concentration in CSTR polymerization (mol/L)
MEHQ	methyl ether of hydroquinone
P	pressure (bar)
$[P]$	polymer concentration (wt%)
T	temperature (°C)
V-65B	2,2′-azobis(2,4-dimethyl-valeronitrile)
τ	average residence time in CSTR polymerization (s)

This paper describes the cross-linking polymerization of acrylic acid in $scCO_2$ in a 20-mL batch reactor and an 800-mL CSTR. The effect of cross-linking on polymer properties was evaluated. By adjusting the degree of cross-linking, water-soluble and water-insoluble polymers were synthesized.

2. Experimental

2.1. Materials

CO_2 (SFC grade, 99.998%) and argon (Research grade, 99.9999%) were purchased from National Specialty Gases. The initiator, 2,2′-azobis(2,4-dimethyl-valeronitrile) (V-65B) (high purity, 98.8%), was donated by Wako Chemicals USA. The 10-h half-life decomposition temperature of this initiator is 51 °C [10]. Acrylic acid (99.5%), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) (HPLC grade, 99.8%), and deionized water (DI water) were purchased from the Fisher Scientific Company. Triallyl pentaerythritol ether (APE3) (76.1%) and tetraallyl pentaerythritol ether (APE4) (90.1%) were obtained from Monomer–Polymer and Dajac Laboratories, Inc. The main impurities in APE3 were diallyl pentaerythritol ether (APE2), 14.7%, and APE4, 7.1%. Similiarly, the main impurities in APE4 were APE2 and APE3. All chemicals were used as received.

2.2. Batch polymerization

The batch polymerization of acrylic acid in $scCO_2$ was carried out in a 20-mL, stainless steel, high-pressure view cell containing a magnetic stir bar. The initial acrylic acid concentration was between 0.73 and 1.46 mol/L, the initial V-65B concentration was between 2.4×10^{-3} and 4.8×10^{-3} mol/L, and the initial cross-linker concentration with respect to acrylic acid was between 0 and 5 wt%. The reactor was purged with SFC grade CO_2 before use. In the beginning of a typical polymerization, acrylic acid, with a known amount of cross-linker, was charged into the reactor. Then, V-65B/Freon 113 solution (0.48 mol/L) was added into the reactor. Liquid CO_2 was then added until it occupied about 2/3 of the reactor volume. The reactor was heated to 50 °C. Additional CO_2 then was added to increase the pressure to 207 bar. At this point, the reactor contents were homogeneous. After a few minutes, polymer particles began to appear. The reaction was allowed to run for 10 h. Then the pressure was slowly released while the reactor was kept at 50 °C. Finally, the reactor was cooled to approximately room temperature, and the product polymer was collected. The yield was above 90% in all experiments.

2.3. Continuous polymerization

The continuous polymerization of acrylic acid in $scCO_2$ was carried out in an 800-mL CSTR using V-65B as the free-radical initiator and APE4 as the cross-linker. The reaction temperature was 70 °C, the pressure was 207 bar, and the average residence time was 25 min. The inlet acrylic acid concentration ($[M]_{\mathrm{in}}$) was 1.25 mol/L, the inlet initiator concentration ($[I]_{\mathrm{in}}$) was 1.0×10^{-3} mol/L, and the inlet cross-linker concentration ($[\mathrm{APE4}]_{\mathrm{in}}$) was 5 wt% with respect to acrylic acid. In a typical experiment, three streams (CO_2, acrylic acid, and V-65B/Freon 113 solution) were fed continuously into the reactor with individual syringe pumps. The polymer precipitated as it was formed, so that the product stream that was withdrawn from the bottom of the reactor consisted of a continuous fluid phase and a dispersed, polymer phase. This stream was cooled and a solution of methyl ether of hydroquinone (MEHQ) in toluene was added to stop the polymerization. The polymer particles were removed from the fluid by filtration, and were extracted with $scCO_2$ to remove unreacted monomer, initiator, Freon 113, toluene, and MEHQ. Details of the equipment and the experimental procedures are available elsewhere [8,11].

2.4. Characterization

The experimental yields were determined by a gravimetric method. The polymer morphologies were observed with a JEOL 6400F field emission scanning electron microscope (SEM). A rheometrics dynamic stress rheometer (DSR, Model

SR-200) operating in the stress–sweep mode at 25 °C with Cuette geometry (cup diameter = 32.00 mm, bob diameter = 29.55 mm, bob length = 44.4 mm) was used for viscosity measurements. A differential scanning calorimeter (DSC, Model Q-100, TA instruments) with a refrigerated cooling accessory was used to determine the polymer glass transition temperatures (T_g). Polymer samples (4–8 mg), which had been dried in a vacuum oven for 2 days at 80 °C to remove any moisture present, were analyzed in crimped aluminum pans under a dry nitrogen purge of 50 mL/min. The sample history was erased by heating the sample to 180 °C at a heating rate of 10 °C/min and cooling it rapidly (20 °C/min) to −40 °C. Then a DSC scan in the temperature range from −40 to 180 °C at a heating rate of 10 °C/min was carried out to determine the T_g of the polymer. The reproducibility of the T_g measurement was ±0.1 °C.

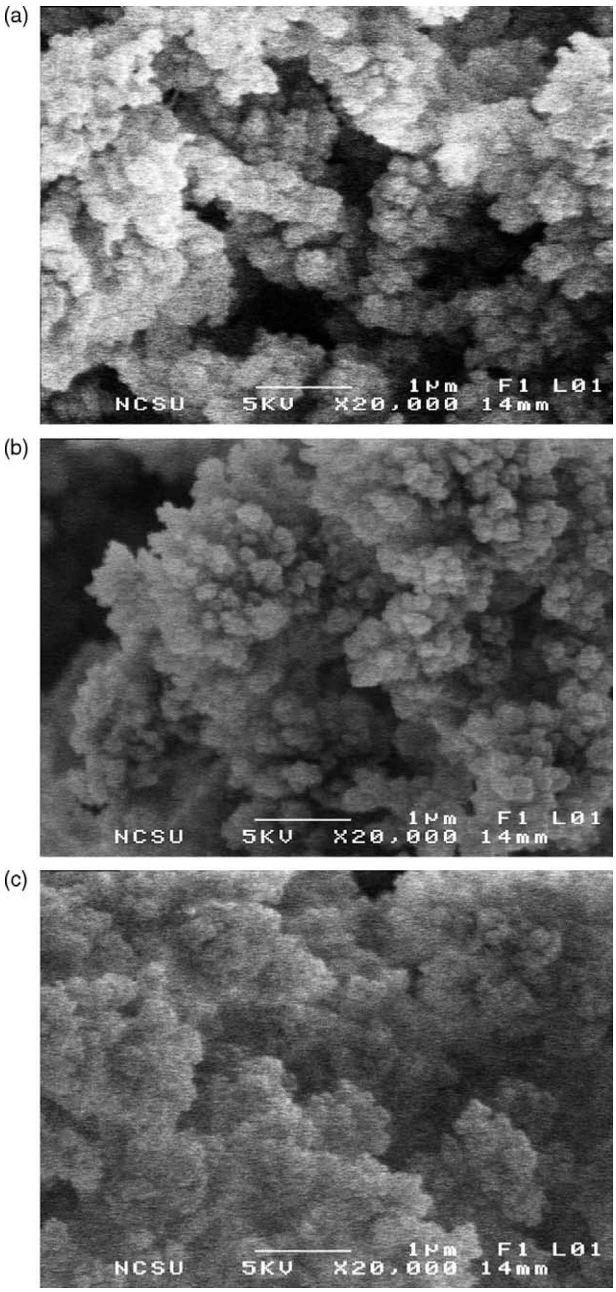

Fig. 1. Comparison of the morphologies of polymers prepared in batch experiments (polymerization conditions: $T = 50$ °C; $P = 207$ bar, $[M]_0 = 1.46$ mol/L; $[I]_0 = 0.0024$ mol/L) a—homopolymer; b—[APE4], 1 wt%; c—[APE4], 5 wt%. The bars in all images are 1 μm.

3. Results and discussion

3.1. Batch polymerization

In all batch experiments, the products were fine, fluffy, free-flowing powders. Electron micrographs of three products are shown in Fig. 1. The polymers are aggregates of primary particles which are about 100–200 nm in diameter. There is no obvious difference between the three samples, although their degrees of cross-linking are different.

The effect of cross-linking on the T_g of polymer is shown in Fig. 2. When the concentration of the cross-linker was low, the T_g decreased as the cross-linker concentration increased. As the cross-linker concentration was increased further, T_g went through a minimum and began to increase. This behavior can be explained as follows: low concentrations of cross-linker only produce branched polymers. The existence of side chains increases the free volume of the polymer, which decreases T_g. However, as the cross-linker concentration is increased further, polymer chains become cross-linked, forming networks. The networks make chain movement difficult, causing the T_g to increase.

Fig. 2 also shows that at a cross-linker concentration of 0.2 wt%, APE3 does not cause as large a decrease in T_g as APE4. This is reasonable because APE3 has only three double bonds while APE4 has four double bonds. For the same amount of cross-linker, APE3 can make fewer branches or cross-links.

Cross-linked, water-soluble PAA is good thickener, while water-insoluble PAA can be neutralized to make SAPs. To evaluate the water-solubility of the present polymers, 0.1 g polymer was dispersed in 10 mL DI water in a 20-mL vial.

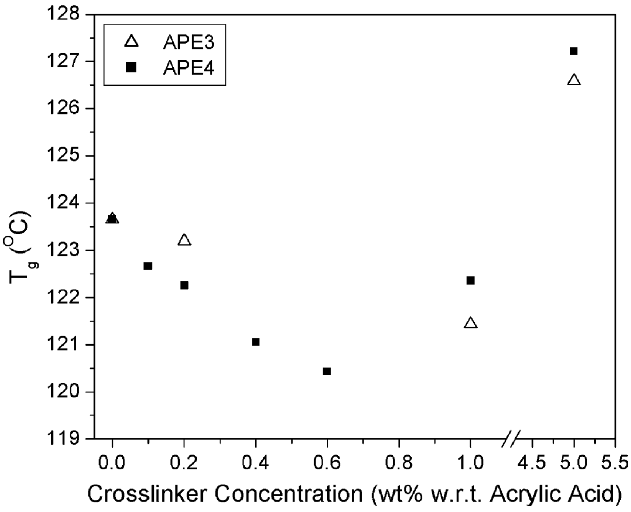

Fig. 2. The effect of cross-linker type and concentration on the polymer glass transition temperature (polymerization conditions: $T = 50$ °C; $P = 207$ bar; $[M]_0 = 1.46$ mol/L; $[I]_0 = 0.0024$ mol/L).

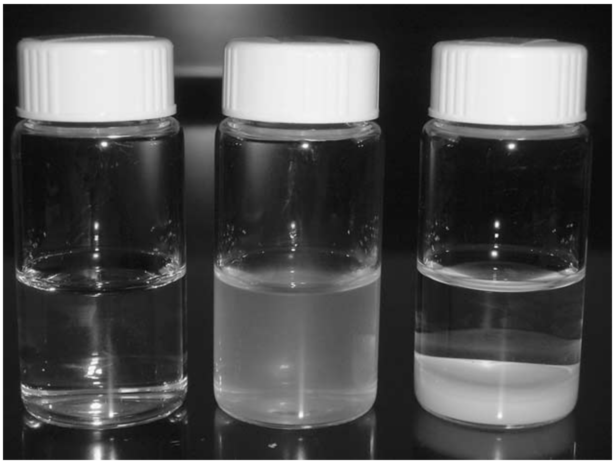

Fig. 3. Solubility behavior of cross-linked PAA in DI water (left—[APE4] = 0.1 wt%; middle—[APE4] = 0.4 wt%; right—[APE4] = 5 wt%).

The mixture was stirred for 24 h at room temperature. The mixture then was allowed to stand for a week at room temperature. Visually, three types of behavior were observed, as shown in Fig. 3: (1) the solutions were clear; the polymers appeared to be completely soluble in water; (2) the solutions were cloudy; the polymers appeared to be only partially insoluble, but there was no settled solid at the bottom of the vial; (3) there was a settled layer at the bottom of the vial; the solution above the settled layer was clear.

The viscosities of the polymer/water mixtures were measured with a DSR at 25 °C. The plots of viscosity versus shear rate are shown in Fig. 4a and b. When the cross-linker concentration was less than 0.2 wt%, the polymers were soluble. Below this cross-linker concentration, the viscosity of the aqueous solution increased dramatically with the cross-linker concentration, as shown in Fig. 4a. When the cross-linker concentration was greater than 0.2 wt%, the polymers were at least partially insoluble in water. In this case, increasing cross-linker concentration decreased the thickening effect of the polymer, as shown in Fig. 4b. The viscosity decrease is probably because less polymer was soluble in water as the cross-linker concentration increased. The mixture finally became a slurry of polymer particles dispersed in water instead of a polymer solution.

The water-insoluble polymer was removed from the mixture by centrifugation. The viscosity of the filtrate then was measured. Fig. 5 shows that the viscosity of the slurry of 1 wt% cross-linked PAA in water was much higher than the slurry of 5 wt% cross-linked PAA, prior to separation. However, the viscosities of their filtrates were both close to the viscosity of water. In other words, there was essentially no polymer left in either filtrate. Therefore, both polymers were insoluble in water. The less cross-linked polymer might have more capacity to swell in water, and it might have more side chains extending into the water, giving it a stronger thickening effect.

For the water-soluble polymers, Fig. 6 shows the two cross-linkers have the same thickening effect. No difference can be observed between the two polymers cross-linked with different

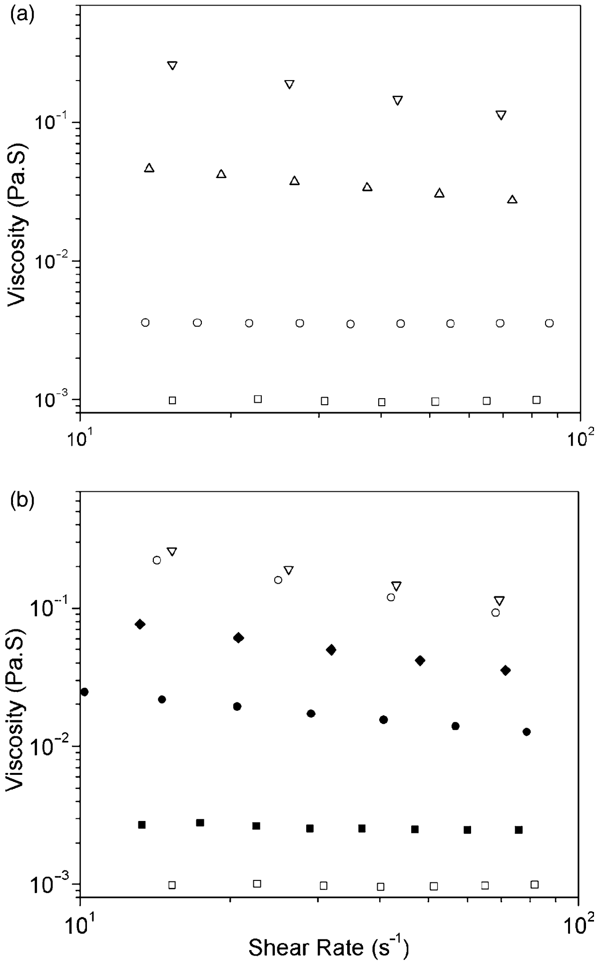

Fig. 4. a The effect of cross-linker concentration on the polymer thickening effect at 25 °C: ([P] = 1 wt%; polymerization conditions: T = 50 °C; P = 207 bar; $[M]_0$ = 1.46 mol/L; $[I]_0$ = 0.0024 mol/L). a. Low cross-linker concentration (□, DI water; ○, [APE4] = 0; △, [APE4] = 0.1 wt%; ▽, [APE4] = 0.2 wt%). b. High cross-linker concentration (▽, [APE4] = 0.2 wt%; ○, [APE4] = 0.4 wt%; ◆, [APE4] = 0.6 wt%; ●, [APE4] = 1.0 wt%; ■, [APE4] = 5.0 wt%; □, DI water).

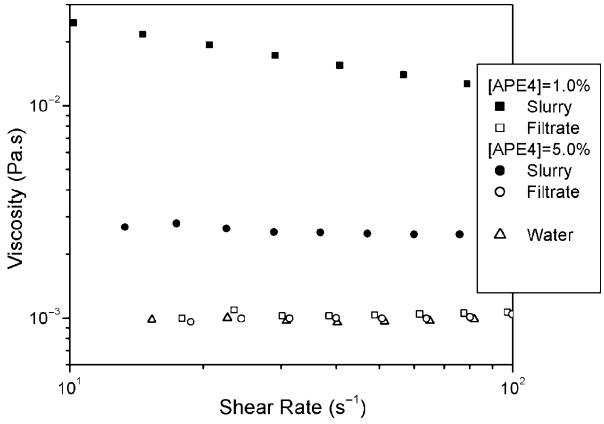

Fig. 5. The viscosities of polymer slurries and their filtrates at 25 °C ([P] = 1 wt%; polymerization conditions: T = 50 °C; P = 207 bar; $[M]_0$ = 1.46 mol/L; $[I]_0$ = 0.0024 mol/L).

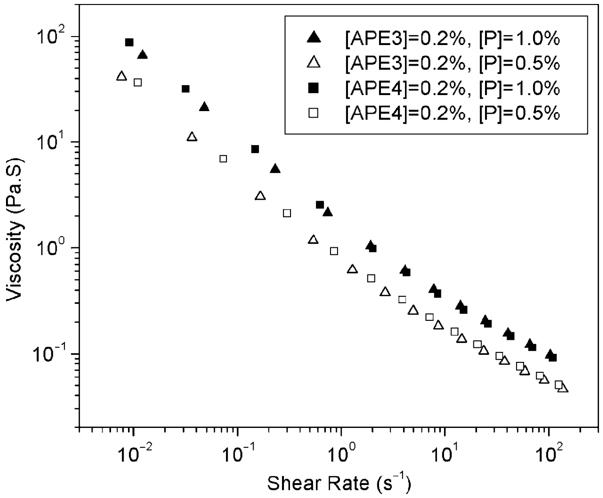

Fig. 6. The viscosities of cross-linked polymer solutions at 25 °C (polymerization conditions: $T=50$ °C; $P=207$ bar; $[M]_0=1.46$ mol/L; $[I]_0=0.0024$ mol/L).

cross-linkers, at the same polymer and cross-linker concentrations. However, the two polymers had somewhat different T_gs, as shown in Fig. 2, which suggests that their degrees of branching were different. Possibly, the DSR measurements were not sensitive to that small structure difference.

The monomer and initiator concentrations used for the polymerization had a strong influence on the polymer thickening effect. Fig. 7 shows that decreasing the monomer concentration or increasing the initiator concentration decreased the viscosity of the polymer solution. These changes could have several effects. First, the length of the main chain should decrease with increasing initiator concentration and decreasing monomer concentration. Second, these changes also should reduce the chain branching and cross-linking. Fig. 7 shows that the solution viscosity decreased faster with the decrease of monomer concentration than it did with the increase of initiator concentration. This is because the kinetic chain length of free radical polymerization depends on the monomer concentration to a higher order than the initiator concentration.

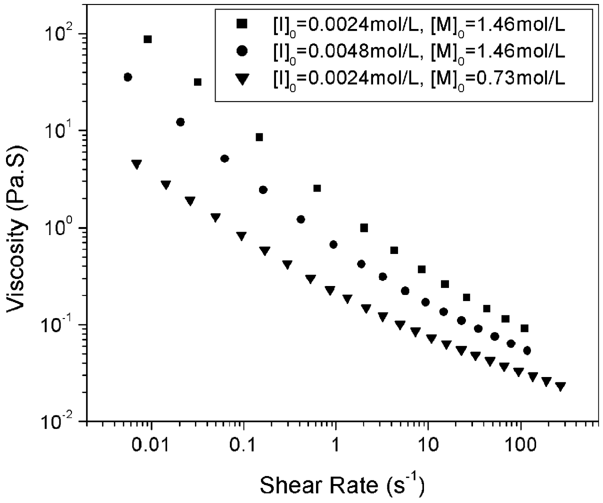

Fig. 7. The effect of monomer concentration and initiator concentration on polymer solution viscosity ($[P]=1$ wt%; polymerization conditions: $T=50$ °C; $P=207$ bar; $[\text{APE4}]_0=0.2$ wt%).

Table 1
Two neutralization experiments carried out at room temperature

Neutralization agent	[APE4] (wt%)	PAA (g)	Neutralization degree (%)	
			Measured value	Theoretical value[a]
0.08 g NH_3	1.0	1.0	38	34
1.5 g NaOH	6.0	4.0	73	72

[a] Assuming that all of the neutralization agent reacts with acid groups in PAA.

The cross-linked PAA, which contains free carboxylic acid groups, has to be partially neutralized for use in certain applications, e.g. SAPs. Table 1 lists two neutralization experiments carried out at room temperature. In the first experiment, 0.08 g of gaseous ammonia was introduced into a 20-mL view cell which contained 1.0 g of cross-linked PAA ([APE4] = 1 wt%). Elemental analysis of the polymer showed that 38% of the carboxylic acid groups were neutralized. In the second experiment, 1.5 g of sodium hydroxide was dissolved in 80 mL ethanol. Then 4.0 g of cross-linked PAA ([APE4] = 6 wt%) was added into the solution. The mixture was stirred for 2 h. Then it was filtered to recover the neutralized polymer. The polymer was dried in a vacuum oven at 80 °C for 2 days. The final mass of the polymer was 4.85 g, which indicates that 73% of the carboxylic acid groups had been neutralized. Table 1 also shows that the theoretical degree of neutralization was close to the measured degree of neutralization for both experiments.

3.2. Continuous polymerization

Table 2 shows the results from two continuous polymerization experiments carried out in an 800-mL CSTR. The conditions were identical, except for the concentration of cross-linker in the feed. The first experiment was a homopolymerization, for which the monomer conversion was 55%. In the second experiment, APE4 was used as the cross-linker, with a feed concentration of 5 wt% with respect to monomer. The monomer conversion was 39%, which indicates that the cross-linker decreased the rate of polymerization. Previous studies [8,9] have shown that, in the precipitation polymerization of acrylic acid in $scCO_2$, chain initiation takes place primarily in the continuous fluid phase while chain propagation and termination mainly take place in the dispersed polymer particles. Therefore, the rate of initiation should not be affected by cross-linking. However, cross-linking could decrease the

Table 2
Two typical continuous polymerization experiments carried out in the CSTR at 70 °C and 207 bar ($[M]_{in}=1.25$ mol/L; $[I]_{in}=0.001$ mol/L; $\tau=25$ min)

$[\text{APE4}]_{in}$ (wt%)	Monomer conversion (%)
0	55
5.0	39

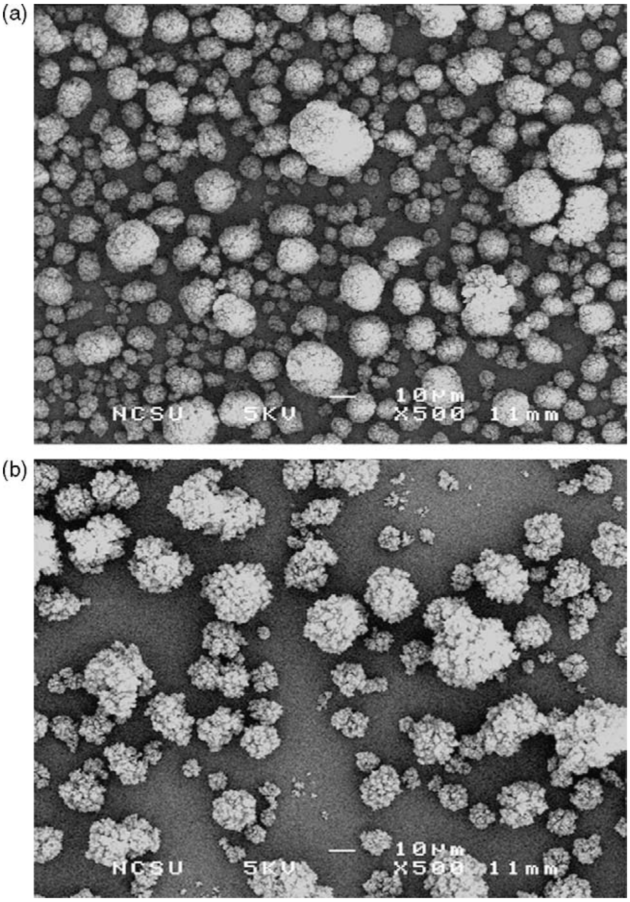

Fig. 8. SEM images of a homopolymer (a) and a cross-linked polymer ([APE4] = 5 wt%) prepared in the CSTR (polymerization conditions: T = 70 °C; P = 207 bar, $[M]_{in}$ = 1.25 mol/L; $[I]_{in}$ = 0.001 mol/L; τ = 25 min). The bars in both images are 10 µm.

permeability of PAA particles to acrylic acid, leading to a lower rate of propagation.

The polymers prepared in the CSTR had different morphologies than those prepared in the batch reactor. Fig. 8 shows the SEM images of the polymers from the two experiments listed in Table 2. Unlike the batch experiments, which produced fine powder with primary particles less than 1 µm in diameter, these two CSTR experiments produced particles of 5–20 µm diameter.

The polymerization temperature appears to have a strong effect on the polymer morphology. In the polymerization, PAA formed and precipitated from the CO_2 phase. The polymer contained dissolved CO_2, at a concentration that was essentially in equilibrium with the CO_2 in the supercritical phase. The glass transition temperature of PAA in the presence of $scCO_2$, T_g, should be lower than that of the pure polymer, T_{g0}. Based on approximate calculations using Chow's equation and measured values of the solubility of CO_2 in PAA, the temperature in the batch polymerization experiments, 50 °C, appears to be below T_g, so that the precipitated polymer was in its glassy state. Therefore, at 50 °C, it seems likely that only small, primary particles precipitated from the CO_2 phase. These particles did not have a tendency to coalesce, although they could form a loose coagulum during the final polymer-collection process. In contrast, the CSTR polymerization temperature, 70 °C, was estimated to be a little higher than T_g. At 70 °C, some or all of the polymer probably was in the melt state, so that the primary particles could coalesce with each other to form larger particles. Under this condition, the intensity of agitation would determine the size distribution of the polymer particles. Further, discussion of this hypothesis can be found elsewhere [11].

4. Conclusions

Cross-linking polymerization of acrylic acid was carried out in $scCO_2$ in a batch reactor at 50 °C and 207 bar with APE3 and APE4 as the cross-linkers and V-65B as the free radical initiator. The polymers were white, fine, fluffy powders. No effect of cross-linking on polymer morphology was observed. By adjusting the cross-linker concentration, water-soluble and water-insoluble polymers could be produced. The thickening effect of the water-soluble polymer depended on the cross-linker concentration and also on the monomer and initiator concentration. The glass transition temperature was affected by the degree of cross-linking. Continuous polymerization of acrylic acid in $scCO_2$ was also carried out in a CSTR at 70 °C and 207 bar. The use of cross-linker in the CSTR decreased the monomer conversion. Several post-polymerization techniques could be used to partially neutralize the polymer.

Acknowledgements

The authors thank Dr Saad A. Khan's research group in the Department of Chemical and Biomolecular Engineering at North Carolina State University for their help in the measurements of DSC and DSR. This research was supported by Kenan Center for the utilization of CO_2 in manufacturing at North Carolina State University and by the STC Program of the National Science Foundation under Agreement no. CHE-9876674.

References

[1] Swift G. In: Bailey J, Kroschwitz JI, editors. Acrylic (and methacrylic) acid polymers. Encyclopedia of polymer science and technology, vol. 1. Hoboken, NY: Wiley; 2003. p. 79–96.
[2] Rindfleisch F, DiNoia TP, McHugh MA. J Phys Chem 1996;100(38):15581–7.
[3] Fukui K, Fujii K, Kagiya T, Toriuchi Y, Yokota H. French Patent No. 1,524,533; 1968.
[4] Fukui K, Fujii K, Kagiya T, Toriuchi Y, Yokota H. US Patent No. 3,522,228; 1970.
[5] Sertage WGJ, Davis P, Schenck HU, Denzinger W, Hartmann H. Canadian Patent No. 1,274,942; 1990.
[6] Hartmann H, Denzinger W. US Patent No. 4,748,220; 1988.
[7] Herbert MW, Huvard GS. European Patent No. 0,301,532 (A2); 1989.
[8] Liu T, DeSimone JM, Roberts GW. J Polym Sci, Part A: Polym Chem 2005;43(12):2546–55.
[9] Liu T, DeSimone JM, Roberts GW. Chem Eng Sci 2006;61(10):3129–39.
[10] Wako Pure Chemical Industries, Ltd. Solvent-soluble Azo Polymerization Initiator (http://www.wako-chem.co.jp/specialty/oilazo/index.htm).
[11] Liu T. Continuous precipitation polymerization of acrylic acid in supercritical carbon dioxide, PhD thesis, North Carolina State University, Raleigh, NC; 2005.