Supercritical CO_2 affects the copolymerization, LCST behavior, thermal properties, and hydrogen bonding interactions of poly(*N*-isopropylacrylamide-*co*-acrylic acid)

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ABSTRACT

Radical copolymerizations of *N*-isopropylacrylamide (NIPAm) with acrylic acid (AA) initiated by azobisisobutyronitrile in supercritical carbon dioxide (scCO$_2$, 55 °C, 27.6 MPa) were compared with those performed in MeOH at 55 °C. The AA compositions of the copolymers in scCO$_2$ were lower than those of the copolymers in MeOH and they increased upon decreasing the pressure of scCO$_2$ from 27.6 to 13.8 MPa. The glass transition temperatures of these copolymers deviated positively from those of respective homopolymers prepared in both media, with the copolymer obtained at a 50/50 feed ratio exhibiting the highest value of T_g. FTIR spectroscopy revealed enhanced H-bonding between the amide group of the NIPAm and the carboxyl group of the AA in the copolymers in scCO$_2$, suggesting that the much higher values of T_g of these copolymers, relative to those in MeOH, arose presumably from the more highly alternating sequences of their NIPAm and AA units.

1. Introduction

Free radical copolymerizations of vinyl monomers in environmentally friendly supercritical CO_2 (scCO$_2$) fluids [1–4] have typically been investigated using either emulsion or dispersion polymerization in perfluorinated polymeric surfactants or stabilizers [5–7] because most polymers are insoluble in CO_2. Only recently has the free radical polymerization of *N*-isopropylacrylamide (NIPAm), yielding temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAm), been studied in CO_2. For example, we have recently compared the kinetics of azobisisobutyronitrile (AIBN)-initiated radical polymerization of NIPAm, without the use of a perfluorinated polymeric surfactant, in scCO$_2$ with that in methanol (MeOH) [8]. The precipitation polymerizations of NIPAm in scCO$_2$ can result in higher yields and molecular weights for PNIPAm than those from the solution polymerizations of NIPAm in MeOH.

Because poly(acrylic acid) (PAA) is a pH-sensitive polymer, copolymers of NIPAm and acrylic acid (AA) exhibit both temperature- and pH-responsiveness. The lower critical solution temperature (LCST) for PNIPAm (ca. 32 °C) would, therefore, vary upon changing the pH of an aqueous solution of poly(NIPAm-*co*-AA) [9–12]. Cao et al. [13] have investigated the copolymerization of NIPAm and AA (equimolar feed ratio) in scCO$_2$ at various pressures at 70 °C for 10 h, using AIBN as the

initiator at various concentrations. These copolymers formed white particles (ca. 50 nm in size) that exhibited thermosensitive and pH-sensitive behavior.

In this study, we have extended our previous investigations [8,14] to the random copolymerizations of NIPAm and AA monomers in scCO$_2$. Here, we compared the copolymerizations performed in scCO$_2$ with those performed in the organic solvent MeOH in terms of yield, molecular weight, and copolymer composition, with a particular focus on the effects of the reaction media on the LCST and glass transition temperatures (T_g) of the copolymers. We conducted these copolymerizations of NIPAm and AA at various feed mole ratios at 55 °C for 8 h in scCO$_2$ (27.6 MPa) and in MeOH.

2. Experimental

2.1. Free radical copolymerizations of NIPAm and AA monomers in scCO$_2$ and MeOH

A monomer mixture (40 mol) of NIPAm and AA (various mole ratios) and AIBN (1 mol) was stirred ultrasonically to obtain a homogeneous mixture and then a part of the mixture was loaded into the thin and tall vial reactor (52 mm in height, 14 mm in diameter, 8 mL in volume) to give 2.2 M of monomer mixture and 0.055 M of AIBN. The

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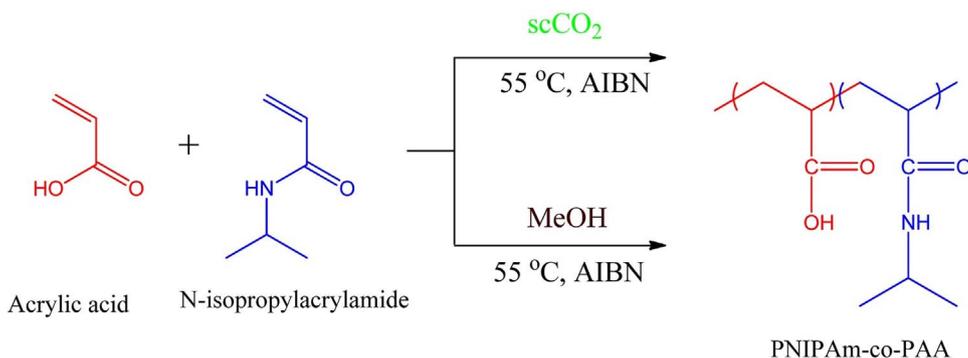
Scheme 1. Preparation of PNIPAm-*co*-PAA random copolymers in scCO$_2$ and MeOH.

vial was then placed in a 200-mL high-pressure vessel that was heated at 55 °C. Carbon dioxide (CO$_2$) was added into the high-pressure vessel and then the free radical copolymerization of NIPAm and AA was performed in scCO$_2$ at 27.6 MPa at 55 °C for 8 h. The variation in temperature within the tall and thin vial reactor during the exothermic copolymerization in scCO$_2$ without stirring was preliminarily determined to be insignificant. During the copolymerization in scCO$_2$, the vial cap was screwed loosely, allowing CO$_2$ to enter the vial without loss of the copolymer. After the copolymerization period, the vessel was then depressurized and the product subjected to purification (see below) by using MeOH and H$_2$O. For comparison, the same homogeneous mixtures reacted in scCO$_2$ were copolymerized in MeOH, also at 55 °C.

To purify PNIPAm homopolymers, the homopolymer was first dissolved in MeOH (80 mL) at 25 °C and then added into deionized H$_2$O (100 mL) at 45 °C to precipitate the polymer; the dissolution/precipitation procedure was repeated three times to give pure PNIPAm, followed by drying at 60 °C for 24 h. For purification of PAA homopolymers, the homopolymer was also dissolved in MeOH (50 mL) at 25 °C, followed by the sequential addition of diethyl ether (50 mL) and petroleum ether (200 mL) to precipitate the PAA; the final product was obtained by vacuum drying for 24 h.

For purification of PNIPAm-*co*-PAA random copolymers, the copolymers were first dissolved in MeOH (50 mL) at 25 °C and diethyl ether (200 mL) was added to precipitate PNIPAm, PAA, and P(NIPAm-*co*-AA). After the top portion of solution was removed, the settled product in the bottom was dried in an oven. The dried precipitate was then dissolved in 0.15 M aqueous NaOH (200 mL). The solution was heated to ca. 60 °C to precipitate PNIPAm, which was filtered off. The filtrate was treated with concentrated HCl (a few drops) and heated to 60 °C to precipitate the copolymer P(NIPAm-*co*-AA), which was washed with diethyl ether until neutral, followed by vacuum drying for 24 h.

2.2. Characterization

The yields of the (co)polymers formed in scCO$_2$ and MeOH were measured by calculating the quotients w_p/w_m, where w_p is the weight of the dried copolymer and w_m is the initial weight for monomer mixture feed. The weight-average molecular weights of the synthesized PNIPAm and PAA homopolymers were determined from their intrinsic viscosities ([η]), measured using an Ubbelohde viscometer in MeOH at 25 °C [15] and in 0.1 M aqueous NaCl at 25 °C [16], respectively. The M_w values of PNIPAm and PAA were calculated using the equations [η] = $2.99 \times 10^{-2} M_w^{0.64}$ [15] and [η] = $1.46 \times 10^{-2} M_w^{0.8}$ [16], respectively. The intrinsic viscosities ([η]) were also measured for poly(NIPAm-*co*-AA) and PAA in 0.1 M NaCl in MeOH at 25 °C. Fourier transform infrared spectroscopy (FTIR, PerkinElmer Spectrum Two) was used to qualitatively characterize the copolymers of NIPAm and AA. Titration was performed to quantitatively characterize the copolymer compositions. In a typical experiment, a copolymer (0.1 g) was dissolved in 0.11 M aqueous NaCl (25 mL) and then added to 0.1 M

aqueous NaOH (26 mL) at 30 °C to deprotonate the COOH groups. After adding phenolphthalein (0.1 wt% aqueous solution, 20 µL) as an indicator, the copolymer solution was titrated using 0.1 M aqueous HCl. The weight and mole fractions of AA (W_{AA} and X_{AA}, respectively) in the copolymer were determined using the equations

$$W_{AA} = \frac{(B - C) \cdot M \cdot 72}{W \cdot 1000} \tag{1}$$

$$X_{AA} = \frac{W_{AA}/72}{W_{AA}/72 + (1 - W_{AA})/113} \tag{2}$$

where B and C are the volumes of the HCl solution (mL) added in the titrations of the blank and copolymer solutions, respectively; M is the molar concentration of the HCl solution; W is the copolymer weight; and 72 and 113 are the M_w of the AA and NIPAm monomers, respectively. The AA compositions in the copolymers were also determined using ^{1}H NMR spectroscopy (Varian Unity Inova–500 MHz) and DMSO-d_6 as the solvent. The LCSTs of aqueous solutions of the copolymers (3 wt%, pH 4) were characterized by measuring the visible light transmittance at 500 nm as a function of temperature (from high to low temperature during measurements); the inflection point of the transmittance–temperature curve was assigned as the LCST. The values of T_g of the copolymers were determined through differential scanning calorimetry (DSC; DSC-Q100, TA Instruments) using the following temperature program: heating at 20 °C/min from 30 to 200 °C, holding for 5 min, cooling at 40 °C/min to 40 °C, and then heating again at 10 °C/min to 200 °C to record the value of T_g.

3. Results and discussion

3.1. Copolymerizations of NIPAm and AA in scCO$_2$ and MeOH solutions

We prepared various PNIPAm-*co*-PAA random copolymers through free radical copolymerization in scCO$_2$ and MeOH solutions (Scheme 1). The AA compositions of these PNIPAm-*co*-PAA random copolymers were determined using ^{1}H NMR spectroscopy and titration experiments. For example, Fig. 1 presents the ^{1}H NMR spectrum of the PNIPAm-*co*-PAA random copolymer former at a 50/50 feed ratio in MeOH. The signals from the main chain of this PNIPAm-*co*-PAA random copolymer were located between 1.18 and 2.32 ppm. The signals of the alkyl CH and CH$_3$ protons of the PNIPAm segments appeared as multiplets at 3.82 and 1.01 ppm, respectively; the signals of the protons of the amide (CONH) and carboxyl (COOH) groups appeared as singlets at 7.20 and 12.05 ppm, respectively, representing the PNIPAm and PAA segments, respectively. The AA composition was calculated from the peak ratio, $A_{COOH}/(A_{COOH} + A_{CONH})$. Table 1 lists the copolymer compositions determined using both ^{1}H NMR spectroscopy and the titration experiments. Gel permeation chromatography (GPC) is an ineffective method for characterizing the molecular weights of PNIPAm homopolymers [17]. In comparison, the viscometric method provides more reliable values of M_w for PNIPAm homopolymers because of their ready dissolution in H$_2$O. Thus, we used an Ubbelohde viscometer to obtain the

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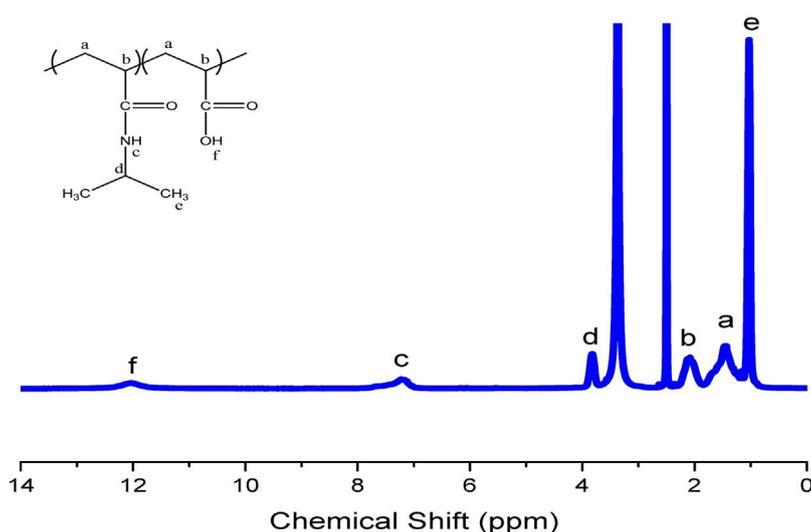
Fig. 1. ^{1}H NMR spectrum of a PNIPAm-*co*-PAA random copolymer synthesized in MeOH.

intrinsic viscosities and determine the molecular weights of the homopolymers and copolymers formed from NIPAm and AA. The yields and values of [η] of the copolymers synthesized at three feed mole ratios (NIPAm/AA: 75/25, 50/50, and 25/75) in scCO$_2$ were significantly lower than those of the corresponding copolymers prepared in MeOH (Table 1). Despite the similar yields of the syntheses of both homopolymers in both media, the value of M_w of PNIPAm prepared in scCO$_2$ was clearly higher than that of PNIPAm prepared in MeOH, but the value of [η] (i.e., M_w) of PAA prepared in scCO$_2$ was much lower than that of PAA prepared in MeOH, suggesting that PAA was difficult to synthesize at high molecular weights in scCO$_2$. The low value of M_w of PAA prepared in scCO$_2$ might be the reason why the three copolymers synthesized in scCO$_2$ had much lower yields and values of [η] than those of the corresponding copolymers prepared in MeOH. Furthermore, for any feed ratio, the AA composition in a copolymer synthesized in scCO$_2$ was lower than that in the corresponding copolymer synthesized in MeOH (Table 1). This finding again demonstrates that AA was less reactive in scCO$_2$ than in MeOH for copolymerization with NIPAm, resulting in much lower values of [η] for the copolymers prepared in scCO$_2$ than for those prepared in MeOH. The lower reactivity of AA in scCO$_2$ was less significant at lower CO$_2$ pressures (Table 2), with the AA composition in poly(NIPAm-*co*-AA) increasing upon decreasing the CO$_2$ pressure. We used the Kelen and Tudos methodology to calculate the reactivity ratios of the copolymers prepared in both scCO$_2$ and MeOH (Fig. 2(a) and (b), respectively) [18,19]. We calculated values of r_{PNIPAm} and r_{PAA} of 0.84 and 0.39, respectively, in scCO$_2$

and 0.67 and 0.50, respectively, in MeOH, implying the tendency toward forming ideal random copolymers. The value of r_{PAA} in scCO$_2$ (0.39) was lower than that in MeOH (0.50), indicating different alternating sequence length distributions of the AA segments in these PNIPAm-*co*-PAA copolymers. In addition, we know that the hydrogen bonding interaction could also affect the polymerization rate, propagation rate constants or reactivity ratios for copolymer system and then induced the different sequence distribution of copolymer system [20,21].

3.2. Thermal properties of poly(NIPAm-co-AA) copolymers formed in scCO$_2$ and MeOH

Fig. 3(A) presents DSC curves (second heating scans) for PNIPAm, PNIPAm-*co*-PAA, and PAA prepared in scCO$_2$. All samples, both homopolymers and copolymers, exhibited single values of T_g; the pure

Table 2
Copolymer compositions and yields from copolymerizations of NIPAm and AA at a feed mole ratio of 50/50 at 55 °C for 8 h in scCO$_2$ at 13.8, 20.7, and 27.6 MPa.

Feed composition (NIPAm/AA)	CO$_2$ pressure (MPa)	Yield (%)	Copolymer composition (PNIPAm/PAA)
50/50	13.8	35.0	54.0/46.0
	20.7	34.2	56.1/43.9
	27.6	28.5	56.4/43.6

Table 1
Copolymer compositions, yields, intrinsic viscosities, molecular weights, LCSTs, and thermal properties of PNIPAm-*co*-AA copolymers synthesized in scCO$_2$ and in MeOH.

Medium	NIPAm/AA mole ratio		Yield (%)	Intrinsic viscosity (η)[a]	M_w[b,c] (g/mol)	LCST[d] (°C)	T_g (°C)
	Feed	Copolymer					
scCO$_2$	100/0	100/0	70.2	–	$4.4 \times 10^{5,b}$	–	138.3
	75/25	75.8/24.2	40.9	0.185	–	28.9	158.4
	50/50	56.4/43.6	28.5	0.357	–	44.4	164.3
	25/75	37.2/62.8	15.5	0.250	–	–	144.1
	0/100	0/100	72.6	0.139	$3.8 \times 10^{4,c}$	–	105.7
MeOH	100/0	100/0	69.1	–	$2.8 \times 10^{5,b}$	–	139.1
	75/25	72.7/27.3	82.0	0.832	–	32.9	159.1
	50/50	51.4/48.6	90.3	0.783	–	48.0	159.6
	25/75	33.3/66.7	86.8	0.767	–	–	141.3
	0/100	0/100	76.2	0.918	$2.5 \times 10^{5,c}$	–	129.0

[a] Intrinsic viscosity determined in 0.1 M NaCl in MeOH at 25 °C
[b] M_w determined from intrinsic viscosity measured in MeOH solution at 25 °C
[c] M_w determined from intrinsic viscosity measured in 0.1 M aqueous NaCl at 25 °C
[d] LCST determined from visible transmittance at 500 nm for copolymers in aqueous solution at 3 wt% and pH 4.

Fig. 2. Kelen–Tudos plots of PNIPAm-*co*-PAA random copolymers synthesized in (a) scCO$_2$ (y = 1.37x-0.53 for red solid line), r_{PNIPAm} = 0.84, r_{PAA} = 0.39 and (b) MeOH (y = 1.25x-0.58 for green solid line), r_{PNIPAm} = 0.67, r_{PAA} = 0.50. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

PNIPAm and PAA homopolymers displayed values of 137 and 107 °C, respectively, while the PNIPAm-*co*-PAA random copolymers had values ranging from 144 to 166 °C—significantly higher than those of the pure homopolymers. The Kwei equation is commonly employed to determine the T_g behavior of strongly intermolecularly hydrogen bonded systems [22]:

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2$$

(3)

where W_i represents the weight fractions of each component (1 and 2); T_{gi} represents the glass transition temperatures of each component (1 and 2); and k and q are fitting constants representing of the strength of intermolecular hydrogen bonding. We calculated values of k and q of 1 and 180, respectively, by using this equation, as displayed in Fig. 3(B) (red line). This positive value of q indicates that intermolecular hydrogen bonding (Scheme 2(c)) was stronger than the self-association

hydrogen bonding of PAA (Scheme 2(a)) and PNIPAm (Scheme 2(b)).

Fig. 4(A) presents DSC curves (second heating scans) for PNIPAm, PNIPAm-*co*-PAA, and PAA prepared in MeOH. The pure PNIPAm and PAA homopolymers provided values of T_g of 140 and 130 °C, respectively. The much lower value of T_g for PAA synthesized in scCO$_2$ than for that synthesized in MeOH was presumably due to the very low value of [η] (i.e., low molecular weight) of the PAA homopolymer synthesized from scCO$_2$ (Table 1). Again, these PNIPAm-*co*-PAA random copolymers exhibited values of T_g (from 142 to 163 °C) significantly higher than those of the individual homopolymers, implying strong intermolecular hydrogen bonding. We calculated values of k and q of 1 and 120, respectively, from the Kwei equation, as displayed in Fig. 4(B) (red line). The values of T_g of the PNIPAm-*co*-PAA random copolymers prepared in scCO$_2$ were higher than those of the copolymers prepared in MeOH, even through the molecular weights of the former were lower than those of the latter (Table 1). This phenomenon may have been
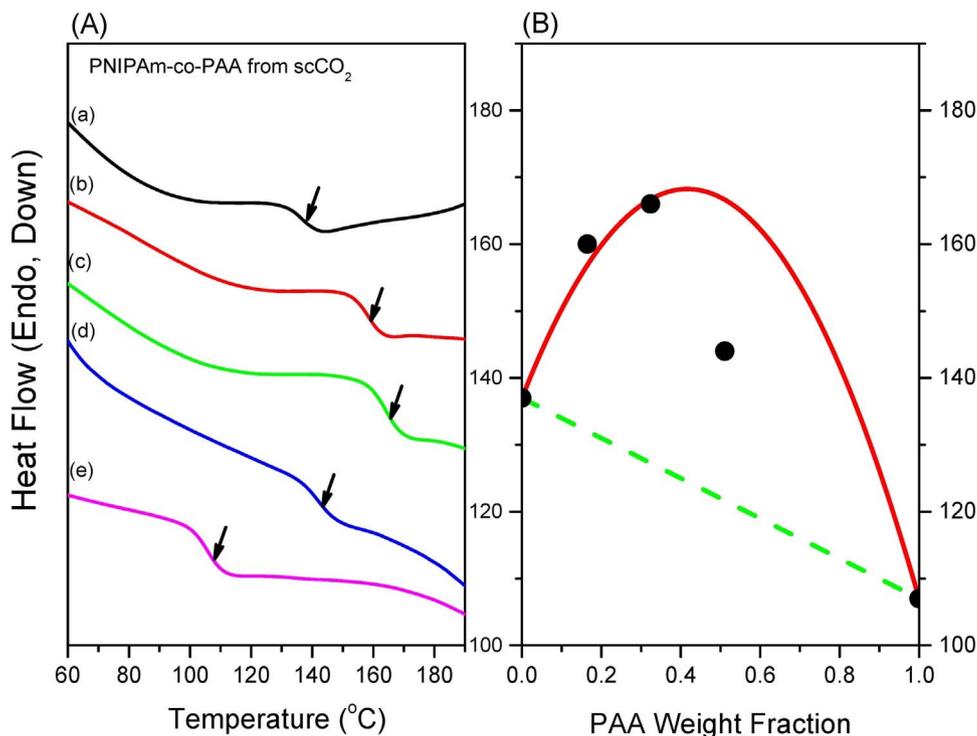
Fig. 3. (A) DSC thermograms of PNIPAm-*co*-PAA random copolymers synthesized in scCO$_2$: (a) pure PNIPAm, (b) PNIPAm76-*co*-PAA24, (c) PNIPAm57-*co*-PAA43, (d) PNIPAm38-*co*-PAA62, (e) pure PAA. (B) Experimental values of T_g (●) and those predicted by the Kwei equation (k = 1, q = 180 for red solid line) and linear rule (green dash line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Self-association of PAA   Self-assoication of PNIPAm   Inter-association of PNIPAm-PAA
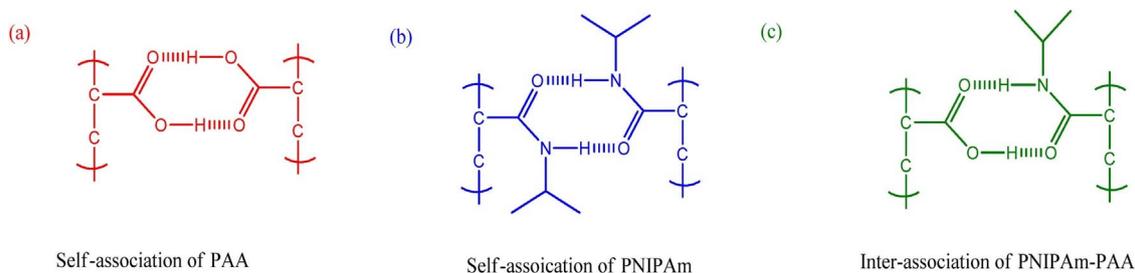
Scheme 2. Hydrogen bonding interactions in PNIPAm-*co*-PAA random copolymers: (a) self-association of PAA segments, (b) self-association of PNIPAm segments, and (c) inter-association between PNIPAm and PAA segments.
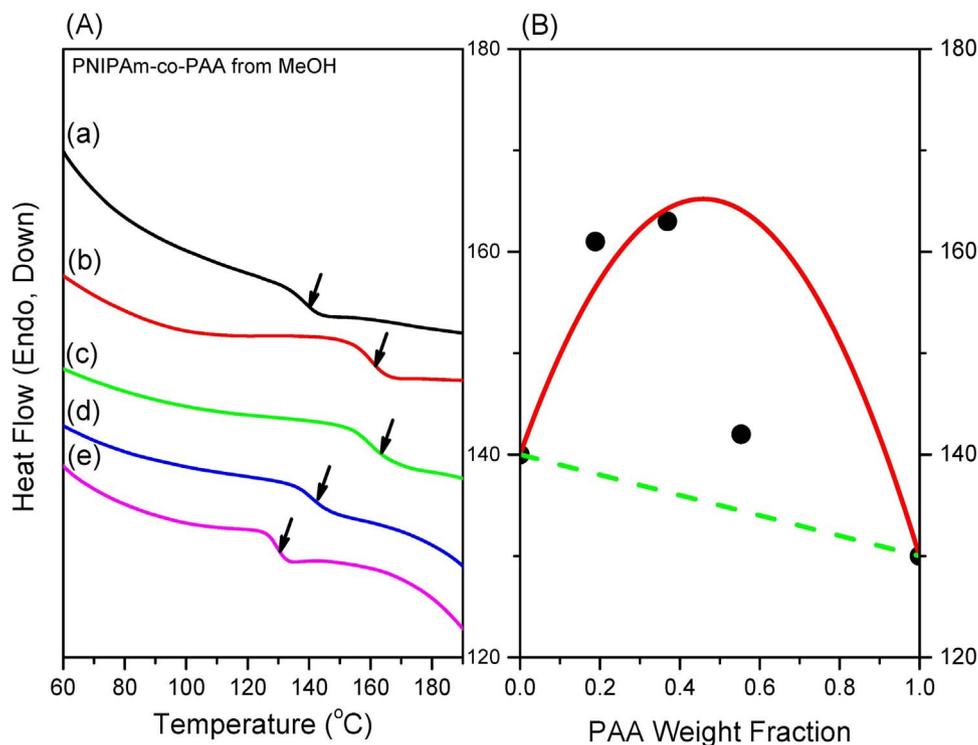
Fig. 4. (A) DSC thermograms of PNIPAm-*co*-PAA random copolymers synthesized in MeOH: (a) pure PNIPAm, (b) PNIPAm73-*co*-PAA27, (c) PNIPAm52-*co*-PAA48, (d) PNIPAm34-*co*-PAA66, (e) pure PAA. (B) Experimental values of T_g (●) and those predicted by the Kwei equation ($k = 1$, $q = 120$ for red solid line) and linear rule (green dash line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

caused by the different sequence length distributions of the AA units in these random copolymers. The more highly alternating sequences in the PNIPAm-*co*-PAA random copolymers prepared in scCO$_2$ (determined from the relatively lower reactivity ratio of r_{PAA} in Fig. 2) imply higher fractions of intermolecular hydrogen bonding interactions, as we have discussed previously [19,23].

To confirm this hypothesis, Figs. 5 and 6 display FTIR spectra of PNIPAm-*co*-PAA random copolymers prepared in scCO$_2$ and MeOH, respectively. In Figs. 5 (A) and 6 (A), the spectra of both pure PAA homopolymers feature broad peaks from 2500 to 3500 cm^{-1}, due to self-association (dimer) hydrogen bonding of COOH units. The spectrum of the pure PNIPAm homopolymer prepared in scCO$_2$ features two obvious peaks at 3290 and 3433 cm^{-1}, corresponding to the self-association hydrogen-bonded and free NH units, respectively; the spectrum of the pure PNIPAm homopolymer prepared in MeOH displays these two peaks at 3304 and 3437 cm^{-1}, respectively. The intensity of the signal for the free NH units decreased and the signal for the self-association hydrogen-bonded NH units shifted to higher wavenumber (to 3359 cm^{-1} for the copolymers prepared in scCO$_2$; to 3356 cm^{-1} for the copolymers prepared in MeOH) upon increasing the AA compositions in both PNIPAm-*co*-PAA random copolymers. This result suggests a switch from self-associated hydrogen-bonded NH···O=C units of the PNIPAm moieties (Scheme 2(b)) to intermolecularly hydrogen bonded NH···O=C units (Scheme 2(c)).

Figs. Fig. 55 (B) and Fig. 66 (B) display the C=O group absorptions

in the FTIR spectra of the PNIPAm-*co*-PAA random copolymers prepared in scCO$_2$ and MeOH, respectively. The spectrum of the pure PNIPAm homopolymer features two absorption signals near 1643 and 1535 cm^{-1}, representing the amide I and amide II absorption modes, respectively, while that of the pure PAA homopolymer has a main peak near 1720 cm^{-1} representing self-association (dimer) hydrogen bonding of COOH units. The amide I absorption unit was split into two signals corresponding to the free amide I units (ca. 1643 cm^{-1}) and amide I units of the PNIPAm segments (ca. 1621 cm^{-1}) involved in intermolecular hydrogen bonding with the carboxyl groups of the PAA segments (Scheme 2(c)). This signal at 1621 cm^{-1} (Scheme 2(c)) was observed upon increasing the AA composition for the polymers prepared in both media. In addition, the amide II absorption at 1535 cm^{-1} shifted to 1549 cm^{-1} upon increasing the AA compositions of the copolymers prepared in both media. The signal from the self-associated (dimer) hydrogen bonded COOH units of the PAA segments also shifted to lower wavenumber (to 1712 cm^{-1}), again representing a switch to intermolecularly hydrogen bonded C=O units of the PNIPAm and PAA segments (Scheme 2(c)). For convenience, to calculate the fractions of intermolecularly hydrogen bonded amide units of the PNIPAm-*co*-PAA random copolymers prepared in scCO$_2$ and MeOH, we split these C=O units into four signals (Fig. 7): (a) COOH units (1712–1720 cm^{-1}), (b) free amide I units (ca. 1643 cm^{-1}), (c) intermolecular amide I units (ca. 1621 cm^{-1}), and (d) amide II units (1535–1549 cm^{-1}); Fig. 8 summarizes the fraction of each. The fraction of hydrogen-bonded amide I
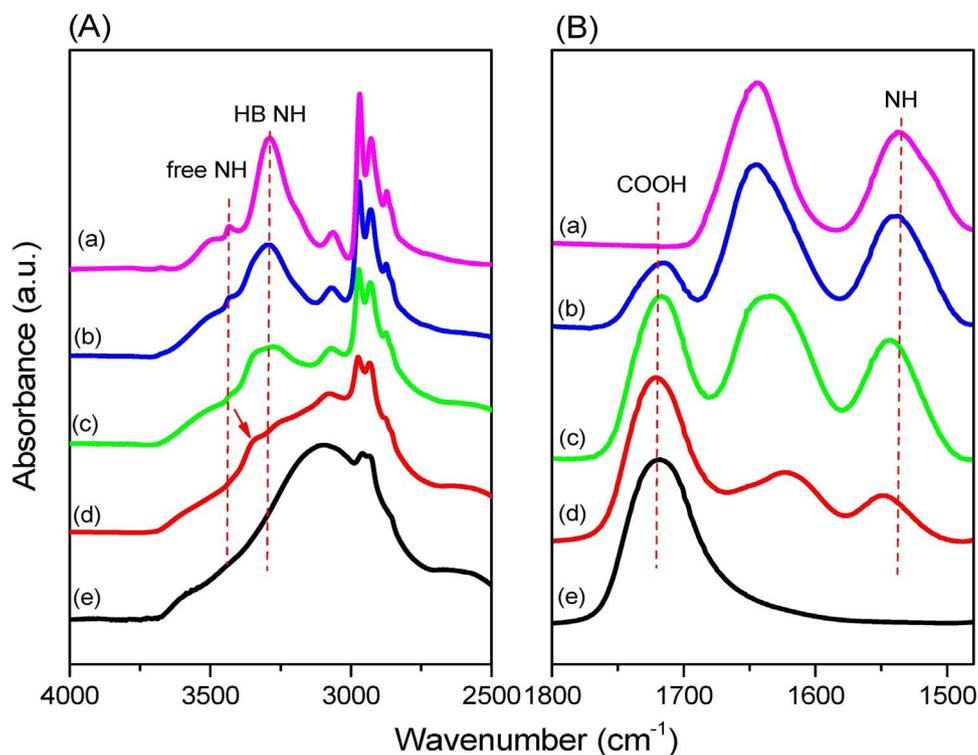
Fig. 5. (A) NH and (B) C=O vibration regions in the FTIR spectra of PNIPAm-*co*-PAA random copolymers synthesized in scCO$_2$: (a) pure PNIPAm, (b) PNIPAm76-*co*-PAA24, (c) PNIPAm57-*co*-PAA43, (d) PNIPAm38-*co*-PAA62, (e) pure PAA.

units increased upon increasing the AA composition in both types of PNIPAm-*co*-PAA random copolymer; these strong intermolecular hydrogen bonds would enhance the glass transition temperatures of the random copolymers, based on the Kwei equation. In addition, the fraction of hydrogen-bonded amide I units of the PNIPAm-*co*-PAA random copolymers prepared in scCO$_2$ was higher than that of the corresponding random copolymers prepared in MeOH for all PAA compositions; thus, the values of T_g for the PNIPAm-*co*-PAA random

copolymers prepared in scCO$_2$ were higher than those of the corresponding random copolymers prepared in MeOH.

3.3. LCSTs of poly(NIPAm-co-AA) copolymers prepared in scCO$_2$ and in MeOH

PNIPAm is a temperature-sensitive polymer having an LCST near 32 °C [24,25]. In this study, we investigated the dependence of the
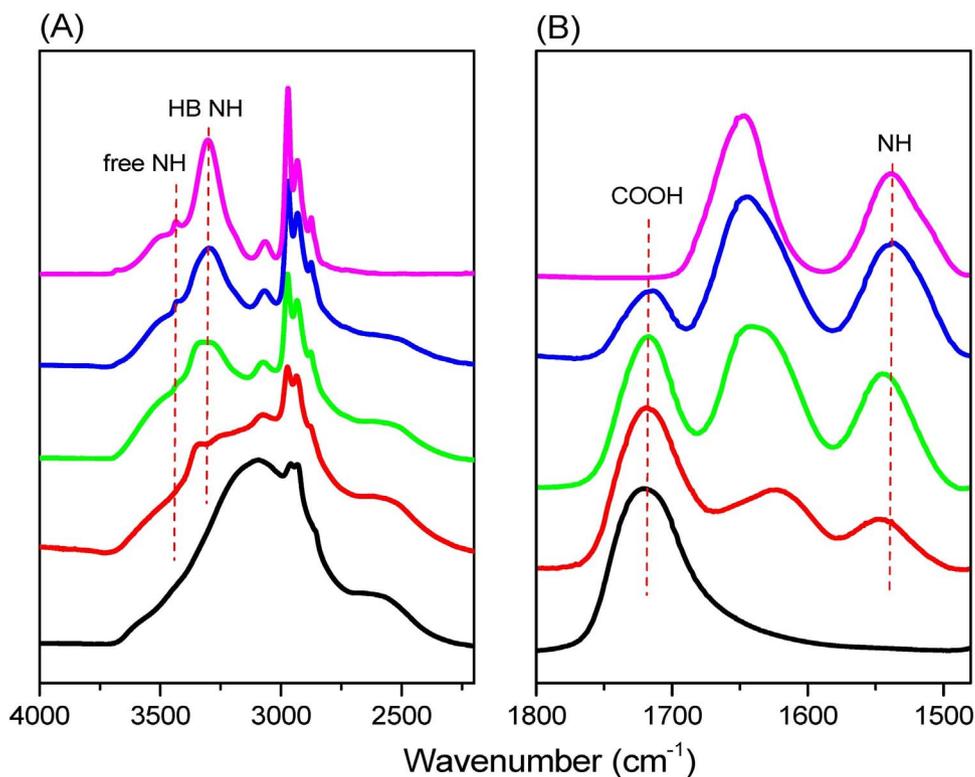
Fig. 6. (A) NH and (B) C=O vibration regions in the FTIR spectra of PNIPAm-*co*-PAA random copolymers synthesized in MeOH: (a) pure PNIPAm, (b) PNIPAm73-*co*-PAA27, (c) PNIPAm52-*co*-PAA48, (d) PNIPAm34-*co*-PAA66, (e) pure PAA.
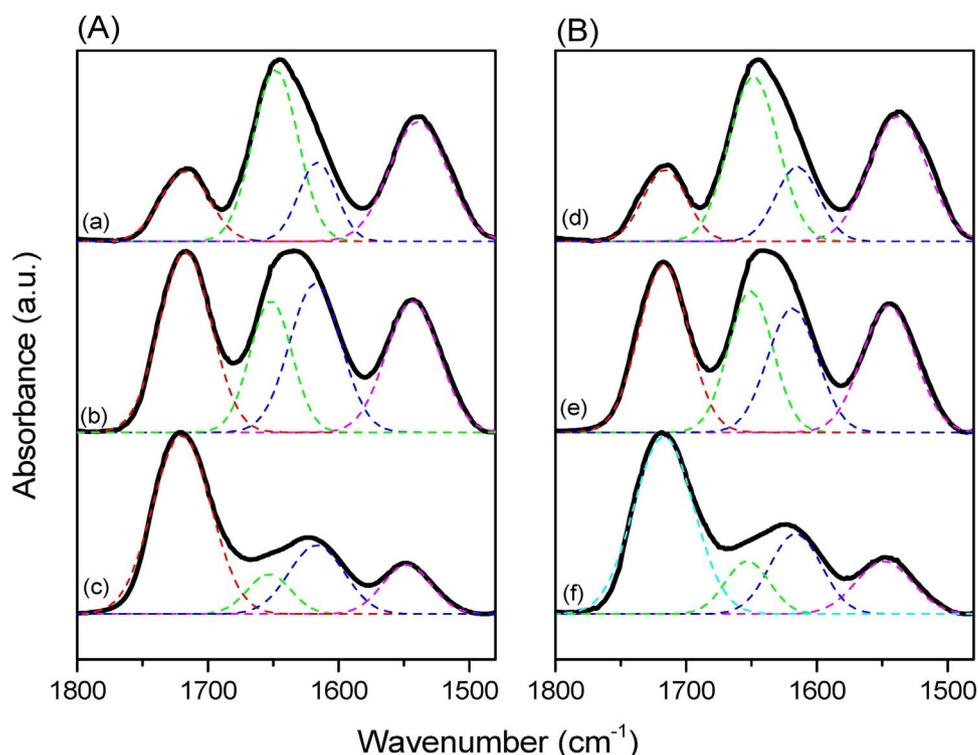
Fig. 7. Curve-fitting results of PNIPAm-*co*-PAA random copolymers synthesized in (A) scCO$_2$ [(a) PNIPAm76-*co*-PAA24, (b) PNIPAm57-*co*-PAA43, (c) PNIPAm38-*co*-PAA62] and (B) MeOH [(d) PNIPAm73-*co*-PAA27, (e) PNIPAm52-*co*-PAA48, (f) PNIPAm34-*co*-PAA66].
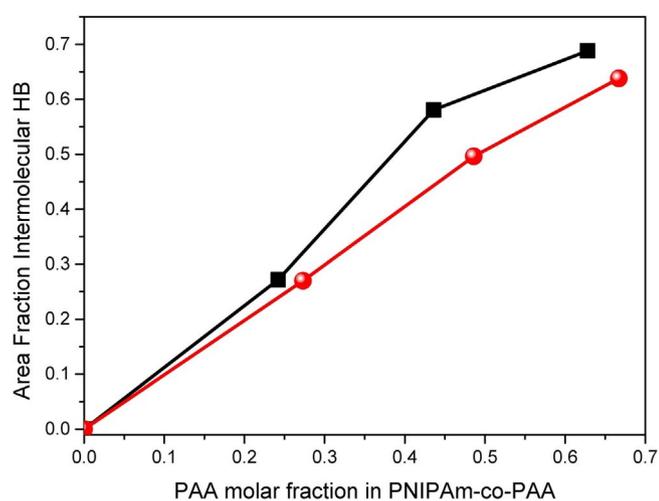
Fig. 8. Area fractions of intermolecularly hydrogen bonded (HB) amide I groups of PNIPAm-*co*-PAA random copolymers synthesized in scCO$_2$ (■) and MeOH (●).

Fig. 9. Visible light transmittance at 500 nm, plotted with respect to temperature, of aqueous solutions (pH 4) of PNIPAm-*co*-PAA copolymers (3 wt%) synthesized in scCO$_2$ [(●) PNIPAm76-*co*-PAA24, (■) PNIPAm57-*co*-PAA43] and in MeOH [(▼) PNIPAm73-*co*-PAA27, (▲) PNIPAm52-*co*-PAA48].

LCST on the composition of the copolymers, in aqueous solutions at pH 4, prepared at feed ratios of 75/25 and 50/50 in scCO$_2$ and MeOH. The copolymers synthesized at a feed ratio of 25/75 were not included for this study because they did not exhibit a phase transition (i.e., no LCST) in aqueous solutions at pH 4. The LCST of poly(NIPAm-*co*-AA) prepared at a 75/25 feed ratio was 28.9 °C (Fig. 9); it was lower than that (ca. 32 °C) for the PNIPAm homopolymer. We suspect that the very low value of [η] (i.e., very low molecular weight) of the copolymer (Table 1) meant that it could readily and efficiently form intermolecular hydrogen bonds between its NIPAm and AA units in different copolymer chains, leading to a decrease in the LCST. A similar discussion of the formation of hydrogen bonds between NIPAm and AA units to lower the LCST of copolymers has been reported previously [11].

The pH of the aqueous solution of the purified copolymer was near 2. The AA units in the copolymer would ionize at pH 4, resulting in the copolymer becoming more hydrophilic than it was near pH 2. Therefore, as expected, the LCST of the PNIPAm-*co*-PAA copolymers in

aqueous solutions at pH 4 increased upon increasing the AA composition in the copolymer (Fig. 9). The LCST for the copolymer synthesized in scCO$_2$ increased from 28.9 to 44.4 °C upon increasing the AA feed ratio from 25 to 75%; for the copolymer synthesized in MeOH, the corresponding increase was from 32.9 to 48.0 °C. For both feed ratios, the LCST of the copolymer synthesized in MeOH was higher than that for the copolymer synthesized in scCO$_2$. We attribute this behavior to the higher contents of hydrophilic AA units (27.3 and 48.6 mol%) in the copolymers synthesized in MeOH than those (24.2 and 43.6 mol%) in the copolymers synthesized in scCO$_2$ (Table 1).

At temperatures below the LCST, the copolymer synthesized in scCO$_2$ (having a relatively low LCST) exhibited relatively low transmittance for its aqueous solutions, as is evident in Fig. 9 where it exhibited approximately 60% transmittance while the copolymer in MeOH exhibited over 80% transmittance for its aqueous solution. The formation of stronger intermolecular hydrogen bonds between the

amide groups of the NIPAm units and the carboxyl groups of the AA units (as in Fig. 8) might be responsible for the relatively low transmittance of the aqueous solutions of the copolymers prepared in scCO$_2$. This observation suggests that the copolymer prepared in scCO$_2$ had a more highly alternating copolymer sequence, allowing strong intermolecular hydrogen bonding to occur more readily between the amide groups of the NIPAm units and the carboxyl groups of the AA units.

4. Conclusions

The yields and values of M_w of copolymers of NIPAm and AA synthesized through radical-initiated copolymerizations at 55 °C, in the absence of a surfactant, in scCO$_2$ at 27.6 MPa were lower than those of the corresponding copolymers prepared in MeOH. The lower reactivity of the AA monomer in scCO$_2$ than in MeOH appears to be responsible for the lower yields, values of M_w, and AA contents of the copolymers prepared in scCO$_2$. The reactivity of the AA monomer in scCO$_2$ increased upon decreasing the scCO$_2$ pressure from 27.6 to 13.8 MPa. The LCSTs of the copolymers synthesized in scCO$_2$ were lower than those of the copolymers prepared in MeOH. In both media, the values of T_g of the copolymers were highest when prepared at a 50/50 feed ratio, presumably because of the stronger intermolecular hydrogen bonds between the amide groups of the NIPAm units and the carboxyl groups of the AA units, relative to those of the amide groups in the pure PNIPAm homopolymer and those of the carboxyl groups in the pure PAA homopolymer. The copolymers prepared with feed ratios of 50/50 and 25/75 in scCO$_2$ both exhibited values of T_g much higher than those of the corresponding copolymers prepared in MeOH, presumably because of the more highly alternating sequences of NIPAm and AA units in the copolymers prepared in scCO$_2$.

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