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

Yeong-Tarng Shieh[a],*, Bo-Hong Chen[a], Tzong-Liu Wang[a], Shiao-Wei Kuo[b],*

[a] *Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 81148, Taiwan*
[b] *Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan*

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ABSTRACT

Radical copolymerizations of *N*-isopropylacrylamide (NIPAm) with acrylic acid (AA) initiated by azobisisobutyronitrile in supercritical carbon dioxide (scCO₂, 55 °C, 27.6 MPa) were compared with those performed in MeOH at 55 °C. The AA compositions of the copolymers in scCO₂ were lower than those of the copolymers in MeOH and they increased upon decreasing the pressure of scCO₂ 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 scCO₂, 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 (scCO₂) 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 scCO₂ with that in methanol (MeOH) [8]. The precipitation polymerizations of NIPAm in scCO₂ 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 scCO₂ 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 scCO₂. Here, we compared the copolymerizations performed in scCO₂ 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 scCO₂ (27.6 MPa) and in MeOH.
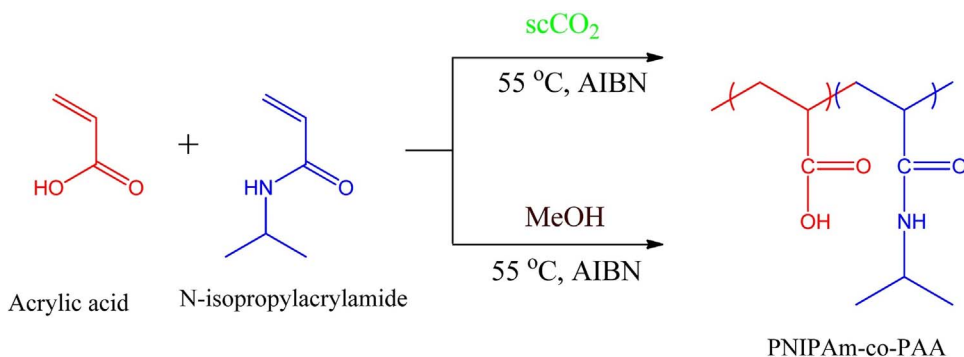
2. Experimental

2.1. Free radical copolymerizations of NIPAm and AA monomers in scCO₂ 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

Acrylic acid   N-isopropylacrylamide

PNIPAm-co-PAA

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_2O. 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_2O (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 ($[\eta]$), 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 $[\eta] = 2.99 \times 10^{-2} M_w^{0.64}$ [15] and $[\eta] = 1.46 \times 10^{-2} M_w^{0.8}$ [16], respectively. The intrinsic viscosities ($[\eta]$) 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

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

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

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_2O. Thus, we used an Ubbelohde viscometer to obtain the