



CrossMark  
click for updates

Cite this: *RSC Adv.*, 2016, 6, 75032

Received 21st June 2016  
Accepted 3rd August 2016

DOI: 10.1039/c6ra16113h

www.rsc.org/advances

## Carbon dioxide affects the phase transition of poly(*N*-isopropylacrylamide)<sup>†</sup>

Yeong-Tarng Shieh,<sup>\*a</sup> Ting-Yu Zhou<sup>a</sup> and Shiao-Wei Kuo<sup>\*b</sup>

The effects of atmospheres of CO<sub>2</sub> and N<sub>2</sub> on the lower critical solution temperature (LCST) of poly(*N*-isopropylacrylamide) (PNIPAAm) in aqueous solution have been investigated using high-pressure differential scanning calorimetry (HP-DSC). In the absence of CO<sub>2</sub> and N<sub>2</sub>, the phase transition—from the hydrated to dehydrated state—of PNIPAAm in aqueous solution was characterized by an endothermic peak near 30.5 °C, namely the LCST. This endothermic peak shifted to relatively lower temperature upon increasing the pressure of CO<sub>2</sub>, but shifted slightly to higher temperature under a higher pressure of N<sub>2</sub>. This behavior appears to be associated with the CO<sub>2</sub> molecules displacing the H<sub>2</sub>O molecules from around the amide groups of PNIPAAm upon increasing the pressure, thereby enhancing the formation of intramolecular hydrogen bonds between the amide groups; in contrast, increasing the N<sub>2</sub> pressure strengthened the interactions of H<sub>2</sub>O with the apolar isopropyl and amide groups. Despite the difference in the effects of CO<sub>2</sub> and N<sub>2</sub> on the LCST, higher pressures of CO<sub>2</sub> and N<sub>2</sub> both led to more positive changes in enthalpy ( $\Delta H$ ) for the phase transition per mole of NIPAAm units. The higher values of  $\Delta H$  at higher CO<sub>2</sub> pressures presumably resulted from the formation of strong intramolecular hydrogen bonds. For a given CO<sub>2</sub> pressure, the value of  $\Delta H$  was less positive at higher concentrations of PNIPAAm, suggesting a lesser degree of disruption of hydrogen bonds during its HP-DSC heating scans. Under a given pressure of CO<sub>2</sub>, the addition of a salt (NaCl, KCl, KBr) led to a further decrease in the LCST and the value of  $\Delta H$  of the aqueous PNIPAAm solution, due to the salt ions coordinating H<sub>2</sub>O molecules.

### Introduction

Poly(*N*-isopropylacrylamide) (PNIPAAm) is soluble in water and adopts a coil conformation at relatively low temperature, whereas it is insoluble and has a globule conformation at temperatures higher than its lower critical solution temperature (LCST, *ca.*

32 °C).<sup>1–5</sup> The coil–globule phase transition of PNIPAAm in aqueous solution at the LCST is an endothermic process that can be observed in DSC heating curves;<sup>6,7</sup> it results from dehydration of ordered H<sub>2</sub>O molecules around the polar amide and apolar isopropyl groups. The Maeda<sup>8</sup> and Sun<sup>9</sup> groups used Fourier transform infrared (FTIR) spectroscopic analyses to investigate the dehydration of the isopropyl groups at higher temperatures, observing the shift to lower wavenumbers of the asymmetric C–H stretching band of the isopropyl groups. Maeda *et al.*<sup>8</sup> also found that dehydration of the polar amide groups occurred at temperatures above the LCST, but most of the C=O functionalities (*ca.* 87%) in the amide groups of PNIPAAm in the globule state remained hydrogen-bonded with H<sub>2</sub>O molecules while the others (*ca.* 13%) formed intra- or interchain hydrogen bonds with the N–H units of PNIPAAm. The addition of metal halide salts (*e.g.*, NaCl, KCl, KBr, KI) can expedite the dehydration, thereby lowering the LCST of PNIPAAm in aqueous solutions.<sup>8,10</sup> These hygroscopic substances are commonly used as salting-out agents to separate less-hydrophilic molecules from H<sub>2</sub>O.

The C=O groups in polymers can interact specifically with CO<sub>2</sub> molecules, leading to much more significant dissolution of CO<sub>2</sub> in these polymers than that of N<sub>2</sub>, which does not interact with C=O groups.<sup>11–13</sup> The presence of CO<sub>2</sub> around the C=O groups of PNIPAAm in aqueous solutions might, therefore, displace H<sub>2</sub>O molecules from around the apolar isopropyl groups and/or the polar amide groups, thereby decreasing the LCST of PNIPAAm. In this study, we used high-pressure differential scanning calorimetry (HP DSC) to monitor the effect of CO<sub>2</sub> on the LCST behavior of PNIPAAm aqueous solutions with respect to the CO<sub>2</sub> pressure. For comparison, we also examined the effects of the N<sub>2</sub> pressure and hygroscopic salts (metal halides) on the phase transitions of PNIPAAm aqueous solutions.

### Experimental section

#### PNIPAAm

The PNIPAAm polymer was prepared through free radical polymerization of NIPAAm monomer (Tokyo Kasei) using

<sup>a</sup>Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 811, Taiwan. E-mail: yts@nuk.edu.tw

<sup>b</sup>Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan. E-mail: kuosw@faculty.nsysu.edu.tw

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra16113h

azobis(isobutyronitrile) (AIBN, Aldrich) as the free radical initiator. To prepare low-molecular-weight PNIPAAm, the purified NIPAAm monomer and AIBN (molar ratio: 50 : 1) were dissolved in MeOH and heated at 55 °C for 2 h under a N<sub>2</sub> atmosphere; the total concentration of NIPAAm and AIBN was 2.2 M. To prepare high-molecular-weight PNIPAAm, a homogeneous reactant mixture (NIPAAm/AIBN molar ratio: 40 : 1) was loaded in an 8 mL vial and then placed in a 200 mL high-pressure vessel. CO<sub>2</sub> was loaded into the high-pressure vessel and the free radical polymerization of NIPAAm was conducted under a CO<sub>2</sub> pressure of 27.6 MPa at 55 °C for 8 h. After polymerization, the vessel was depressurized and the settled product inside the vial was subjected to purification as described previously.<sup>14</sup> Using an Ubbelohde viscometer, the intrinsic viscosity ( $[\eta]$ ) was measured; the molecular weight was calculated using the equation<sup>15</sup>

$$[\eta] = 2.99 \times 10^{-2} M_w^{0.64}$$

The calculated molecular weights of the low- and high-molecular-weight PNIPAAm samples were  $3.90 \times 10^5$  and  $1.13 \times 10^6$  g mol<sup>-1</sup>, respectively.

### HP-DSC measurements of phase transitions of aqueous PNIPAAm solutions

Certain amounts of PNIPAAm were dissolved in deionized water to prepare aqueous PNIPAAm solutions having concentrations of 1.5, 5, and 10 wt%. A portion (*ca.* 5 mg) of the aqueous solution was taken (micropipette) and placed into an aluminum sample pan and weighed; the pan loaded without a lid was into the heating chamber of a HP-DSC apparatus (HP DSC-Q20p, TA Instruments). The chamber was then purged with CO<sub>2</sub> for 5 min before heating under CO<sub>2</sub> at pressures of 0.69, 1.38, 2.07, 2.76, 3.45, and 4.14 MPa while increasing the temperature from 20 to 40 °C at a rate of 2 °C min<sup>-1</sup>. For comparison, the HP-DSC apparatus was also purged with N<sub>2</sub> for 5 min before heating under N<sub>2</sub> at pressures of 1.38 and 2.76 MPa while increasing the temperature from 20 to 40 °C at a rate of 2 °C min<sup>-1</sup>. The peak temperature and area of the endothermic peak in the first heating curve of each sample were recorded and taken to be the LCST and enthalpy, respectively, of the phase transition of the PNIPAAm aqueous solution. A 5 wt% PNIPAAm aqueous solution containing 1 wt% of a salt (KBr, KCl, or NaCl) was also heated under CO<sub>2</sub> at various pressures in the HP-DSC apparatus to investigate the effects of salts on the phase transitions of aqueous PNIPAAm solutions.

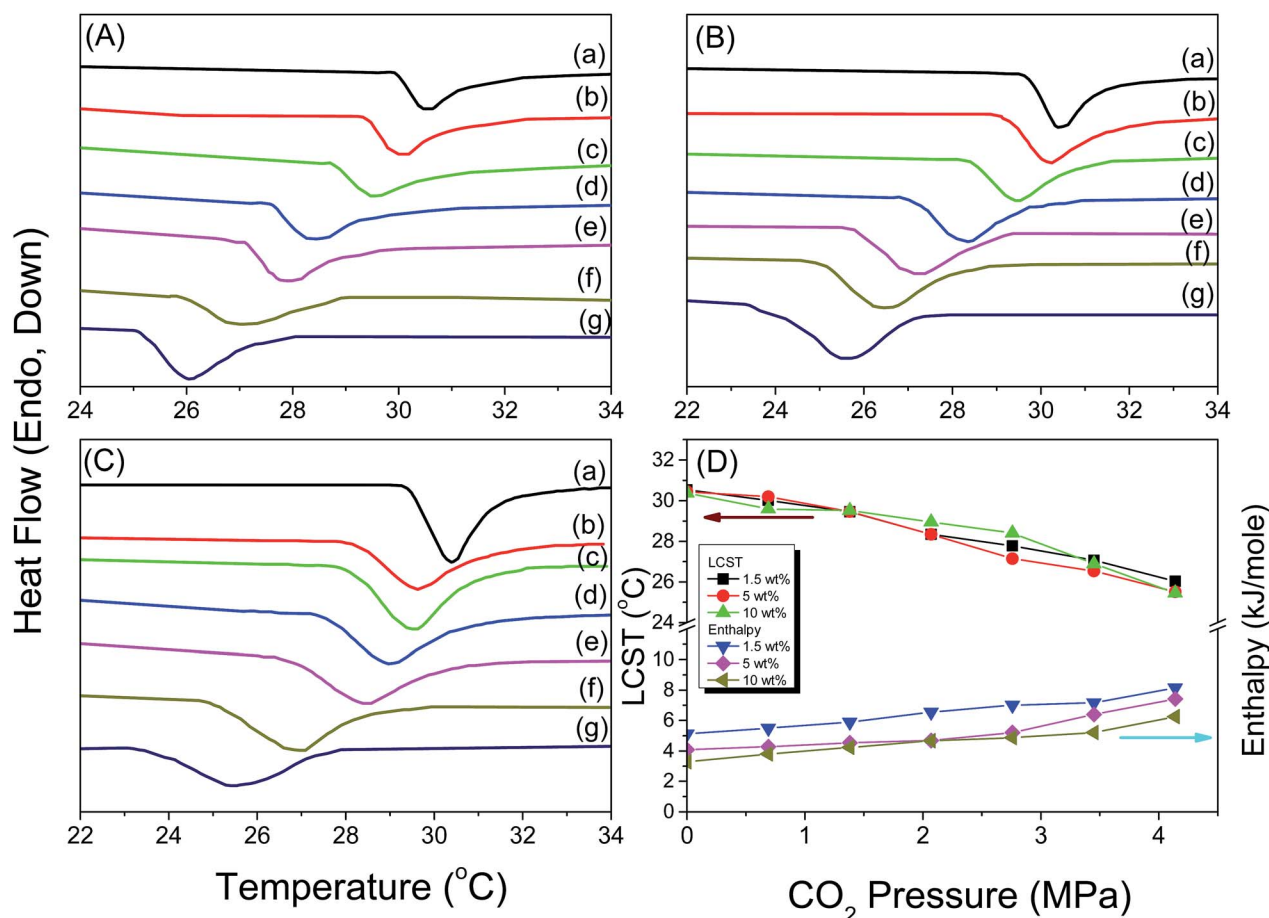


Fig. 1 (A–C) HP-DSC first-heating curves (2 °C min<sup>-1</sup>) of (A) 1.5, (B) 5, and (C) 10 wt% aqueous PNIPAAm solutions under CO<sub>2</sub> at pressures of (a) 0, (b) 0.69, (c) 1.38, (d) 2.07, (e) 2.76, (f) 3.45, and (g) 4.14 MPa. (D) Summary of the corresponding LCSTs and values of  $\Delta H$ .

## Results and discussion

### Effects of CO<sub>2</sub> and N<sub>2</sub> on LCST behavior of aqueous PNIPAAm solutions

Fig. 1 and 2 present the HP-DSC first heating curves for aqueous PNIPAAm solutions of 1.5, 5, and 10 wt% in CO<sub>2</sub> and N<sub>2</sub>, respectively, at various pressures. An endothermic peak appears in every heating scan, corresponding to the coil-to-globule phase transition<sup>16</sup> of the aqueous PNIPAAm solution from the dissolved state to the turbid state.<sup>6,7</sup> For PNIPAAm solutions with different concentrations without CO<sub>2</sub>, the peaks were *ca.* 30.5 °C and the peak in Fig. 1(A)–(C) shifted to lower temperatures upon increasing the CO<sub>2</sub> pressure; in contrast, it remained almost unchanged upon increasing the pressure of N<sub>2</sub>, as revealed in Fig. 2(A)–(C). In other words, the LCST of aqueous PNIPAAm solutions could decrease upon increasing the CO<sub>2</sub> pressure, but slightly increase upon increasing the N<sub>2</sub> pressure.

Because the C=O groups in polymers can interact specifically with CO<sub>2</sub>,<sup>11</sup> but not with N<sub>2</sub>, the dissolution of CO<sub>2</sub> in such polymers can be much greater than that of N<sub>2</sub>.<sup>12,13</sup> Fig. 1(D) reveals that the LCSTs of the aqueous PNIPAAm solutions clearly decreased upon increasing the pressure of CO<sub>2</sub> at various concentrations. In contrast, the LCST increased slightly upon increasing the N<sub>2</sub> pressures, as displayed in Fig. 2(D). This behavior can be attributed to CO<sub>2</sub>, but not N<sub>2</sub>, displacing the H<sub>2</sub>O molecules around the apolar isopropyl

groups and/or the polar amide groups in PNIPAAm. Upon increasing the CO<sub>2</sub> pressure, the displacement of H<sub>2</sub>O molecules increased and the formation of intramolecular hydrogen bonds between the amide groups in PNIPAAm was, thereby, promoted, leading to a decrease in its LCST. Upon increasing the N<sub>2</sub> pressure, the increase in the LCST might be attributable to the pressure effect of N<sub>2</sub>: enhancing the interactions of H<sub>2</sub>O with the apolar isopropyl and polar amide groups of PNIPAAm and, thereby, promoted the solvation and/or hydrogen bonding of these groups with H<sub>2</sub>O, leading to an increase in the LCST. Scheme 1 summarizes the possible interactions of PNIPAAm in aqueous solutions under N<sub>2</sub> and CO<sub>2</sub>.

### Effects of CO<sub>2</sub> and N<sub>2</sub> on value of $\Delta H$ of phase transition of PNIPAAm solution

Fig. 1(D) and 2(D) and Table S1† summarize the enthalpy changes ( $\Delta H$ ) and LCST behavior of the coil-to-globule phase transitions of aqueous PNIPAAm solutions at three different concentrations, as measured through HP-DSC under various pressures of CO<sub>2</sub> and N<sub>2</sub>, respectively. The coil-to-globule phase transition of PNIPAAm in H<sub>2</sub>O upon heating is an endothermic process resulting from disruption of the interactions of H<sub>2</sub>O with the apolar isopropyl groups and the hydrogen bonds of H<sub>2</sub>O with the polar amide groups. Despite the difference in the effects of the pressure of CO<sub>2</sub> and N<sub>2</sub> on their LCST as discussed

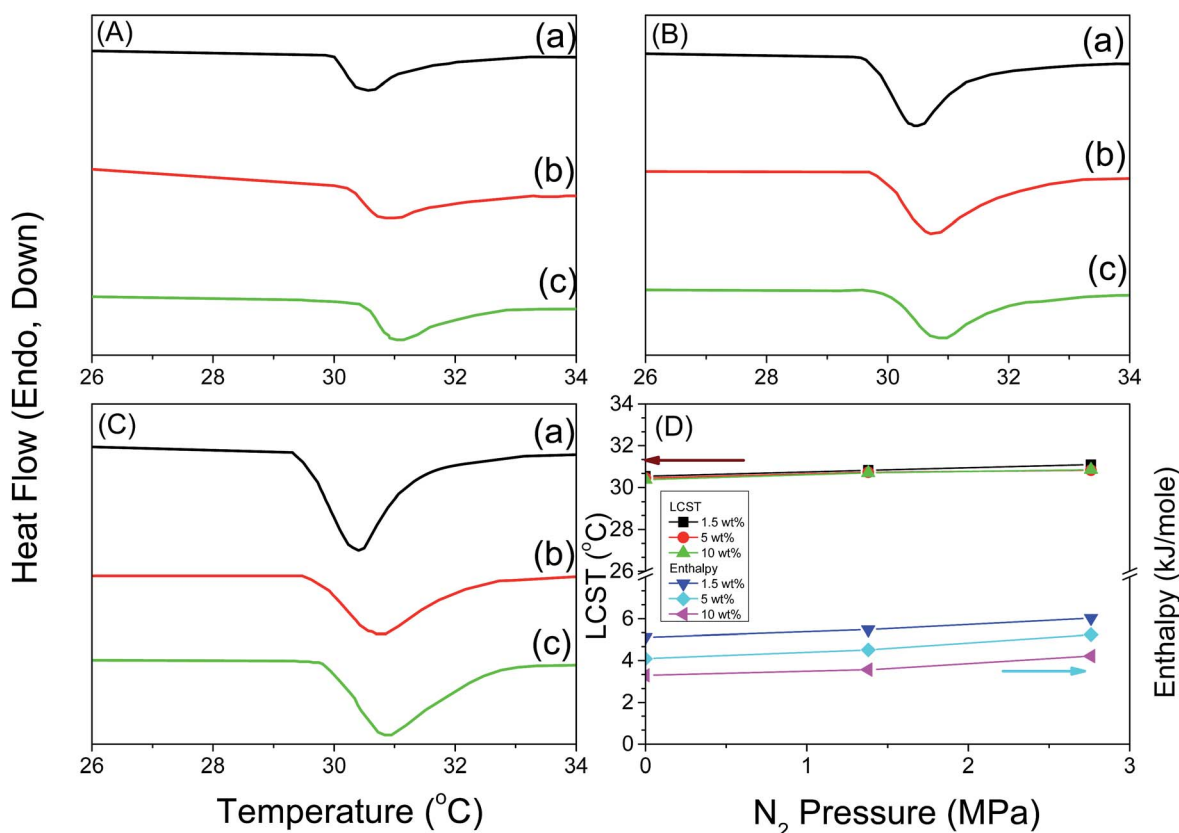
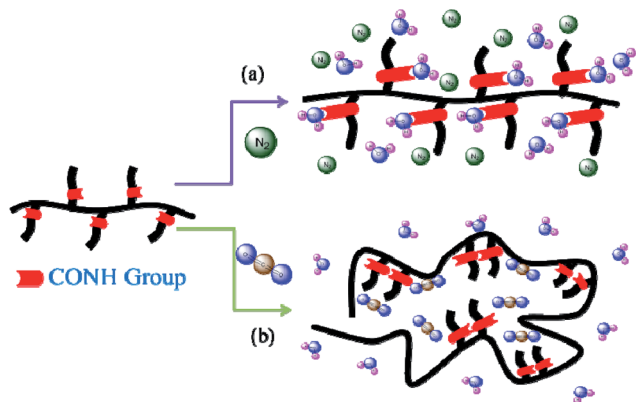


Fig. 2 (A–C) HP-DSC first-heating curves (2 °C min<sup>-1</sup>) of (A) 1.5, (B) 5, and (C) 10 wt% aqueous PNIPAAm solutions under N<sub>2</sub> at pressures of (a) 0, (b) 1.38, and (c) 2.76 MPa. (D) Summary of the corresponding LCSTs and values of  $\Delta H$ .



Scheme 1 Cartoon representation of the possible interactions of PNIPAAm under (a) N<sub>2</sub> and (b) CO<sub>2</sub> atmospheres.

above, relatively high pressures of CO<sub>2</sub> and N<sub>2</sub> both led to more positive values of  $\Delta H$  for the phase transition per mole of NIPAAm units. Because the LCST of the aqueous PNIPAAm solution decreased upon increasing the pressure of CO<sub>2</sub>, we were surprised that a higher CO<sub>2</sub> pressure provided a more positive value of  $\Delta H$  for the phase transition of PNIPAAm. This finding suggests that although the displacement of H<sub>2</sub>O molecules by CO<sub>2</sub> molecules led to a decrease in LCST, the formation

of intramolecular hydrogen bonds among the amide groups was promoted under CO<sub>2</sub>, thereby increasing the value of  $\Delta H$  upon increasing the CO<sub>2</sub> pressure. For a given pressure of CO<sub>2</sub> or N<sub>2</sub>, the endothermic value of  $\Delta H$  was lower at higher concentrations of PNIPAAm, as is evident in Fig. 1(d) and 2(d). This behavior might be associated with less disruption of the hydrogen bonds during the heating of PNIPAAm at higher concentrations.

#### Effect of salts on LCST and value of $\Delta H$ of phase transition of PNIPAAm solution

NaCl, KCl, and KBr are hygroscopic salts that can be used as salting-out agents to separate less-hydrophilic molecules from H<sub>2</sub>O. They are soluble in H<sub>2</sub>O and dissociate into their constituent anions and cations, which interact strongly with the positive and negative ends, respectively, of H<sub>2</sub>O dipoles, leading to hygroscopicity in air and rapid dissolution in H<sub>2</sub>O. Fig. 3 displays the variations in the LCSTs of 5 wt% PNIPAAm solutions containing 1 wt% of KBr, KCl, or NaCl, plotted with respect to the pressure of CO<sub>2</sub>. The LCST of each sample decreased upon the addition of each salt at each CO<sub>2</sub> pressure. This behavior is consistent with these salts coordinating to H<sub>2</sub>O molecules and, thereby, decreasing the solvation power of H<sub>2</sub>O molecules to the apolar isopropyl groups and the hydrogen bonding of H<sub>2</sub>O molecules to the polar amide groups of PNIPAAm. In the absence of CO<sub>2</sub>, the solvation power and/or

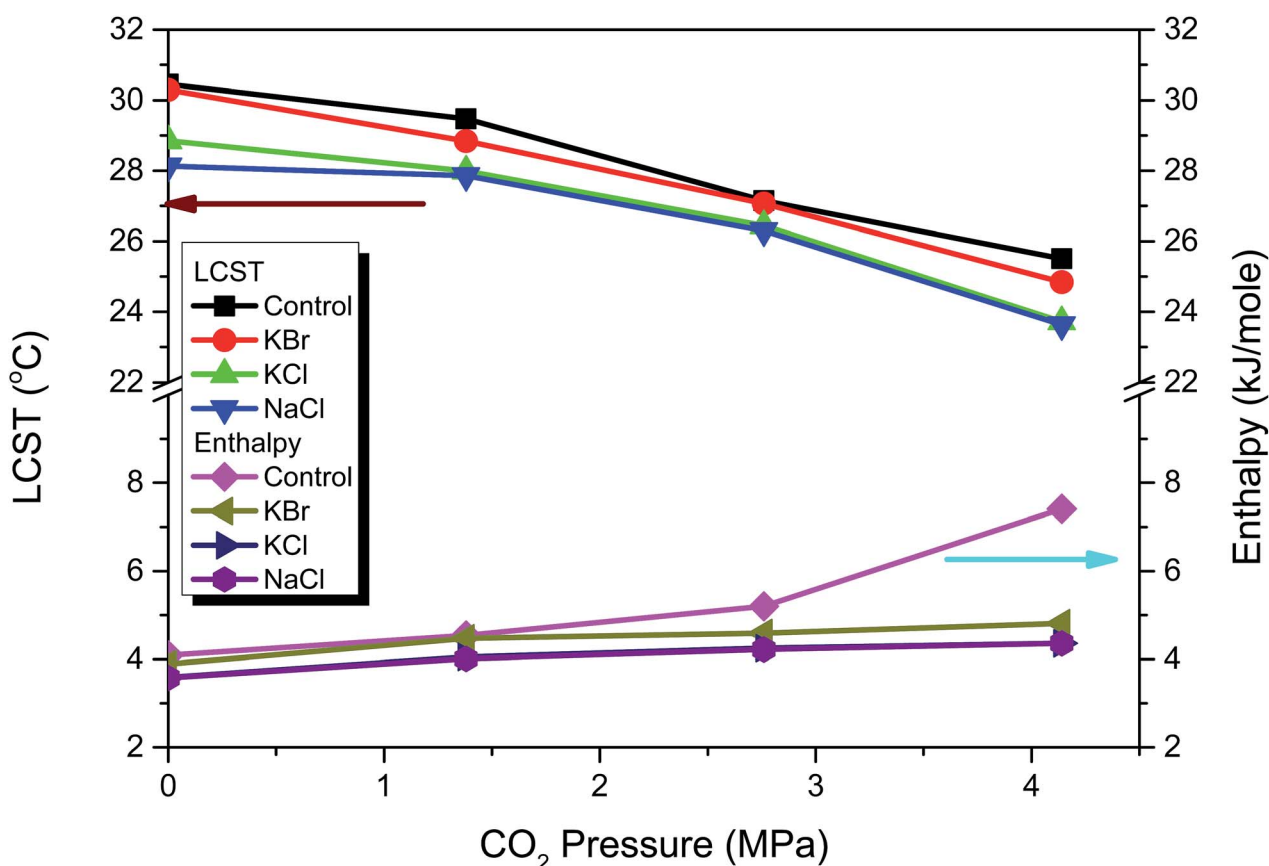


Fig. 3 LCSTs and values of  $\Delta H$  for the phase transitions of 5 wt% aqueous PNIPAAm solutions containing 1 wt% of a salt (KBr, KCl, or NaCl), determined from HP-DSC first-heating scans (2 °C min<sup>-1</sup>) under CO<sub>2</sub> at various pressures.

hydrogen bonding of H<sub>2</sub>O decreased the most in the presence of NaCl, followed by KCl and, to the least extent, KBr. This sequence suggests that NaCl absorbs H<sub>2</sub>O the most and KBr the least, with KCl in between the two extremes. A Na<sup>+</sup> cation is smaller than a K<sup>+</sup> cation, and a Cl<sup>-</sup> anion is smaller than a Br<sup>-</sup> anion. Because the weight concentration of each added salt was 1 wt%, a smaller cation or anion would give a higher molar concentration of the dissociated ions and, thus, a higher ionic strength, resulting in greater absorption of H<sub>2</sub>O molecules.

Fig. 3 and Table S2† also summary the values of  $\Delta H$  for the phase transitions of aqueous PNIPAAm solutions in the presence of these salts. For a given pressure of CO<sub>2</sub>, the endothermic value of  $\Delta H$  decreased upon the addition of a salt. NaCl, with its greatest ionic strength, caused the greatest decrease in the value of  $\Delta H$ , while KBr, of lowest ionic strength, induced the lowest decrease. Upon the addition of a salt, the decrease in the value of  $\Delta H$  for the phase transition of PNIPAAm in aqueous solution indicated greater disruption of the interactions/hydrogen bonds of H<sub>2</sub>O with the apolar isopropyl groups and the polar amide groups of PNIPAAm, suggesting that the H<sub>2</sub>O molecules around the apolar isopropyl groups and the polar amide groups had been absorbed by the added salt. Thus, the decreases in the LCST of PNIPAAm induced by CO<sub>2</sub> or the salts arose through different mechanisms: the CO<sub>2</sub> molecules displacing H<sub>2</sub>O molecules and the salts absorbing H<sub>2</sub>O molecules from around the apolar isopropyl groups and the polar amide groups of PNIPAAm.<sup>17,18</sup>

#### Effect of molecular weight of PNIPAAm on CO<sub>2</sub>-dependent LCST

Two PNIPAAm polymers having different weight-average molecular weights ( $M_w$ ) were used to investigate the effect of molecular weight on the CO<sub>2</sub>-dependent LCST and values of  $\Delta H$  as shown in Table S3.† Fig. 4 reveals that, for both polymers, the LCST decreased and the value of  $\Delta H$  increased upon increasing the pressure of CO<sub>2</sub>. The higher- $M_w$  polymer provided the lower LCST at any CO<sub>2</sub> pressure observed through HP-DSC. The lower

LCST for the higher- $M_w$  PNIPAAm may have arisen from greater entanglement, more intrachain hydrogen bonds, and more hydrophobic interactions; similar phenomena have been reported previously.<sup>19–25</sup> The greater degree of intrachain hydrogen bonding and hydrophobic interactions in the higher- $M_w$  PNIPAAm should lead to less intermolecular hydrogen bonding between PNIPAAm and H<sub>2</sub>O at any CO<sub>2</sub> pressure; if so, less heat would be required to disrupt the intermolecular hydrogen bonds during the phase transition at the LCST. Indeed, the enthalpy change ( $\Delta H = 3.44 \text{ kJ mol}^{-1}$ ) for the phase transition at the LCST for the higher- $M_w$  PNIPAAm was lower than that ( $\Delta H = 4.09 \text{ kJ mol}^{-1}$ ) for the lower- $M_w$  PNIPAAm.

## Conclusions

The interactions of CO<sub>2</sub> with the C=O units of PNIPAAm can displace H<sub>2</sub>O molecules from around the amide groups of PNIPAAm in aqueous solution leading to a decrease in the LCST of the polymer. In contrast, under N<sub>2</sub>, which does not interact with the C=O units of PNIPAAm, the H<sub>2</sub>O molecules can interact more strongly with the apolar isopropyl and polar amide groups of PNIPAAm in aqueous solution, resulting in an increase in the LCST of the polymer. Despite the difference in the effects of CO<sub>2</sub> and N<sub>2</sub> on the shifting LCST, higher pressures of CO<sub>2</sub> and N<sub>2</sub> both led to increases in the endothermic value of  $\Delta H$  for the phase transition of PNIPAAm. The addition of salts (NaCl, KCl, KBr) further decreased the LCST of PNIPAAm in aqueous solution at any CO<sub>2</sub> pressure, due to the absorption of H<sub>2</sub>O by the salts in addition to the displacement of H<sub>2</sub>O molecules by CO<sub>2</sub> molecules.

## Acknowledgements

We thank the Ministry of Science and Technology of Taiwan for supporting this study financially under contract MOST 103-2221-E-390-030.

## References

- 1 C. T. Lai, R. H. Chien, S. W. Kuo and J. L. Hong, *Macromolecules*, 2011, **44**, 6546–6556.
- 2 Y. W. Lai, S. W. Kuo and J. L. Hong, *Langmuir*, 2012, **28**, 15725–15735.
- 3 C. W. Tu and S. W. Kuo, *J. Polym. Res.*, 2014, **21**, 476.
- 4 K. Liu, P. Pan and Y. Bao, *RSC Adv.*, 2015, **5**, 94582–94590.
- 5 J. Gan, X. X. Guan, J. Zheng, H. Guo, K. Wu, L. Liang and M. Lu, *RSC Adv.*, 2016, **6**, 32967–32978.
- 6 C. Boutris, E. G. Chatzi and C. Kiparissides, *Polymer*, 1997, **38**, 2567–2570.
- 7 J. Zhang and N. A. Peppas, *Macromolecules*, 2000, **33**, 102–107.
- 8 Y. Maeda, T. Higuchi and I. Ikeda, *Langmuir*, 2000, **16**, 7503–7509.
- 9 B. J. Sun, Y. N. Lin, P. Y. Wu and H. W. Siesler, *Macromolecules*, 2008, **41**, 1512–1520.
- 10 Y. W. Lai, S. W. Kuo and J. L. Hong, *RSC Adv.*, 2012, **2**, 8194–8200.

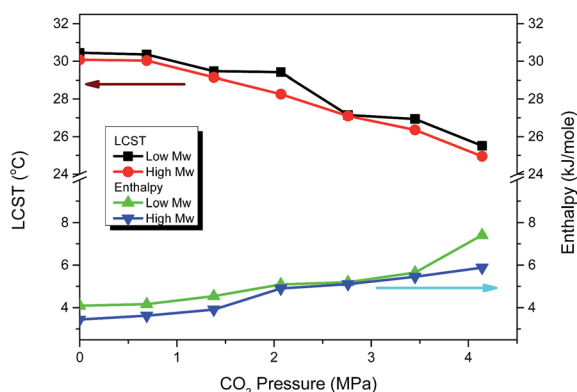


Fig. 4 LCSTs and values of  $\Delta H$  for the phase transitions of 5 wt% aqueous PNIPAAm solutions [weight-average molecular weights:  $0.39 \times 10^6$  (low  $M_w$ ) and  $1.13 \times 10^6$  (high  $M_w$ ) g mol<sup>-1</sup>], determined from HP-DSC first-heating scans (2 °C min<sup>-1</sup>) under CO<sub>2</sub> at various pressures.

- 11 S. G. Kazarian, M. F. Vincent, F. V. Bright and C. L. Liotta, *J. Am. Chem. Soc.*, 1996, **118**, 1729–1736.
- 12 Y. T. Shieh and K. H. Liu, *J. Supercrit. Fluids*, 2003, **25**, 261–268.
- 13 Y. T. Shieh and K. H. Liu, *J. Polym. Res.*, 2002, **9**, 107–113.
- 14 Y. T. Shieh, C. Zhao, T. L. Wang and C. H. Yang, *J. Supercrit. Fluids*, 2014, **91**, 1–6.
- 15 O. Chiantore, M. Guaita and L. Trossarelli, *Makromol. Chem.*, 1979, **180**, 969–973.
- 16 C. Wu and X. Wang, *Phys. Rev. Lett.*, 1998, **80**, 4092–4094.
- 17 J. Spevacek, J. Dybal, L. Starovoytova, A. Zhigunov and Z. Sedlakova, *Soft Matter*, 2012, **8**, 6110–6119.
- 18 J. Spevacek, R. Konefal and E. Vadova, *Macromol. Chem. Phys.*, 2016, **217**, 1370–1375.
- 19 H. G. Schild and D. A. Tirrell, *J. Phys. Chem.*, 1990, **94**, 4352–4356.
- 20 T. Baltes, F. Garret-Flaudy and R. Freitag, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 2977–2989.
- 21 S. Furyk, Y. Zhang, D. Ortiz-Acosta, P. S. Cremer and D. E. Bergbreiter, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1492–1501.
- 22 Y. T. Shieh and B. H. Chen, *J. Supercrit. Fluids*, 2016, **107**, 624–629.
- 23 V. O. Aseyev, H. Tenhu and F. M. Winnik, *Adv. Polym. Sci.*, 2006, **196**, 1–85.
- 24 V. O. Aseyev, H. Tenhu and F. M. Winnik, *Adv. Polym. Sci.*, 2016, **242**, 29–89.
- 25 F. Messussen, E. Nies, H. Berghmans, S. Verbrugghe, E. Goethals and F. Du-Prez, *Polymer*, 2000, **41**, 8597–8602.