Understanding the UCST-type transition of P(AAm-co-AN) in H₂O and D₂O: dramatic effects of solvent isotopes†

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The UCST-type transition of poly(acrylamide-co-acrylonitrile) (P(AAm-co-AN)) (molar fraction of AN: 13.3%; PDI = 3.2) in H₂O and D₂O is explored and compared by applying turbidity, DLS as well as FTIR measurements. The transition temperature of P(AAm-co-AN) in D₂O is observed to be almost 10 °C higher than that in H₂O at the same concentration, demonstrating a dramatic solvent isotope effect. Such a phenomenon could be rooted from a stronger interaction among polymer chains in D₂O than in H₂O, as indicated from DLS results. It is also observed in second-derivative analysis of FTIR spectra in the ν(C=O) region, where all C=O groups participate in the formation of inter-/intra-chain hydrogen bonds (C=O...H–N) in D₂O while there is still part of relatively "free" C=O groups in H₂O. Moreover, we find in the temperature-dependent FTIR spectra that C≡N groups exhibit hydrating behavior while C=O groups present increased inter-/intra-molecular hydrogen bonding interaction (C=O...H–N) upon cooling, revealing the later process to be the driving force of the UCST-type transition.

1. Introduction

Water-soluble thermal-responsive polymers, exhibiting drastic variations in the physical properties upon small changes in temperature in aqueous solutions, have been subject to an extensive study in both academia and industry over the past few decades. Because of their “smart” nature, those thermal-responsive polymers hold great potential in applications including temperature-triggered drug release, targeted drug delivery, tissue engineering, bioseparation, sensing, etc.¹⁻⁴ Generally, this group of polymers can be divided into two categories, depending on whether the miscibility gap is located at a low or a high temperature in the temperature-composition phase-diagram of polymer solution: one is polymers displaying a lower critical solution temperature (LCST) above which polymers separate from the aqueous solution, and the other one is polymers displaying upper critical solution temperature (UCST) above which polymers become soluble in water. Much attention has been paid to those LCST-type polymers, while only a small part of the concern was devoted to the UCST-type ones.⁵⁻⁸ Under such a circumstance, the development and improvement of polymers that exhibit sharp UCST-type transition in water is highly imperative, so that the broad applications of thermally responsive polymers could be extended.

Very few polymers are known to show UCST-type behavior in aqueous media under practically conditions, for example, with UCST in the range between 0 and 100 °C at atmospheric pressure. It is widely considered that polymer–polymer interactions must be stronger than water–polymer interactions at lower temperatures to afford a UCST-type transition. In this way, all the recognized polymers that exhibit UCST-type phase transition in water are achieved by engineering electronic interactions (such as poly(betaines),⁷,⁸ poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) in the presence of Multivalent Counterions⁹⁻¹⁰) or thermally reversible hydrogen bonding (i.e., poly(ureacil acrylate),¹¹ urea-modified polymers¹² and derivatives of poly(N-acryloylglycinamide)¹³⁻¹⁴) within the polymer chains. Due to the strong sensitivity of phase transition behavior to electrolytes (ions) of charged polymers, uncharged UCST-type polymers relying on hydrogen bonding, whose thermosensitivity is relativity stable, present more promising candidates for biomedical applications. Recently, Seuring and Agarwal have demonstrated that free radical copolymerization of commercially available acrylamide (AAM) and acrylonitrile (AN) could yield random copolymers P(AAm-co-AN) with a sharp UCST in water.
or electrolyte solution conveniently tunable by varying the composition of the monomers, which shows to be the most noteworthy contribution to the investigation of UCST-type polymers.\textsuperscript{15,16} Since then, it has aroused increasing interest in both fundamental and applied arena. In the report of Zhao et al.,\textsuperscript{17} a common block of P(AAm-co-AN) was coupled with either hydrophobic polystyrene (PS) or hydrophilic poly(dimethylacrylamide) (PDMA) or the LCST-type polymer of PDMAEMA via reversible addition-fragmentation chain-transfer (RAFT) polymerization. It was demonstrated that the corresponding block copolymers displayed reversible dispersion-aggregation of micelles, dissolution-formation of micelles, and reversal of the micelle core and corona in water under the perturbation of temperature, respectively. Agarwal et al.\textsuperscript{18} then fabricated thermophilic hydrogel films from photo cross-linkable thermoresponsive copolymers based on P(AAm-co-AN-co-4-acryloyloxybenzophenone), which exhibited continuous positive volume transition behavior in water with increasing temperature and was utilized for the design of micro-actuators. More recently, self-assembled UCST-type micelles that derived from P(AAm-co-AN) have also been explored for drug delivery systems.\textsuperscript{19,20} However, to the best of our knowledge, comprehensive investigations of the UCST-type transition behavior of P(AAm-co-AN) in water at the molecular level are still lacking.

Deuterium isotopic substitution is a useful probe to study intramolecular forces, especially hydrogen-bonding interactions, in the condensed phase.\textsuperscript{21} With regard to thermally responsive systems, the isotope effect on the phase transition behavior has been intensively inspected as well. For poly(N-isopropylacrylamide) (PNIPAM), which is a famous LCST-type polymer, the results can be summarized as follows: (i) the LCST of PNIPAM in D\textsubscript{2}O is ca. 1 °C higher than that in H\textsubscript{2}O. (ii) The magnitudes of the hysteresis are not affected or are only weakly affected by isotopic substitutions.\textsuperscript{22} Meanwhile, the deuterium isotope effects on the swelling behavior of a typical aqueous PNIPAM gel and a polyacrylamide (PAAm) gel have also been investigated and compared.\textsuperscript{23,24} It was demonstrated that the deuterium isotopic substitution affected the size in the equilibrium state of the PNIPAM gel and the PAAm gel oppositely, which could be originated from different polymer–solvent interactions caused by the isotopic substitution. Moreover, they have also investigated the deuterium isotope effect on phase separation in aqueous zipper-type hydrogen-bonding polymer solutions.\textsuperscript{25} It was observed that the phase separation temperature of poly(acrylic acid) (PAA)–PAAm in heavy water was about 16 °C higher than that in water. And they attributed such a large isotope effect to be the polymer–polymer interaction of cooperative hydrogen bonds in the polymer–polymer complex. Additionally, Cai et al.\textsuperscript{26} have examined the solvent isotopic effect on the temperature-induced phase transition process of pyrrolidone-based polymers and discovered that the cloud point of poly[N,N-dimethyl-N-(3-methacrylamido)propyl] ammoniopropanesulfonate determined in D\textsubscript{2}O were generally higher by about 6 °C in H\textsubscript{2}O, implying that hydrogen bonding played a major role in the effective hydration of the polyzwitterion. Nevertheless, how the UCST-type transition of P(AAm-co-AN) is influenced by deuterium isotopic substitution still remains a blank.

In this work, we firstly utilized dynamic light scattering (DLS) and turbidity measurements to examine the transition points and features of P(AAm-co-AN) in H\textsubscript{2}O and D\textsubscript{2}O, which provides an overall view of the transition process. Further, Fourier transform infrared spectroscopy (FTIR), which is rather sensitive to morphological or conformational variations and has been proved to be a powerful method in recording the molecular motion and interactions between chemical groups, is employed to probe the change in hydration states and hydrogen bonds within the polymer chains during the UCST-type transition and reveal the distinctive effect of solvent isotopes thereinto.

2. Experimental

2.1 Materials

Acrylamide and acrylonitrile were purchased from Aladdin Reagent Co. and used as received. Azobis(isobutyronitrile) (AIBN) was also purchased from Aladdin Reagent Co. and recrystallized from ethanol. Dimethyl sulfoxide (DMSO) and methanol were vacuum distilled before use. Pure H\textsubscript{2}O was distilled-deionized water obtained from a Millipore Milli-Q gradient machine. D\textsubscript{2}O was purchased from Cambridge Isotope Laboratories Inc. (D 99.9%, chemical purity > 99.5%). P(AAm-co-AN) was synthesized by radical polymerization in DMSO using AIBN as an initiator. And the corresponding reaction was illustrated in Fig. S1 (ESI\textsuperscript{†}). Herein, the acrylonitrile feed content was 16 mol% for P(AAm-co-AN) and 20 mol% for P(AAm-co-AN), respectively. After three freeze–pump–thaw cycles, the polymerization reaction proceeded at 60 °C for 5.5 h under vacuum. The synthesized copolymers were purified by precipitation in methanol three times and further vacuum-dried for 24 h at 40 °C. The GPC traces of synthesized copolymers were shown in Fig. S2 (ESI\textsuperscript{†}). For P(AAm-co-AN), \(M_w = 85.4\) kDa and \(PDI = 3.2\); for P(AAm-co-AN), \(M_w = 80.8\) kDa and \(PDI = 2.6\). The molar fraction of AN in the copolymers was determined to be 13.3% for P(AAm-co-AN) and 17.1% for P(AAm-co-AN) by IR spectroscopy using a calibration curve. (Fig. S3, ESI\textsuperscript{†}) The FTIR and \(^1\text{H} NMR\) characterization of P(AAm-co-AN) was shown in Fig. S4 and S5 (ESI\textsuperscript{†}), respectively.

2.2 Instruments and measurements

The turbidity measurements were carried out on a Lambda 35 UV-vis spectrometer at 500 nm with deionized water as a reference (100% transmittance). Temperatures were programmed to be under control using a water-jacketed cell holder at a rate of ca. 0.4 °C min\textsuperscript{−1} with an interval of 1 °C. Before each measurement, the temperature point was held for 2 min to ensure the thermal
equilibrium of the sample cell. DLS measurements were performed on a Malvern Zetasizer Nano ZS instrument with a scattering angle of 90° at a heating rate of ca. 0.4 °C min⁻¹. The interval was 1 °C and each temperature point was also maintained for 2 min before measurements for equilibration of the sample. For FTIR measurements of copolymer solutions, the concentration was fixed at 10 wt%. Herein, the copolymer solutions were sealed between two pieces of CaF2 tablets, which had no absorbance in the middle infrared bands. All the temperature-dependent FTIR spectra during cooling were recorded on a Nicolet Nexus 6700 FTIR spectrometer equipped with a DTGS detector. To achieve an acceptable signal-to-noise ratio, 32 scans at a resolution of 4 cm⁻¹ were accumulated. Temperatures were manually controlled with an electronic cell holder at a rate of ca. 1 °C/min with a decrement of 1.0 °C (accuracy: 0.1 °C). The neat P(AAm-co-AN) film for FTIR measurement was prepared by drop-casting on a CaF2 tablet from its hot aqueous solution. Baseline correction was performed using the software OMINIC 6.1a.

3. Results and discussion

3.1 Turbidity measurements

The phase transition behavior of P(AAm-co-AN) aqueous solution is firstly investigated by turbidity measurements. Hereby, we not only choose the solutions with different concentrations (1, 0.5 and 0.1 wt%) in H2O, but also solvents with varied deuterium isotopic substitution. In this way, both the concentration effect and the solvent isotope effect on the UCST-type transition behavior of P(AAm-co-AN) during the cooling and heating cycle could be examined, as shown in Fig. 1.

The cloud points are taken as the initial turn point in the obtained transmittance versus temperature curves. Thus the cloud point temperatures (Tc) of 1, 0.5 and 0.1 wt% P(AAm-co-AN) in H2O during the cooling process can be easily determined to be 34, 32 and 29 °C, respectively (Fig. 1(a)), indicating that Tc would slightly decrease with dilution. Such a phenomenon is consistent with what was reported previously, where the phase separation temperature of P(AAm-co-AN) was, to some extent, a little concentration dependent. In addition, it is clearly demonstrated in the turbidity curves that the phase separation would transform from a sharp transition to a relatively continuous one when the concentration is decreased from 1 to 0.1 wt%, suggesting that a broadening of the transition occurs upon dilution. From those points of view, we may say that the UCST-type transition of P(AAm-co-AN) should involve multiple polymer aggregating processes and polymer chains could not “find” each other as quickly in dilute solutions. Furthermore, it is observed that the transmittance can go back exactly to the initial one after a cooling and heating cycle and only a small hysteresis of 1–2 °C takes place thereinto, implying a good reversibility in the phase transition.

As for the solvent isotope effect, it is discovered that the phase separation temperature of P(AAm-co-AN) in D2O is almost 10 °C higher than that in H2O at a concentration of 1 wt% (Fig. 1(b)). Moreover, it is observed that with increasing AN content in the copolymer, the difference between the cloud points of P(AAm-co-AN)* in H2O and D2O is weakened, implying that such a strong isotope effect could, in some extent, come from PAAm parts.

Furthermore, in order to study the effect of pH and salt concentration on the cloud point, turbidity measurements have been performed as well on the UCST-type transitions of P(AAm-co-AN) in H2O with varied pH and NaCl concentration. As demonstrated in Fig. 2(a), the cloud points are nearly unchanged at pH = 5, 7, and 9, indicating that the UCST-type transition of P(AAm-co-AN) in H2O is relatively stable with pH. Moreover, the cloud point dependency of P(AAm-co-AN) as a function NaCl concentration is displayed in Fig. 2(b). It is shown that the cloud point is slightly decreased with the addition of NaCl, which is in accordance with Hofmeister series of ions. Under such a circumstance, it is inferred that the UCST-type transition only suffers a little from the addition of NaCl, which is far different from that of zwitterionic systems. Nevertheless, the cloud points of P(AAm-co-AN) are only decreased about 5 °C after the addition of 150 mM NaCl, while the phase separation temperature is lowered by about several tens of degree with comparable NaCl concentration in zwitterionic systems. Under such a circumstance, it is inferred that the UCST-type transition only suffers a little from the addition of NaCl, which is far different from that of zwitterionic systems. Tentatively, we would ascribe such relatively stable cloud points of P(AAm-co-AN) in H2O against various pH and NaCl concentrations due to the fact that P(AAm-co-AN) possesses strong hydrogen donors and acceptors and it contains no or very few ionic groups.
with varied concentration and isotopic substitution, as presented in Fig. 3. As expected, upon cooling, the hydrodynamic diameter ($D_h$) exhibits an abrupt increase at the cloud point, indicating the aggregation of polymer chains. With regard to concentration-dependence, it is displayed that $T_{cp}$ of 1 wt% solution is slightly higher than that of 0.1 wt% solution in H$_2$O, which is in consistence with the outcome of turbidity curves. What is more, the gradual aggregation of polymer chains in the phase separation process is demonstrated in the DLS profile, where $D_h$ manifests a continuous increase upon cooling under $T_{cp}$. Concerning the effect of deuterium isotopic substitution, we also find that the transition temperature in D$_2$O is as much as 10 °C higher than that in H$_2$O, confirming a strong solvent isotopic effect as illustrated in the turbidity curves.

For more minute information regarding DLS measurements, number-average size distributions of P(AAm-co-AN) in H$_2$O and D$_2$O with a concentration of 0.1 wt% at varied temperatures are portrayed in Fig. 4. At temperatures higher than $T_{cp}$, polymer chains are well dissolved in both H$_2$O and D$_2$O with small sizes. After cooling below $T_{cp}$, the phase separation takes place, accompanied by diameters jumping abruptly to obvious bigger ones. Looking into the number-average size distributions more carefully, we should find that the sizes of “unimers” above $T_{cp}$ are relatively higher than that of normal ones, which are always smaller than 10 nm. For clarity, the number-average size distributions of P(AAm-co-AN) in H$_2$O and D$_2$O at 50 °C are plotted in Fig. 4(c). Meanwhile, the number-average size distribution of P(AAm-co-AN) in DMSO at 50 °C, where polymers are supposed to be dissolved molecularly, has been presented for comparison. As is demonstrated, the size of polymer chains in DMSO is obviously smaller than that in H$_2$O and D$_2$O. Moreover, the size of polymer chains that dissolved in H$_2$O and D$_2$O lies in between 10–40 nm, which is usually considered to be “small associations” rather than unimers of polymer chains. Thereupon, it is inferred that strong interactions among P(AAm-co-AN) chains in water have not been totally spoiled even after heating above $T_{cp}$. It has been reported that PAAm could form associates or “multimacroion domains” even it was dissolved in water. Then, such a strong interaction is believed to arise from the inter/intra-chain hydrogen bond of C=O⋅⋅⋅H–N among the PAAm part. Furthermore, when comparing the situation in H$_2$O and D$_2$O, we can apparently notice that the size of P(AAm-co-AN) chains in D$_2$O is larger than that in H$_2$O at 50 °C, hinting that the interactions among P(AAm-co-AN) chains in D$_2$O should be stronger than that in H$_2$O. In a sense, this discovery might be the origin of different phase separation temperatures of P(AAm-co-AN) in H$_2$O and D$_2$O.

### 3.3 FTIR analysis

FTIR has been proved to be a quite useful technique to probe changes in molecular interactions of individual chemical groups of polymers, especially thermally responsive polymers. According to what we know, compared with common LCST-type polymers such as PNIPAM, poly(N-vinylcaprolactam) (PVCL), poly(vinyl methyl ether) (PVME) and oligo(ethylene glycol) (meth)acrylate (OEGMA)-based polymers, FTIR investigations of the thermosensitive behavior of UCST-type polymers still remain limited. Hence, FTIR is employed to depict the UCST-type transition of P(AAm-co-AN) aqueous solution and interpret the dramatic solvent isotope effect from the view of specific chemical groups.

Fig. 5(a) and (b) present temperature-dependent FTIR spectra of P(AAm-co-AN) in H$_2$O (46–26 °C) and D$_2$O (56–36 °C) with a concentration of 10 wt% upon cooling, respectively. Herein, we

![Fig. 3 DLS curves of (a) (AAm-co-AN) in H$_2$O with various concentrations and (b) P(AAm-co-AN) in H$_2$O and D$_2$O at 0.1 wt% upon cooling.](image1)

![Fig. 4 DLS analyses: size distributions by a number of P(AAm-co-AN) in H$_2$O (a) and D$_2$O (b) at 0.1 wt% during the cooling process; (c) comparison of size distributions by a number of P(AAm-co-AN) in DMSO, H$_2$O and D$_2$O at 50 °C with a concentration of 0.1 wt%.](image2)

![Fig. 5 Temperature-dependent FTIR spectra of P(AAm-co-AN) in H$_2$O (46–26 °C) (a) and D$_2$O (56–36 °C) (b) with a concentration of 10 wt% upon cooling.](image3)
will mainly focus on two spectral regions: the C≡N stretching region (2260–2233 cm\(^{-1}\)) and the C=O stretching region (1690–1590 cm\(^{-1}\)). In this way, we can trace the group motions of both PAAm and PAN parts on the polymer chains during the phase transition. It should be noticed that D\(_2\)O is used as a solvent to probe the behavior of C=O groups so that overlap of the \(\delta(\text{O–H})\) band of H\(_2\)O at around 1640 cm\(^{-1}\) with the \(\nu(\text{C}=\text{O})\) band of PAAm can be eliminated. Meanwhile, since the \(\nu(\text{D–O})\) band of D\(_2\)O overlaps with the \(\nu(\text{C}≡\text{N})\) band of PAN, H\(_2\)O is used as a solvent to monitor the change of C≡N groups.

From Fig. 5(a), we can clearly find that C≡N groups exhibit a continuous shift to higher wavenumber upon cooling. As a hydrophobic moiety of water soluble polymers, the C≡N group is believed to be surrounded by water clathrates in which water molecules have a well-ordered structure.\(^{41}\) The higher the number of water molecules surrounding C≡N groups is, the higher the vibrational wavenumber is.\(^{42}\) Accordingly, it is inferred that C≡N groups on the polymer chains experience a hydration process upon cooling. To some extent, this observation within C≡N groups goes against the phase separation process, where polymer chains should undergo dehydration. Referring to the \(\nu(\text{C}=\text{O})\) band, it displays a somewhat red-shift upon cooling. It is generally known that a lower frequency implies a stronger interaction in the C=O stretching region of FTIR spectra. Then, we can figure that interactions relating to C=O groups along the polymer chains are increased with temperature going down. Considering both the occurrence of phase separation behavior and strong hydrogen bonding interaction among PAAm parts, it is supposed that the increased interaction within C≡O groups is attributed to the strengthening of C≡O⋅⋅⋅D–N in PAAm parts. Under such a circumstance, we can conclude that the enhanced hydrogen bonding interaction of C≡O⋅⋅⋅D–N in PAAm upon cooling is the driving force of the UCST-type transition. Moreover, by comparing the temperature-resolved spectra of \(\nu(\text{C}≡\text{N})\) and \(\nu(\text{C}=\text{O})\) bands, we see that the former presents a continuous change while the latter shows a sort of sudden one around the transition point (temperature-dependent maximum IR absorbance shown in Fig. S6, ESI\(^+\)), further confirming that PAN dominates the UCST-type transition while PAN plays an assistant role in adjusting the hydrophilic-lipophilic balance of the whole polymer chains.\(^{15}\)

To discern the effect of hydration on the states of C≡N and C=O groups, some contrast FTIR curves of P(AAm-co-AN) and the neat P(AAm-co-AN) film in H\(_2\)O or D\(_2\)O before and after the phase transition were obtained upon cooling, and have been presented in Fig. 6. Due to the absence of water, both C≡N and C=O groups are free of hydrophobic hydration or hydrogen bonds with water in the neat film. It is noted that there exist two peaks in the region 1720–1565 cm\(^{-1}\) of the neat film. And from a higher wavenumber to a lower wavenumber, those two bands can be corresponded to the amide I and II region, respectively.\(^{43}\) Once the polymer is dissolved into water, hydrophobic hydration of C≡N groups and hydrogen bonding of C=O groups with water molecules take place evidently, leading to the obvious shift of those two bands. Herein, the disappearance of the amide II band is caused by deuterium of N–H into N–D. Compared with the neat film, C≡N and C=O groups are in partially hydrated states both before and after the phase transition. Moreover, both the blue-shift of \(\nu(\text{C}≡\text{N})\) and the red-shift of \(\nu(\text{C}=\text{O})\) are rather slight, indicating that the changes in interactions of the polymer chains are relatively small during the UCST-type transition.

For more detailed information on the variations in C≡N and C=O groups and the effect of solvent isotopes, the second-derivative analysis of FTIR spectra of 2265–2222 and 1740–1560 cm\(^{-1}\) regions in pure H\(_2\)O and D\(_2\)O before and after the phase transition as well as the neat film is conducted, and the results are shown in Fig. 7. The sharpened minima in the second-derivative curves correspond to the maxima in the original absorption spectra. Then, the overlapped peaks in the original spectra can be told apart. For C≡N groups, they are always in well hydrated status in water with vibrational frequency obviously higher than that in the neat film. And a slight frequency shift during the phase transition can be also substantiated here. In addition, there is nearly no difference of fine structure within C≡N groups in those two solvent systems, revealing that the drastic solvent isotope effect should not come from PAN parts. As for C=O groups, we will firstly focus on the neat film. In the amide I region of the neat film, two peaks, located at 1690 and 1660 cm\(^{-1}\), are visibly identified. In consideration of the chemical structure of the polymer chains, these two bands can be assigned to free C=O and hydrogen bonded C=O with N–H, respectively. After dissolving polymer chains into D\(_2\)O, only one band at around 1650 cm\(^{-1}\) could be recognized, meaning that there exists just one kind of C=O group. As has been discussed above, the inter-/intra-molecular hydrogen bond

![Fig. 6 Spectral comparison of P(AAm-co-AN) in H\(_2\)O (a) and D\(_2\)O (b) before and after the UCST-type transition and neat P(AAm-co-AN) film.](image)

![Fig. 7 Second-derivative spectra of P(AAm-co-AN) in H\(_2\)O (solid line) and D\(_2\)O (dashed line) and the neat P(AAm-co-AN) film (black) in 2265–2222 (a) and 1740–1560 cm\(^{-1}\) (b) region (red lines represent temperature higher than phase separation temperature while blue ones represent temperature lower than phase separation temperature).](image)
C–O···H–N plays an important role in the UCST-type phase transition. Thus, the observed band of 1650 cm\(^{-1}\) should be related to C–O···D–N in the PAAm part. Due to its lower frequency compared with that in the neat film (1660 cm\(^{-1}\)), we can attribute the band at 1650 cm\(^{-1}\) to C–O groups that hydrogen bond with both D–N and D–O. Being aware that this band exists all the time and suffers only a slight change during the UCST-type transition, we might suppose that hydrogen bonding interactions among the polymer chains are strong and stand even at temperatures higher than phase separation temperature. When H\(_2\)O is used as a solvent, the second-derivative spectra are interrupted by δ(O–H) in the region lower than 1660 cm\(^{-1}\). However, the appearance of a band at 1690 cm\(^{-1}\) is very clear, suggesting that there is a new kind of C–O group that does not exist in the D\(_2\)O system. Taking the band of 1690 cm\(^{-1}\) in the neat film into consideration, we can assign the new band at 1680 cm\(^{-1}\) to C–O groups hydrogen bonded with one water molecule (C–O···H–O). In other words, this new band is corresponded to hydrated C–O groups that are free from the inter-/intra-molecular hydrogen bond.

Until now, the inherent difference between the UCST-type transition of P(AAm-co-AN) in H\(_2\)O and D\(_2\)O has been emphasized, which provides a concrete view to the unearthing of the root of this interesting solvent isotope effect. In D\(_2\)O, almost all the C=O groups participate in the formation of inter-/intra-chain hydrogen bonds. While, in H\(_2\)O, there is part of “free” C=O groups that only interact with water molecules along the polymer chains. Then, it is believed that the interactions among polymer chains in D\(_2\)O are relatively stronger than that in H\(_2\)O. Such a delicate distinction herein might be explained by the fact that C–O···D–N is more stabilized than C–O···H–N.\(^{22,25}\) Hence, during the cooling procedure, polymer chains in D\(_2\)O are more inclined to aggregate, further resulting in obviously higher phase separation temperature. For limpidty of demonstration, the illustration and comparison of the UCST-type transitions of P(AAm-co-AN) in H\(_2\)O and D\(_2\)O upon cooling are displayed in Fig. 8.

4. Conclusion

In this work, we mainly employed turbidity, DLS and FTIR measurements to explore and compare the UCST-type transitions of P(AAm-co-AN) in H\(_2\)O and D\(_2\)O. It is displayed in turbidity curves that the UCST-type transition behavior is a kind of concentration-dependent, namely, the transition temperature is slightly decreased and the transition range is obviously broadened upon dilution. In addition, the phase separation temperature of P(AAm-co-AN) (13.3 mol\% AN) in D\(_2\)O is discovered to be almost 10°C higher than that in H\(_2\)O at the same concentration, which is also confirmed in DLS measurements. As demonstrated in further DLS analysis, the size of polymer chains above transition temperature is larger than normal ones and moreover, the size in D\(_2\)O is larger than that in H\(_2\)O, indicating that there exists a strong interaction among P(AAm-co-AN) chains and such an interaction is especially stronger when D\(_2\)O is used as a solvent. From temperature-dependent FTIR spectra, we can find that C=O groups exhibit hydrating behavior while C–O groups present increased inter-/intra-molecular hydrogen bonding interaction (C–O···H–N) upon cooling, revealing that C=O groups on the PAAm part play a predominant role in the UCST-type transition. Moreover, stronger interaction among polymer chains in D\(_2\)O is then verified by second-derivative analysis of the FTIR spectra, where all the C–O groups participate in the formation of inter-/intra-chain hydrogen bonds in D\(_2\)O while there is still a part of C–O groups free from C–O···H–N in H\(_2\)O. This observation provides a direct view at the molecular level of the explanation of obviously higher phase transition temperature of P(AAm-co-AN) in D\(_2\)O than H\(_2\)O with the same concentration.

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Notes and references