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Control of the lower critical solution temperature—type cononsolvency properties of poly(*N*-isopropylacrylamide) in water—dioxane mixtures through copolymerisation with acrylamide

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Abstract

The behaviour of the homopolymers poly(*N*-isopropylacrylamide) (PNIPAM), polyacrylamide (PAM) and random copolymers of *N*-isopropylacrylamide (NIPAM) with acrylamide (AM) was studied by turbidimetry and viscometry in mixtures of water with dioxane. It was found that the well-known lower critical solution temperature-type cononsolvency properties of PNIPAM in water–dioxane mixtures, observed in the water-rich region, can be effectively controlled by copolymerisation of NIPAM with AM. Thus, the cononsolvency properties of the copolymers in water–dioxane mixtures are shifted to higher temperatures and restricted within a narrower solvent composition region as the acrylamide content of the copolymers increases. A significant decrease of the reduced viscosity of the systems exhibiting phase separation properties was observed upon heating, indicative of the collapse of the (co)polymer chains as temperature approaches the corresponding cloud point temperature. Furthermore, when temperature is fixed close to the cloud point temperature, the reduced viscosity decreases with increasing the volume fraction of dioxane, φ, as far as the solvent mixtures are rich in water. On the contrary, the reduced viscosity of PNIPAM in dioxane-rich mixtures is found significantly higher, indicative of an expansion of the polymer chain, as compared to the reduced viscosity of this polymer in the two pure solvents.

Keywords: Poly(*N*-isopropylacrylamide); Polyacrylamide; Random copolymers

1. Introduction

The wide scientific and technological interest on the water-soluble polymer poly(*N*-isopropylacrylamide), PNIPAM, arises from its well-known and largely studied lower critical solution temperature (LCST) behaviour in aqueous solution. This phenomenon takes place within a narrow temperature range and it is revealed as a polymer phase separation from water when temperature increases above ~33 °C [1,2]. Although mainly studied in aqueous solution, this LCST-type thermosensitivity of PNIPAM is also extended to mixtures of water with several polar organic solvents and it is related to the phenomenon of cononsolvency.

Cononsolvency refers to the situation of polymers soluble in two pure solvents but insoluble in their mixtures, for some mixture compositions [3]. Regarding water-soluble polymers, apart PNIPAM, cononsolvency is also found with poly(*N*,*N*-diethylacrylamide) [16] and poly(vinyl alcohol) [4,5] in water–dimethyl sulfoxide mixtures, poly(vinyl methyl ether) in water–alcohol mixtures [6] and poly(*N*,*N*-dimethylacrylamide) in water–dioxane and water–acetone mixtures [7].

As far as it concerns PNIPAM, it has been found that water form cononsolvents for this polymer when mixed with methanol, tetrahydrofuran, dioxane and other polar organic solvents [8,9]. This solvent-composition-induced transition of PNIPAM has been studied both in the form of linear polymer chains [10–15] and in the form of polymer hydrogels [16–20] or microgels [21]. The molecular origin of the cononsolvency behaviour of PNIPAM chains (or the corresponding reentrant behaviour of PNIPAM hydrogels) remains an open question since the discovery of these phenomena. The best studied case is probably the behaviour of PNIPAM in mixtures of water with methanol. In this case, cononsolvency may be qualitatively explained in terms of competitive interactions between methanol, water and PNIPAM [8,9,22]. In addition, the formation of different water/methanol

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complexes, which are worse solvents for PNIPAM compared to pure water or pure methanol, has been recently suggested as the origin of cononsolvency of PNIPAM in water–methanol mixtures [13,15,23,24].

Although the cononsolvency properties of the homopolymer PNIPAM in mixed solvents have been investigated in detail, similar studies have not yet been extended to *N*-isopropylacrylamide-based copolymers, as far as we are aware. However, it is well established that copolymerisation of *N*-isopropylacrylamide, NIPAM, with other more hydrophilic or hydrophobic comonomers may be applied to effectively tune the LCST properties of the copolymer in aqueous solution [25–27]. As a consequence, copolymerisation is expected to provide us with a variety of products in order to modulate at will the cononsolvency properties of NIPAM-based copolymers, as these are closely related to their corresponding LCST behaviour. As a result, by using such copolymers, both the temperature range and the solvent composition range for the observation of cononsolvency phenomena may be effectively controlled.

In the present work, we apply these concepts using random copolymers, P(NIPAM-*co*-AM), of NIPAM with a very hydrophilic monomer, namely acrylamide, AM. As a consequence of its high hydrophilicity, the introduction of AM units in the PNIPAM chain leads to an effective elevation of the LCST of the copolymers in pure water [26,28]. Here, we study the phase separation behaviour of the P(NIPAM-*co*-AM) copolymers in water–dioxane mixtures and we follow the reduced viscosity changes in dilute solutions as a function of the solvent composition and temperature.

2. Experimental

2.1. Materials

NIPAM, AM, sodium metabisulphite, and methylene bisacrylamide (BIS) were purchased from Aldrich, while ammonium persulphate was a Serva product. HPLC grade dioxane was used. Water was purified by means of a Seralpur Pro 90C apparatus combined with a USF Elga laboratory unit.

The homopolymer PNIPAM was prepared by free radical polymerisation in water at 29 °C, using the redox couple ammonium persulphate/sodium metabisulphite as initiator [29]. The copolymers were prepared similarly at 35 °C. The products were purified by dialysis and recovered by freeze-drying. The composition of the copolymers was determined by ^{1}H NMR spectroscopy. The copolymers will be denoted as P(NIPAM-*co*-AM*x*), where *x* is the feed mol percentage of AM units in the copolymer. The reduced viscosity of the (co)polymers was determined in pure water at $T=25$ °C. The characterization results are summarized in Table 1.

2.2. Methods

2.2.1. Turbidimetry

The optical density of the (co)polymer solutions as a function of temperature or solvent composition was determined with a U-2001 Hitachi UV–vis spectrophotometer equipped with a thermostated circulation system. The solutions were let for 5 min under stirring to equilibrate at each temperature before measurement. For the detection of the cloud point temperature by visual observation of the polymer solution upon heating, a thermostated water bath equipped with a magnetic stirrer was used. The heating rate was adjusted manually to ~0.5 °C/min.

Table 1
Composition of the (co)polymers used in the present study

(Co)polymer	Feed composition (%mol AM)	Product composition by ^{1}H NMR (%mol AM)	[η] (cm^3/g)
PNIPAM	0	–	88.2
P(NIPAM-*co*-AM25)	25	19	33.2
P(NIPAM-*co*-AM35)	35	38	24.7
PAM	100	–	19.4

For all the turbidity experiments the polymer concentration was 1×10^{-2} g/cm^3.

2.2.2. Viscometry

The reduced viscosity studies were carried out with an automated viscosity measuring system (Schott-Gerate AVS 300) equipped with a micro-Ostwald-type viscometer. The (co) polymer concentration was fixed at 2.5×10^{-3} g/cm^3.

3. Results and discussion

3.1. Thermosensitivity in pure water

As mentioned, the introduction of the hydrophilic AM units in the copolymers leads to the elevation of the LCST of the products, when dissolved in pure water. This is evidenced in Fig. 1, where the optical density of aqueous solutions of PNIPAM, P(NIPAM-*co*-AM25), P(NIPAM-*co*-AM35) and PAM is presented as a function of temperature. As expected, the hydrophilic and not thermosensitive PAM is well-soluble in

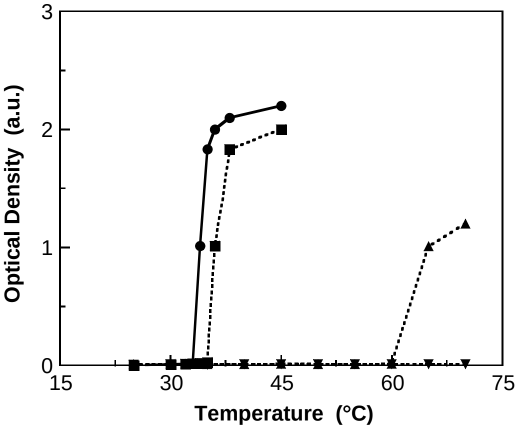

Fig. 1. The temperature-dependence of the optical density of aqueous solutions of PNIPAM (●), P(NIPAM-*co*-AM25) (■), P(NIPAM-*co*-AM35) (▲) and PAM (▼). The polymer concentration is 1×10^{-2} g/cm^3.

water and the PAM solution remains transparent within the whole temperature range studied. On the contrary, the thermosensitivity of PNIPAM is evidenced by an abrupt turbidity increase at ~34 °C. The copolymer P(NIPAM-*co*-AM25) presents a similar behaviour, but now the cloud point is observed at ~39 °C. Finally, the cloud point of the AM-richer copolymer, P(NIPAM-*co*-AM35), is elevated about 30 °C as compared to the homopolymer, and it is observed at 62 ± 2 °C. The observed cloud points are in a rather good agreement with the results reported by Taylor et al. [25] and Chiklis et al. [28], whereas they are somewhat higher than the results reported by Priest et al. [26].

In the case of PNIPAM, the phase separation behaviour is accompanied by a coil to globule transition of the single PNIPAM chain [30]. At a first approximation, this phenomenon can be evidenced by reduced viscosity, η_{sp}/c, changes of the PNIPAM solution [31]. In Fig. 2, we follow the temperature-dependence of the reduced viscosity of the aqueous solutions of our polymers. As the reduced viscosities of the four polymers at 20 °C vary significantly, due to variations in their nature and their molar mass, the results are presented in terms of the ratio r_{20}

$$r_{20} = \frac{(\eta_{sp}/c)}{(\eta_{sp}/c)_{20}} \tag{1}$$

of the reduced viscosity η_{sp}/c of the sample at the temperature of the experiment over its reduced viscosity $(\eta_{sp}/c)_{20}$ at 20 °C. Thus, using this representation, values of r_{20} close to unity are an indication that the quality of the solvent is similar to that of water at 20 °C for the polymer studied. Moreover, values of r_{20} higher than unity indicate that the polymer chains expand further, whereas values of r_{20} lower than unity are an indication of chain shrinkage, as the polymer chains now 'sense' a worse solvent, as compared to water at 20 °C. As seen, the ratio r_{20} of PAM is very close to unity and decreases very smoothly with increasing temperature. This indicates that the properties of the aqueous PAM solution do not depend significantly on temperature. On the contrary, the temperature-dependence of the ratio $r_{20\,°C}$ for the NIPAM-containing derivatives is much more important, especially for the NIPAM-richer samples. Thus, for the aqueous PNIPAM and P(NIPAM-*co*-AM25) solutions, the gradual decrease of r_{20} at the initial stages of warming is followed by an abrupt decrease as temperature reaches the corresponding phase separation temperature for each polymer. This is indicative of the collapse of the polymer chain and the abrupt worsening of the solvent quality, which finally becomes a nonsolvent at temperatures higher than the corresponding cloud point. Finally, for the AM-richer copolymer, P(NIPAM-*co*-AM35), just a monotonic decrease of the ratio r_{20} with temperature is observed within the temperature range studied, as the phase separation of this copolymer is observed at a higher temperature (~62 °C, Fig. 1).

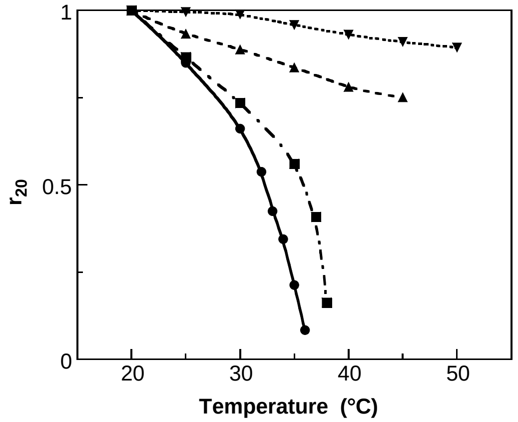

Fig. 2. The temperature-dependence of the reduced viscosity ratio, r_{20}, of aqueous solutions of PNIPAM (●), P(NIPAM-*co*-AM25) (■), P(NIPAM-*co*-AM35) (▲) and PAM (▼). The polymer concentration is 2.5×10^{-3} g/cm^3.

3.2. Cononsolvency in water–dioxane mixtures

We investigated the dependence of the cononsolvency abilities of water–dioxane mixtures upon heating on the copolymer composition by visual observation and by measuring the optical density of the (co)polymers solution. All the NIPAM-containing polymers studied phase separate upon heating in pure water and in water–dioxane mixtures for some mixtures composition. The cloud point temperatures determined by both methods are presented in Fig. 3, as a function of the volume fraction of dioxane, φ:

$$\varphi = \frac{V_D}{(V_W + V_D)} \tag{2}$$

where V_W and V_D are the volumes of water and dioxane, respectively, used for the preparation of the solvent mixture.

The curve obtained for the homopolymer PNIPAM is in good agreement with the results reported by Schild [9]: the cloud point of PNIPAM from ~34 °C in pure water initially decreases upon addition of dioxane, reaching a minimum of ~31 °C at $\varphi = 0.4$. Further addition of dioxane leads to a gradual elevation of the cloud point to ~45 °C at $\varphi = 0.55$.

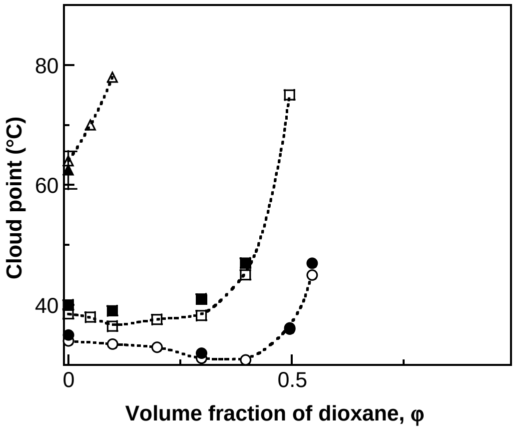

Fig. 3. The variation of the cloud point of PNIPAM (●, ○), P(NIPAM-*co*-AM25) (■, □) and P(NIPAM-*co*-AM35) (▲, △) with the volume fraction of dioxane, φ. Open symbols refer to visual observation results, whereas full symbols refer to optical density results. The polymer concentration is 1×10^{-2} g/cm^3.

Finally, for higher volume fractions of dioxane, $0.55<\varphi\leq 1$, no phase separation is observed within the whole temperature range studied, as dioxane and dioxane-rich mixtures are good solvents of PNIPAM. The 'phase separation behaviour' of the copolymer P(NIPAM-*co*-AM25) is quite similar to that of the homopolymer PNIPAM, but displaced to slightly higher temperatures and restricted to somewhat water-richer solvent compositions: the cloud point of this copolymer from ~39 °C in pure water initially decreases to ~37 °C at $\varphi=0.1$ and then increases to ~75 °C at $\varphi=0.5$, before disappearing at higher volume fractions of dioxane. This change is more striking for the AM-richer copolymer P(NIPAM-*co*-AM35): the 'phase separation behaviour' for this copolymer is displaced to much higher temperatures as the cloud point of P(NIPAM-*co*-AM35) in pure water is ~62 °C, while the phase separation region is limited in the region $0\leq\varphi<0.15$. We should note that no cloud point depression has been observed for this copolymer upon addition of dioxane. Moreover, this AM-richer copolymer, as well as PAM, is not soluble in pure dioxane. Therefore, strictly speaking, the phase behaviour of P(NIPAM-*co*-AM35) in water–dioxane mixtures cannot be described as cononsolvency.

The temperature-dependence of the reduced viscosity of PNIPAM and P(NIPAM-*co*-AM25) has been investigated for water–dioxane mixtures covering the whole solvent composition region, $0\leq\varphi\leq 1$. In Fig. 4 we present representative results concerning the homopolymer PNIPAM, using the ratio r_{20}. When the solvent composition is within the limits where phase separation is detected upon heating ($0\leq\varphi<0.6$), the behaviour is similar to that of PNIPAM in pure water ($\varphi=0$), discussed earlier: at low temperatures the ratio r_{20} decreases gradually, but when temperature approaches the cloud point of each system a sharp decrease of the ratio r_{20} is observed, indicating the collapse of the polymer chains as the solvent mixture turns to a nonsolvent. In pure dioxane ($\varphi=1$), the ratio r_{20} is smoothly increasing, probably indicating that pure dioxane becomes gradually a better solvent for PNIPAM upon heating. This trend is inversed upon addition of water to dioxane ($\varphi=0.6$) and the change of the ratio r_{20} turns gradually to a decreasing function of temperature.

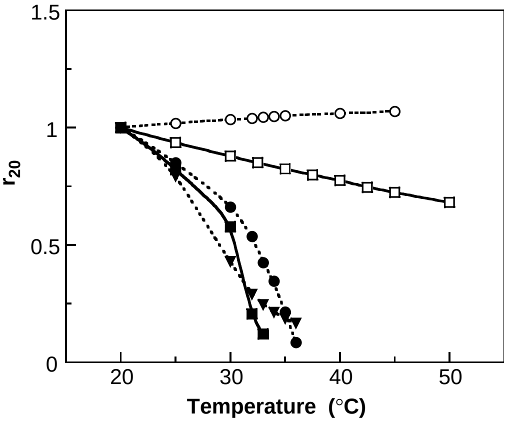

Fig. 4. The temperature-dependence of the ratio r_{20} of PNIPAM in water–dioxane mixtures with $\varphi=0$ (●), $\varphi=0.2$ (■), $\varphi=0.4$ (▼), $\varphi=0.6$ (□) and $\varphi=1$ (○). The polymer concentration is 2.5×10^{-3} g/cm^3.

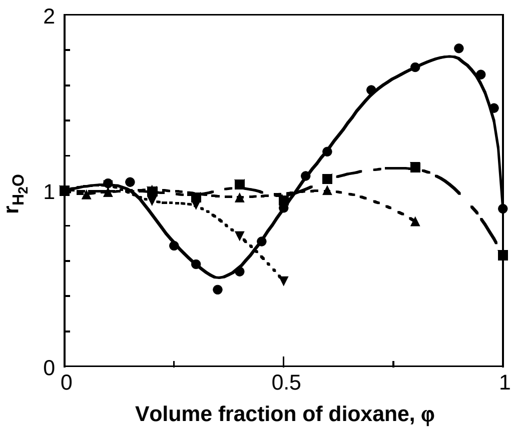

Fig. 5. The variation of the ratio r_{H_2O} of PNIPAM (●), P(NIPAM-*co*-AM25) (■), P(NIPAM-*co*-AM35) (▲) and PAM (▼) with the volume fraction of dioxane, φ, at $T=30$ °C. The polymer concentration is 2.5×10^{-3} g/cm^3.

To investigate the dependence of the reduced viscosity of the polymers on the solvent composition we fixed the temperature at $T=30$ °C. This temperature is very close to the phase separation temperature of the homopolymer PNIPAM, but lower enough from the phase separation temperature (if any) of the rest (co)polymers in pure water and in water–dioxane mixtures. The results are plotted in Fig. 5, in terms of the ratio r_{H_2O}

$$r_{H_2O}=\frac{(\eta_{sp}/c)}{(\eta_{sp}/c)_{H_2O}} \tag{3}$$

where η_{sp}/c and $(\eta_{sp}/c)_{H_2O}$ is the reduced viscosity of the (co)polymer in the solvent mixture studied and in pure water, respectively. At a first approximation, the ratio r_{H_2O} could be a qualitative measure of the expansion or contraction of the polymer chain in the solvent mixture at 30 °C, taking as a reference the behaviour of the polymer in pure water under the same conditions.

As seen, for the homopolymer PNIPAM the ratio r_{H_2O} is around 1 both in pure water and in pure dioxane. On the contrary, for the copolymer P(NIPAM-*co*-AM25) the ratio r_{H_2O} for PNIPAM passes through a minimum at $\varphi\sim 0.35$–0.4. The minimum value of r_{H_2O} is about 0.4, i.e. at this solvent composition the homopolymer chain is shrunken at less than the half of its original hydrodynamic volume in pure water under the same conditions. This reflects the decrease of the solvent quality with increasing φ in this solvent composition region. Note that at $\varphi=0.4$ the experimental temperature (30 °C) is just 1 °C lower than the observed cloud point (31 °C), while for $\varphi=0$ the temperature difference from the cloud point is about 4 °C (the cloud point was observed at ~34 °C). The consequent increase of r_{H_2O} with further addition of dioxane reflects the improvement of the solvent quality, as expressed by the cloud point increase with φ in this region. A respective minimum is absent for all the other samples, as the experimental temperature is far from the phase separation temperature (if any). As a consequence, for the two copolymers and for PAM the ratio r_{H_2O} is close to unity and changes monotonically in a large composition region, φ.

It is noteworthy that at the solvent composition region $0.6<\varphi<1$, the ratio r_{H_2O} of PNIPAM is higher than unity, passing through a maximum at $\varphi\sim 0.9$. At this solvent composition the ratio r_{H_2O} reaches a value of about 1.8, i.e. the reduced viscosity of the PNIPAM solution is almost doubled as compared to the reduced viscosity of PNIPAM in the two pure solvents. To our knowledge, no reports are found in literature concerning such a behaviour of polymers in mixtures of cononsolvents. Although it merits further and deeper investigation, it could be interpreted to a better solvation of the polymer chain for this solvent compositions, as compared to the two pure solvents. This behaviour is also observed for the copolymer P(NIPAM-*co*-AM25), although the increase of the ratio r_{H_2O} is now smoother. Finally, the AM-richer copolymer P(NIPAM-*co*-AM35) and the homopolymer PAM present a decrease of the ratio r_{H_2O} in dioxane-rich mixtures, indicative of a chain collapse as the systems approach the two phase region.

The relative strength of at least three kinds of interactions, presumably hydrogen-bonding, would decisively govern the solubility behaviour of PNIPAM in water–dioxane mixtures. These are the NIPAM–water, NIPAM–dioxane and water–dioxane interactions. So far, the studies on the cononsolvency behaviour of PNIPAM in water–dioxane mixtures are very limited and a quantitative evaluation of these interactions is not possible. However, several investigations suggest that dioxane is involved in water/dioxane micelle-like clusters or complexes [32–35]. In fact, three specific molar fractions χ of dioxane, $\chi=0.13$, 0.3 and 0.7 (corresponding to volume fractions $\varphi=0.41$, 0.67 and 0.92, respectively), are characteristic in water–dioxane mixtures [34]. Thus, (a) within the region $0\leq\varphi\leq 0.41$ pure water coexists with (dioxane)$(H_2O)_{6-7}$ complexes, (b) within the region $0.41\leq\varphi\leq 0.67$ several micelle-like clusters with structures (dioxane)$n(H_2O)_m$ with $n=1$–3 and $m=7$–21 are observed, (c) within the region $0.67\leq\varphi\leq 0.92$ micelle-like clusters of the form (dioxane)$_7(H_2O)_{21}$ coexist with dioxane clusters, while (d) within the region $0.92\leq\varphi\leq 1$ no micelle-like clusters are detected. The slight depression of the cloud point of PNIPAM (Fig. 3) and the considerable shrinkage of the PNIPAM chain (Fig. 5) observed in the solvent composition region $0\leq\varphi\leq 0.4$ suggest that probably the (dioxane)$(H_2O)_{6-7}$ complexes are worse solvents for PNIPAM, compared to pure water or pure dioxane. The cononsolvency behaviour of PNIPAM in water–methanol mixtures has been also attributed to the existence of methanol/water complexes of a similar structure [13,15,23,24]. On the other hand, the cloud point increase and the important reswelling of the PNIPAM chain observed in water–dioxane mixtures for $\varphi>0.4$ are possibly related with the appearance of the micelle-like structures, detected within the region $0.41\leq\varphi\leq 0.92$. The disappearance of these structures for $\varphi\geq 0.92$, seeming to be better solvents for the homopolymer PNIPAM, is probably related with the maximum observed at $\varphi\sim 0.9$ in Fig. 5.

The system is much more complicated regarding the P(NIPAM-*co*-AM*x*) copolymers, because we have also to consider the interactions of AM units with water and dioxane, as compared to the water–dioxane interactions. The insolubility of PAM in dioxane indicates that the AM-dioxane contacts are not favourable, while the strong hydrophilic character of this polymer indicates strong hydrogen-bonding interactions between AM and water. Thus, it seems that within the water-rich region the ability of AM to form strong hydrogen-bonds with water prevails over the unfavourable interactions between the NIPAM units and the (dioxane)$(H_2O)_{6-7}$ complexes, so that the cononsolvency behaviour of the copolymers is displaced to higher temperatures as x increases. On the other hand, the need to avoid the unfavourable contacts between AM units and dioxane molecules leads to the gradual decrease of the maximum observed in Fig. 5 or, even, to phase separation, with increasing x, within the dioxane-rich region.

4. Conclusions

The lower critical solution temperature behaviour and the cononsolvency properties of PNIPAM and copolymers of NIPAM with AM, (P(NIPAM-*co*-AM*x*)), were studied in water–dioxane mixtures by means of turbidimetry and viscometry in dilute solutions. Increasing the content x of the very hydrophilic AM units in the copolymers shifts the cloud point to higher temperatures and limits the cononsolvency behaviour within a narrower solvent composition region. In addition, a drastic decrease of the reduced viscosity of the (co) polymer solutions is observed either by warming prior to phase separation or with increasing the volume fraction of dioxane if the temperature is fixed very close to the cloud point temperature, indicative of the collapse of the (co)polymer chains as temperature approaches the corresponding cloud point temperature. On the contrary, the reduced viscosity of PNIPAM in dioxane-rich mixtures is found significantly higher, as compared to the reduced viscosity of this polymer in the two pure solvents, indicative of an expansion of the polymer chains for these solvent mixtures compositions.

The results reported here show that such LCST-type solvent-composition-induced transitions of NIPAM-based polymers may be effectively controlled by using adequate copolymers of NIPAM. In the present study, we focused on copolymers of NIPAM with AM, using water and dioxane as cononsolvents. Other cononsolvent pairs, like water–methanol or water–acetone, or other comonomers, more or less hydrophilic than NIPAM, may be used to demonstrate and enlarge the possibilities for effectively controlling the solvent-composition-induced transitions of the respective (co) polymers.

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