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Temperature- and solvent-sensitive hydrogels based on *N*-isopropylacrylamide and *N,N*-dimethylacrylamide

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Summary

The swelling behaviour in water-dioxane mixtures of hydrogels containing *N*-isopropylacrylamide (NIPAM) and *N,N*-dimethylacrylamide (DMAM) is investigated as a function of dioxane content and temperature. The composition of the hydrogels, reported as the mol percentage of DMAM units, x, varies from 0 up to 100. It is found that the hydrogel containing only NIPAM units, GPNIPAM, deswells significantly in the water-rich region, while the hydrogel containing only DMAM units, GPDMAM, presents a pronounced deswelling in the dioxane-rich region. This deswelling becomes less significant with decreasing the DMAM content x, when using the hydrogels of the copolymers GP(NIPAM-*co*-DMAMx). This swelling behaviour of the hydrogels results from a combination of the lower critical solution temperature-type cononsolvency behaviour of poly(*N*-isopropylacrylamide) with the upper critical solution temperature-type cononsolvency behaviour of poly(*N,N*-dimethylacrylamide) in water-dioxane mixtures.

Introduction

Water-soluble polymers and hydrogels responsive or sensitive to external stimuli like temperature, pH, ionic strength, solutes or solvent composition, represent nowadays an important and active research area due to the many possible applications of such smart materials in diverse technological fields. Recently, research focused on multi-stimuli materials, i.e. on polymers or hydrogels responsive or sensitive to more than one external stimulus.

In the present work we focus on polymers and hydrogels sensitive both to temperature and solvent composition. To achieve this, we have exploited the cononsolvency properties of poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N,N*-dimethylacrylamide) (PDMAM) in mixtures of water with polar organic solvents, like dioxane. It is well known that the PNIPAM homopolymer exhibits a lower critical solution temperature (LCST)-type cononsolvency behaviour in water-rich mixtures of water with polar organic solvents, i.e. the PNIPAM phase separates from such

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mixtures upon heating. This behaviour has been investigated either in the form of linear chains [1-9] or in the form of hydrogels [10-15]. On the other hand, we have recently shown [16] that the PDMAM homopolymer exhibits the inverse cononsolvency behaviour in water-dioxane mixtures, i.e. the PDMAM phase separates from water-dioxane mixtures rich in dioxane upon cooling (upper critical solution temperature (UCST)-type cononsolvency).

To combine the UCST-type cononsolvency properties of PDMAM with the LCST-type cononsolvency properties of PNIPAM in water-dioxane mixtures, we have prepared a series of hydrogels containing *N*-isopropylacrylamide (NIPAM) and *N,N*-dimethylacrylamide (DMAM) units by random copolymerisation in water of the two monomers in the presence of *N,N′*-methylenebisacrylamide. These hydrogels are denoted GP(NIPAM-*co*-DMAM*x*), where *x* is the mol percentage of DMAM units varying from $x = 0$ up to 100. The degree of swelling of these hydrogels in water-dioxane mixtures was studied as a function of temperature and solvent composition.

Experimental

Materials

NIPAM, DMAM, sodium disulfite, *N,N,N′,N′*-tetramethylethylenediamine (TEMED) and *N,N′*-methylenebisacrylamide (BIS) were purchased from Aldrich, while ammonium persulfate was a Serva product. Dioxane of HPLC grade was used. Water was purified in a Seralpur Pro 90C apparatus combined with a USF Elga laboratory unit.

Synthesis of linear polymers and hydrogels

The homopolymer PNIPAM was prepared by radical polymerisation in water at 29 °C, using the redox pair ammonium persulfate/sodium disulfite as initiator [17]. The PDMAM homopolymer was prepared similarly at 35 °C. The products were purified by dialysis and recovered by freeze-drying.

The hydrogels were prepared by dissolving the appropriate monomers and BIS (2 mol % of the total monomer concentration) in water under stirring at room temperature. The total monomer concentration for the preparation of the hydrogels was in all cases 1 M. The solution was deoxygenated and then ammonium persulfate and TEMED were added. The formation of the gel was almost immediate. The reaction was left to proceed for some hours and then the gel was immersed in pure water for one week. Water was renewed daily. Finally, the hydrogel was cut into ~0.2 g pieces and freeze-dried. Five hydrogels were prepared, following the above-described procedure: the hydrogels of the two homopolymers, GPNIPAM and GPDMAM, and the three copolymer hydrogels GP(NIPAM-*co*-DMAM33), GP(NIPAM-*co*-DMAM50) and GP(NIPAM-*co*-DMAM67), with molar DMAM/NIPAM feed compositions 33/67, 50/50 and 67/33, respectively.

Measurements

The absorbance of the homopolymer solutions as a function of temperature was determined with a U-2001 Hitatchi UV-vis spectrophotometer equipped with a thermostatted circulation system. The solutions were left 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 thermostatted water bath equipped with a magnetic stirrer was used. The heating rate was adjusted to ~0.5 °C/min.

For the swelling measurements, a preweighed dry gel sample was immersed in 10 cm^3 of the solvent with the desired mixture composition and left to swell. The mass of the gel was measured daily. The gel was considered to reach equilibrium when its mass did not change (within experimental error) for at least two days. For each experimental point, at least two samples were measured. The differences in the results were less than 5 %. The swelling ratio *S* was defined as the mass of the swollen gel relative to the initial mass of the freeze-dried gel.

Results and discussion

In Figure 1, we present the temperature dependence of the absorbance of solutions of the two homopolymers, PNIPAM and PDMAM, in water-dioxane mixtures for selected volume fractions of dioxane, φ, of the mixed solvents. As we can see, both homopolymers present a cononsolvency behaviour in water-dioxane mixtures. Thus, the solutions of PNIPAM in mixed solvents with rather low volume fractions of dioxane ($0 \leq \varphi < 0.55$) turn turbid upon heating. On the contrary, phase separation of solutions of PDMAM is observed upon cooling for mixed solvents very rich in dioxane ($0.8 < \varphi < 1$).

These inverse cononsolvency properties of the two homopolymers lead to pronounced changes in the swelling ratios of the corresponding hydrogels in water-dioxane

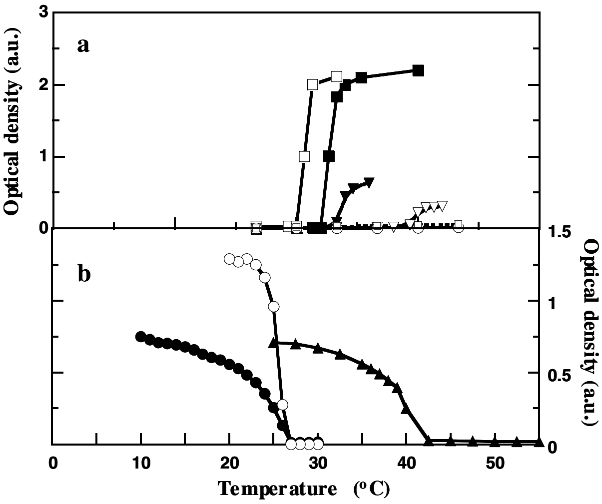

Figure 1. The temperature dependence of the absorbance (optical density) of the PNIPAM homopolymer (a) and PDMAM (b) in water-dioxane mixture for selected volume fractions of dioxane, φ. (■): $\varphi = 0$, (□): $\varphi = 0.3$, (▼): $\varphi = 0.5$, (▽): $\varphi = 0.55$, (●): $\varphi = 0.8$, (▲): $\varphi = 0.83$, (○): φ=0.98. The concentration of PNIPAM is $2.5x10^{-3}$ g/cm^3 and the concentration of PDMAM is $1x10^{-3}$ g/cm^3.

mixtures. The results are presented in Figures 2 and 3, for the hydrogels GPNIPAM and GPDMAM, respectively.

For the hydrogel GPNIPAM a smooth deswelling is observed at 25 °C in the dioxane-poor region, while an important reswelling follows in the dioxane-rich region. At a higher temperature, 34 °C, the behaviour in the dioxane-rich region is practically unaffected, whereas in the dioxane-poor region the deswelling of the GPNIPAM hydrogel is now very important. As we can see in Figure 1, the temperature T = 34 °C is higher than the observed cloud point temperatures in the dioxane-rich region. As a result, the hydrogel now "senses" a poor solvent, explaining the low swelling ratios measured.

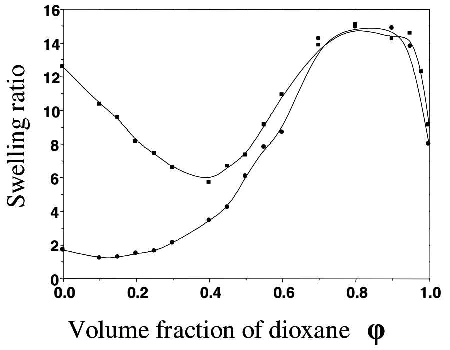

Figure 2. Variation of swelling ratio of GPNIPAM in water-dioxane mixtures with the volume fraction of dioxane (■): T = 22 °C and (•): T = 34 °C.

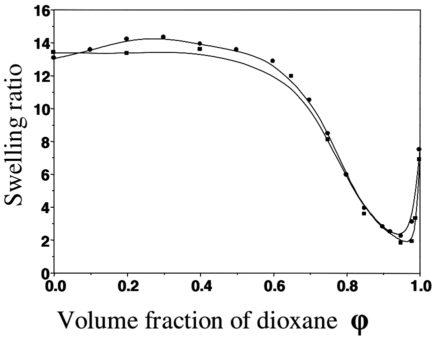

Figure 3. Variation of swelling ratio of GPNIPAM in water-dioxane mixtures with the volume fraction of dioxane (■): T = 22 °C and (•): T = 34 °C.

Contrary to the behaviour of GPNIPAM, the swelling behaviour of GPDMAM is practically not influenced by the dioxane content in the water-rich region. On the other hand, strong deswelling behaviour is observed in solvent mixtures very rich in dioxane ($0.8 < \varphi < 1$). Temperature increasing from 22 °C to 34 °C has no significant effect on the swelling behaviour of GPDMAM and the two curves obtained practically coincide. The behaviour of GPDMAM can also be explained from the results presented in Figure 1. In the water-rich region, no phase separation is observed and, thus, the hydrogel "senses" a good solvent. On the contrary, the temperatures 22 °C and 34 °C are within the phase separation region for $0.8 < \varphi < 1$. As a result, a pronounced deswelling is observed in this region.

Similar swelling experiments were performed at 22 °C and 34 °C for the three hydrogels P(NIPAM-*co*-DMAM33), P(NIPAM-*co*-DMAM50) and P(NIPAM-*co*-DMAM67). The results are presented in Figures 4 and 5, respectively for T = 22 °C and T = 34 °C. It is clearly observed that increasing the DMAM content of the hydrogels has an important effect mainly in the dioxane-rich region. Thus, in both Figures we observe that the swollen hydrogel for x=0 deswells gradually and a minimum of the swelling ratio appears as x increases. Furthermore, deswelling is somewhat less significant at the higher temperature. As a result, at T = 34 °C, the minimum is observed only for GPDMAM and GP(NIPAM-*co*-DMAM67) and not for the DMAM-poorer hydrogels, GP(NIPAM-*co*-DMAM33) and GP(NIPAM-*co*-DMAM67). On the other hand, in the water-rich region, the temperatures 22 °C and

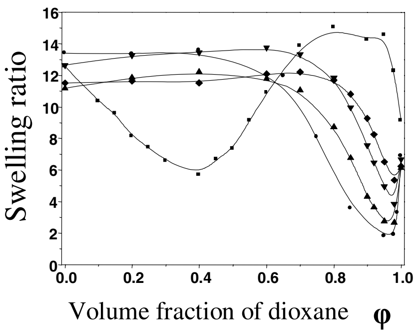

Figure 4. Variation of swelling ratio of hydrogels GP(NIPAM-*co*-DMAMx) in water-dioxane mixtures with the volume fraction of dioxane at 22 °C. x=0 (■), x=1 and (●), x=33 (◆), x=50 (▼), and x=67 (▲).

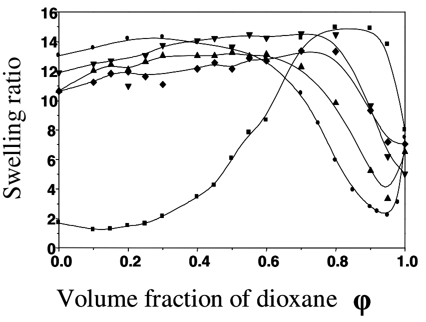

Figure 5. Variation of swelling ratio of hydrogels GP(NIPAM-*co*-DMAMx) in water-dioxane mixtures with the volume fraction of dioxane at 34 °C. x=0 (■), x=1 and (●), x=33 (◆), x=50 (▼), and x=67 (▲).

34 °C are within the one-phase region for all the other hydrogels, with the exception of GPNIPAM. As a result, no significant changes are observed in this region.

The exact nature of the cononsolvency behaviour of linear chains (and the corresponding re-entrant phenomenon observed with hydrogels) is still an open question. The most studied case may be 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 [1, 2, 18]. In fact, the formation of different water/methanol complexes which are poor solvents for PNIPAM has been recently proposed as the origin of cononsolvency of PNIPAM in water-methanol mixtures [6, 19, 20]. On the other hand, the studies on the cononsolvency behaviour of PNIPAM or PDMAM in water-dioxane mixtures are very rare. However, several investigations suggest that water/dioxane micelle-like clusters or complexes are present in water-dioxane mixtures, depending on the mixture composition [21-24]. Similarly to the water/methanol complexes, these water/dioxane clusters could possibly be involved in the cononsolvency behaviour observed with PNIPAM and PDMAM.

Conclusion

In the present study we investigated the swelling behaviour in water-dioxane mixtures of hydrogels, GP(NIPAM-*co*-DMAMx), of copolymers containing NIPAM and DMAM. Our intention was to combine the lower critical solution temperature-type cononsolvency of PNIPAM with the upper critical solution temperature-type cononsolvency of PDMPAM. In fact, we observed that the phase separation behaviour of the linear polymers is revealed as an important deswelling of the corresponding hydrogels. In accordance, deswelling is very sensitive to solvent composition as the two-phase region is approached. The swelling behaviour of the hydrogels is also sensitive to temperature. Nevertheless, this temperature sensitivity is important only when the temperature range studied crosses the two-phase region, as is the case of GPNIPAM. Otherwise, a gradual change of the swelling ratio with temperature is observed.

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