Polymers with a lower or an upper critical solution temperature (LCST or UCST) can precipitate in a very narrow temperature range. Cross-linking of such polymers and adding them to suited solvent results in smart gels that are capable of greatly changing their dimensions with changing temperature. This transition occurs very often in a broad temperature range, which limits the applicability of smart materials. To shed some light into the design of thermo-responsive hydrogels with a narrow phase transition, poly(2-ethyl-2-oxazoline) (PEtOx), poly(2-isopropyl-2-oxazoline), and statistical copolymers of 2-butyl-2-oxazoline and 2-ethyl-2-oxazoline, respectively, are synthesized and the concentration-dependent cloud point temperatures ($T_{cp}$) of the free polymers in aqueous media are determined in relation to the thermo-responsive swelling behavior of the respective hydrogels. A narrow thermal transition of the hydrogels can only be achieved when the $T_{cp}$ of the free polymers in water is independent on the concentration. Aqueous salt solutions can render even PETOx into a concentration independent LCST polymer. However, this salt effect does not work for hydrogels.

1. Introduction

Smart or responsive polymeric materials react to external stimuli, such as temperatures ranging from room or body temperature$^{[1,2]}$ up to 350 °C$^{[3,4]}$ chemicals or chemical vapors$^{[5]}$, radiation$^{[6]}$ or mechanical stress$^{[7,8]}$ by changing at least one of their properties, such as shape$^{[9,10]}$, conductivity$^{[11]}$, stiffness$^{[12,13]}$ or optical properties$^{[14]}$. Besides reacting to signals, smart polymers can also memorize environmental changes$^{[15]}$ or selectively react changing signal such as to the speed of heating$^{[16,17]}$. While bulk materials, such as shape memory polymers, can reversibly switch up to the 15-fold of their initial length$^{[18]}$ swollen polymer networks, referred to as gels, can reversibly undergo volume changes of 800%$^{[19]}$. Especially, water-swollen polymer networks—hydrogels—that undergo a temperature triggered phase transition in aqueous solution are of great interest, for example, for medical applications or microfluidic devices$^{[20]}$. One class of such polymers are the lower critical solution temperature (LCST) polymers, which are fully soluble in water at low temperatures and phase-separate upon heating$^{[21]}$. This phase separation is indicated by a visible precipitation appearing at the cloud point temperature ($T_{cp}$). The polymer volume transition at LCST can be understood as a transition from an expanded coil-like state to a collapsed state$^{[22-24]}$. LCST polymers with a very narrow molecular weight distribution or a high molecular weight of more than 20,000 g mol$^{-1}$ undergo this phase transition within a temperature range of 1 to 2 K.

Such a narrow phase transition is usually not found for water-swollen polymer networks that are composed of cross-linked LCST polymers, which limits the application of these interesting thermo-switching materials. Only a few thermo-responsive hydrogels with a narrow phase transition have been described so far, such as Poly(N-isopropylacrylamide) (PNiPAM)$^{[25,26]}$, cellulose-ether hydrogels$^{[27]}$, and polyacrylamide in acetone-water mixtures$^{[28]}$. Hydrogels with narrow transitions have in common that they are composed of LCST polymers that are low cross-linked. Further, these LCST polymers show no concentration-dependency on the cloud point temperature ($T_{cp}$) in solution. Based on this, the broadness of the swelling-deswelling phase transition might be explainable as follows: In cross-linked macromolecules the molecular weight between cross-links ($M_c$) is the responsible for the properties of the polymers. Thus, the cross-linked LCST polymers rather act as low molecular weight polymers, which have LCST phase transitions that are strongly dependent on molecular weight distribution and the nature of the end groups$^{[29]}$. Since the molecular weight distribution in cross-linked systems...
is often broad, this also results in a broad phase transition. If \( M_c \) is very high, the phase transition is less dependent on the dispersity, enabling a narrower phase transition as well. Further, if an LCST polymer has a concentration dependence on \( T_{cp} \), the respective hydrogel does not show a discrete transition either. \( T_{cp} \) at a certain concentration can be translated into a degree of swelling of the cross-linked polymer at a respective temperature. Thus, the swelling is continuous and does not abruptly change with temperature. Altogether, only hydrogels composed of lowly cross-linked LCST polymers with a concentration independent \( T_{cp} \) curve should be able to perform a narrow thermo-induced phase transition.

The present manuscript investigates this phenomenon on the example of hydrogels composed of different lowly cross-linked LCST poly(2-oxazoline)s in water and salt solutions.

2. Experimental Section

2.1. Materials

The chemicals and solvents were obtained from various suppliers and used as received.

Merck: Acetone (laboratory grade). VWR Chemicals: sodium chloride (NaCl). Acros Organics: ammonium sulfate (AS), valeronitrile, calcium hydride (CaH₂), methyl tosylate (99%), 2-ethyl-2-oxazoline (EtOx) (99%). Alfa Aesar: guanidine hydrochloride (GHCl), zinc acetate dihydrate (98%), isobutyronitrile (99%). Fisher Scientific: ethanolamine (99%), diethyl chlororide (GHCl), sodium chloride (NaCl). Acros Organics: ammonium sulfate (AS), and used as received. LiBr, 20 mmol, was used as a sulfonating agent. Methyl tosylate was distilled under reduced pressure. Acetonitrile was dried with a solvent drying system from MBRAUN of type SPS-800 via activated aluminum oxide column under argon atmosphere. All these chemicals were stored in an argon atmosphere and over molecular sieves (4 Å) at −20 °C. All other chemicals were of analytical grade or purer and used without further purification if not noted otherwise. Methyl tosylate was distilled under reduced pressure. The synthesis of 2-iso-propyl-2-oxazoline (iPropOx) from isobutyronitrile and 2-ethyl-2-oxazoline (EtOx) was performed with polymerization methyl tosylate (1 eq) and 5 mL of the respective monomer(s) were dissolved in 15 mL of dry acetonitrile under an argon atmosphere. The mixture was stirred in closed vessels at 80 °C for 72 h. The product was precipitated in 150 mL cold diethyl ether (Et₂O). The precipitant was separated from the Et₂O phase by centrifugation (5000 rpm, 5 min). After decantation of the Et₂O phase, the polymer was re-dissolved in chloroform and precipitated in ether again. The procedure was repeated three times. The resulting polymer was dialyzed against methanol for 6 h using conditioned benzoylated cellulose membranes (ZelluTrans, Roth, 1000 g mol⁻¹ molecular weight cutoff). The methanol was removed using a rotary evaporator apparatus to obtain a white powder and the yield of the polymer products were ≤50–70%. The composition of the polymers was calculated from the ¹H NMR spectrum in deuterated chloroform (CDCl₃). The molecular weight distribution was calculated via SEC in N,N-dimethylformamide (DMF) using polystyrene standards for calibration.

2.2. Monomer Synthesis

EtOx was distilled twice from CaH₂ under reduced pressure and argon atmosphere. Acetonitrile was dried with a solvent drying system from MBRAUN of type SPS-800 via activated aluminum oxide column under argon atmosphere. All these chemicals were stored in an argon atmosphere and over molecular sieves (4 Å) at −20 °C. All other chemicals were of analytical grade or purer and used without further purification if not noted otherwise. Methyl tosylate was distilled under reduced pressure. The syntheses of 2-iso-propyl-2-oxazoline (iPropOx) from isobutyronitrile and 2-butyl-2-oxazoline (ButOx) from valeronitrile were carried out according to literature. The reaction times were 72 h for ButOx and 48 h for iPropOx.

2.3. Polymer Synthesis

For polymerization methyl tosylate (1 eq) and 5 mL of the respective monomer(s) were dissolved in 15 mL of dry acetonitrile under an argon atmosphere. The mixture was stirred in closed vessels at 80 °C for 72 h. The product was precipitated in 150 mL cold diethyl ether (Et₂O). The precipitant was separated from the Et₂O phase by centrifugation (5000 rpm, 5 min). After decantation of the Et₂O phase, the polymer was re-dissolved in chloroform and precipitated in ether again. The procedure was repeated three times. The resulting polymer was dialyzed against methanol for 6 h using conditioned benzoylated cellulose membranes (ZelluTrans, Roth, 1000 g mol⁻¹ molecular weight cutoff). The methanol was removed using a rotary evaporator apparatus to obtain a white powder and the yield of the polymer products were ≤50–70%. The composition of the polymers was calculated from the ¹H NMR spectrum in deuterated chloroform (CDCl₃). The molecular weight distribution was calculated via SEC in N,N-dimethylformamide (DMF) using polystyrene standards for calibration.

2.4. Polymer Characterization

SEC was performed on a Viscotek GPCMax equipped with a refractive index detector (tempered to 55 °C) using a Tosoh TSKgel GMHHR-M (5.0 µm pores, 2 x ∞ 1x precolumn) column set to determine the molecular weight \( M_w \) and the dispersity \( D \) of the synthesized polymers. Saline DMF + LiBr, 20 mmol, was used as eluent at 60 °C at a flow rate of 0.70 mL min⁻¹. Calibration was performed with poly(styrene) standards (from Viscotek).

¹H NMR spectra were recorded in CDCl₃ using a Nanobay AVANCE-III HD-400 spectrometer with a 5 mm BBFosmart probe from Bruker BioSpin GmbH operating at 400 MHz and a DD2-500 spectrometer with 5 mm triple resonance H(C,X) probe from Agilent Technologies operating at 500 MHz to determine the composition of the different copolymers. The ¹H NMR spectra are displayed in Figures S7–S9, Supporting Information.

The results are displayed in Tables 1 and 2.

2.5. Network Synthesis

The different polymers were radically crosslinked with a combination of DCP (radical starter) and TAIC (crosslinker) as described elsewhere. The crosslinking was controlled by varying the amount of DCP added to the polymer, while keeping the DCP:TAIC ratio of 1:8 constant. The amounts used in the experiments are summarized in Table 3.

| Polymer | \( M_n,SEC \) [kg mol⁻¹] | \( D_{SEC} \) | ButOx NMR [mol%] |
|---------|----------------|----------------|------------------|
| P(EtOx-stat-ButOx) | 23.6 | 2.8 | 15 |
| 26.6 | 2.7 | 25 |
| 25.2 | 3.0 | 43 |
| Table 2. Average molecular weight \( M_n \), dispersity \( D \), and composition of the synthesized P(EtOx-stat-ButOx) copolymers. |

| Polymer | \( M_n,SEC \) [kg mol⁻¹] | \( D_{SEC} \) |
|---------|----------------|----------------|
| PiPropOx | 18.6 | 1.9 |
| 17.7 | 1.9 |
| Table 1. Average molecular weight \( M_n \), dispersity \( D \), and composition of Poly(2-isopropyl-2-oxazoline) (PiPropOx). |

Table 3. Molecular characterization of the synthesized P(EtOx-stat-ButOx) copolymers.
DCP and TAIC were dissolved in 30 mL acetone before 10 g of powdered polymer were added and stirred until a high viscous liquid formed. Subsequently, the acetone was completely removed by tempering in an oven at 80 °C for at least 24 h. The remaining mixture of polymer, DCP and TAIC was compression molded to sheets with the dimensions 50 mm × 30 mm × 1 mm (length, width, thickness) and cured for 30 min under exclusion of air in a heating press using a force of 35 kN and a temperature of 160 °C.

### 2.6. Network Characterization

The number of repeating units between crosslinks \( N_{\text{rep}} \) of the differently composed polymer-networks was calculated from the Young’s modulus determined by a dynamic thermomechanical analyzer (DMA2980). The respective Young’s modulus versus temperature curves are shown in Figures S1–S3, Supporting Information.

The \( N_{\text{rep}} \) s were calculated according to Flory’s theory of viscoelasticity in Equation (1) as the quotient of the netchain molecular weight \( M_c \) of the hydrogel and the molecular weight of the repeating unit \( M_{\text{rep}} \), which can be expressed as

\[
N_{\text{rep}} = \frac{2(1 + \theta) \cdot \rho(T) \cdot R \cdot T \cdot g^4}{E(T) \cdot M_{\text{rep}}} \tag{1}
\]

where \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( \rho(T) \) the density, \( g \) the gel content, \( T \) the absolute temperature and \( E(T) \) the equilibrium storage modulus. The equilibrium moduli were taken from the respective DMA measurements at 160 °C. The thermal expansion coefficient was measured with a thermomechanical analyzer (TMA2940) and used for calculating the density \( \rho(T) \) to 1.01 g cm\(^{-3}\) at 160 °C. The respective gel contents \( g \) were determined by extracting the respective network with deionized water and calculated as the ratio of the dry masses after and before the extraction. The gel contents \( g \) of the PiPropOx- and PEtOx-stat-ButOx-networks are displayed in Table S1, Supporting Information, while \( g \) of the PEtOx-networks can be taken from Ref. [36]. The Poisson ratio \( \nu \) is assumed as 0.4 as published in various papers.

### 2.7. Measurement of the Degree of Swelling

The differently crosslinked hydrogels were swollen in water and water/salt mixtures of varying concentrations. After extraction of the sol content with water, the weight \( m_{\text{dry}} \) of the dried samples was determined. The samples were swollen for at least 48 h in the respective solvent at temperatures ranging between −10 and 95 °C using a Lauda Eco Silver Thermostat. The equilibrium weight of the swollen samples \( m_{\text{swollen}}(T) \) was measured at the respective temperature after removal of excess water from the samples. The swelling temperature was decreased stepwise from 95 to up to −10 °C, depending on the used solvent, and increased again stepwise to 95 °C.

The gravimetrical degree of swelling \( S(T) \) is calculated as stated in Equation (2).

\[
S(T) = \frac{m_{\text{swollen}}(T)}{m_{\text{dry}}} \tag{2}
\]

### 2.8. Cloud Point Temperature \( T_{\text{cp}} \)

The polymers were dissolved in the chosen solvent at different concentrations and stored at 6 °C until the polymer was completely dissolved. This takes up to 2 weeks at high polymer concentrations, since the liquid becomes highly viscous. The aqueous polymer solutions were then transferred into a quartz-glass cuvette and placed into a photometer (Specord S 600 from Analytik Jena). The transmission was measured at a wavelength of 500 nm. The cuvette was heated using a peltier element with a heating rate of 30 K h\(^{-1}\). The temperature at which the transmission reached 50% was considered to be the cloud point temperature.

The respective transmission-temperature curves are shown in Figures S4–S6, Supporting Information.

### 3. Results and Discussion

We propose that the discrete switching of LCST hydrogels depends on the concentration-dependent \( T_{\text{cp}} \) of the free polymer in aqueous solutions and on a narrowly distributed netchain molecular weight \( M_c \). In this work, the number of repeating units between crosslinks \( N_{\text{rep}} \), which is expressed as the quotient of the netchain molecular weight \( M_c \) of the hydrogel and the molecular weight of the repeating unit \( M_{\text{rep}} \) is used to describe and compare the differently structured hydrogels. In contrast to the poly(2-oxazoline) networks cross-linked by the end groups,[40,41] we chose to cross-linked these polymers via their side groups. Previously reported PEtOx hydrogels cross-linked this way show a nearly linear decrease of swelling in water with increasing temperature over a very wide temperature range.[36] Given the concept above, the transition of PEtOx hydrogels should be more discrete in an environment, where the free PEtOx shows no concentration dependency on \( T_{\text{cp}} \). The LCST behavior of PEtOx in aqueous salt environments has been performed for selected low polymer concentrations and these studies revealed that the LCST of PEtOx shifts to lower temperatures.[42–46] The \( T_{\text{cp}} \) versus concentration curve of PEtOx was only determined in lowly concentrated aqueous sodium chloride (NaCl) solutions, which resulted
in a shift of the curve to lower temperatures without changing the shape of the curve.\[47\] In order to find an environment that might also reduce concentration dependency of the curve, we investigated the cloud point temperatures of PEtOx with an average molecular weight $M_w$ of 122 kg mol$^{-1}$ in different highly concentrated aqueous salt solutions. The salts were chosen according to their classification in the Hofmeister series.\[48\] Kosmotropes are well-hydrated ions that cause a salting-out effect by destabilizing the hydrogen bonds between water and the polar groups of the polymer. This increases the cost of hydration and enhances hydrophobic interactions and thus, results in a decrease of the $T_{cp}$ and solubility with increasing salt concentration.\[49–51\] Chaotropes on the other hand are poorly hydrated ions, which increase $T_{cp}$ and the solubility. GHCl was chosen as a chaotrope, NaCl as a weak kosmotropic salt and AS as a strong kosmotrope.

As seen in Figure 1, PEtOx greatly reacts to salts in the surrounding aqueous environment. The LCST of PEtOx in water is 64 °C at a PEtOx concentration of 2 wt%. Higher polymer concentrations result in increased $T_{cp}$s. When adding the chaotropic salt GHCl to water (Figure 1a), the LCST increases. This effect gets more pronounced with higher salt concentrations. Interestingly, the aqueous solution of the 2.5 wt% GHCl affords an untypical $T_{cp}$ curve, changing the type 1 LCST PEtOx to a type 3 LCST polymer. The latter polymers are known to show a maximum and a minimum of the $T_{cp}$ versus concentration curve. Further increasing the salt concentration seems to diminish this effect. Altogether, the $T_{cp}$ of PEtOx strongly increases with higher polymer concentrations for all GHCl concentrations.

When adding the weakly kosmotropic salt NaCl (Figure 1b), the transition temperatures shift as well, but in this case to overall lower $T_{cp}$s. The polymer concentration dependence of PEtOx on $T_{cp}$ becomes less pronounced with higher salt concentrations and nearly diminishes at 15 wt% NaCl. The $T_{cp}$ is even slightly decreasing by 3–4 K at higher polymer concentrations.

The kosmotropic salt AS also results in lowered $T_{cp}$s (Figure 1c). Interestingly, here the $T_{cp}$s of PEtOx become nearly independent on the concentration at an AS concentration of only 2.5 wt%. Further increasing the AS concentration to 5 wt% is not only decreasing the cloud points of PEtOx, but also renders the slope of the $T_{cp}$ versus concentration curve negative. A possible explanation for this behavior is that the lower critical solution concentration (LCSC), the concentration at which the LCST occurs, is shifted to higher values due to the kosmotropic salts. The LCSC shifts from $\approx$2 wt% PEtOx in pure water to $\approx$30 wt% PEtOx at an AS concentration of 2.5 wt%. The LCSC at 5 wt% AS is supposedly at a higher concentration. It seems reasonable to assume that the concentration-dependence of LCST polymers in aqueous solution is diminished by salts, because they form a corona (diffusion layer) around the polymer coil, which hinders intermolecular interactions and, thus, precipitation.

Thus, all three salt solutions afford changed $T_{cp}$s and the two kosmotropic salts NaCl and AS at certain concentrations render PEtOx a concentration-independent LCST polymer.
This should make the resulting hydrogels thermo-responsive with narrow phase transitions. The temperature-dependent swelling-deswelling of PEtOx hydrogels in different media is discussed in the following. During the swelling experiments, no differences between degrees of swelling were measured during the heating or cooling cycle, even at highest salt concentration. This means the hydrogels were at the equilibrium during testing.

First, the swelling of PEtOx hydrogels in aqueous GHCl is examined. To this end, solutions with salt concentrations of 0.5, 2.5, and 10 wt%, respectively, were prepared and PEtOx networks with different degrees of cross-linking were swollen in these solutions.

All swelling curves seen in Figure 2 converge at a break point temperature $T_{BP}$ similar to the one reported for PEtOx in pure water. The chaotropic salt GHCl has two effects on the swelling behavior of the PEtOx hydrogels. On the one hand, the degree of swelling $S$ increases for every degree of crosslinking and temperature. On the other hand, $T_{BP}$ of the networks also increases toward higher values. Both is in accordance with the behavior of PEtOx shown in Figure 1 and reported in the literature. $T_{BP}$ increased from 60 to $\approx 90^\circ C$ at a concentration of 10 wt% GHCl. The overall shape of the swelling curve did not change. This was expected, since the $T_{cp}$-curves of PEtOx show the same concentration dependence at all GHCl concentrations.

In contrast to aqueous GHCl, a solution of NaCl in water renders PEtOx into a concentration independent LCST polymer.

The results of the PEtOx hydrogels swollen in differently concentrated aqueous NaCl solutions at different temperatures are shown in Figure 3. Instead of increasing $S$, like it was the case for GHCl, $S$ decreases with increasing NaCl concentration for every degree of crosslinking and temperature. $T_{BP}$ is also decreased from $\approx 67^\circ C$ for 0.5 wt% NaCl to $42^\circ C$ for 15 wt% NaCl. The change of swelling is linear over the whole temperature range in all cases. Thus, the salt does not afford a more discrete thermal switching, as would be expected from the $T_{cp}$-curve in Figure 1 at the highest NaCl concentration. However, the swelling-deswelling rate $dS/dT$ slightly increases with rising NaCl concentration, most notably for the hydrogel with the lowest $N_{rep}$.

As seen in Figure 4, the kosmotropic AS, which has a strong effect on the concentration-dependence of $T_{cp}$, also lowers $S$ and $T_{BP}$ in the PEtOx hydrogels with increasing concentration. The temperature-induced swelling is still linear at 0.5 and 5 wt%. In contrast, the swelling-deswelling curve in 2.5 wt% aqueous AS solution is diverging from the linear slope to a somewhat sigmoidal shape, indicating that the $T_{cp}$-dependence of PEtOx on the concentration in this medium (Figure 1) is influencing the swelling deswelling/curve. However, the effect cannot be interpreted as discrete switching of the thermo-responsive hydrogel.

Altogether, aqueous salts particularly those with kosmotropic character are capable of influencing the concentration-dependence of $T_{cp}$ of PEtOx. Optimal salt concentrations of
NaCl and AS have the potential to render PETOx a concentration-independent LCST polymer similar to PNIPAM in water. The PETOx hydrogels, however, only react to the aqueous salt solutions by changing their break point temperature, but still show a broad nearly linear shrinking with higher temperatures and not the expected more discrete, sigmoidal-like switching curve of PNIPAM hydrogels. Only a 2.5 wt% aqueous AS solution affords a weak effect that indicates a slight influence of the salt. One reason for the weak influence of the salts on the volume transition of PETOx hydrogels could be that the salting-out effect does not work within hydrogels, because it might need more free space to form an effective diffusion layer on the surface of the polymers. Another reason could be that the here used cross-linking strategy renders $M_f$ very broad and, thus, the transition as well. In order to investigate this, poly(2-oxazoline)s without concentration dependence on $T_c$ were cross-linked applying the strategy above.

Poly(2-iso-propyl-2-oxazoline) (PiPropOx), which is similar to PNIPAM, was synthesized in molecular weights of $\approx 18$ kg mol\(^{-1}\). The $T_c$ versus concentration curve in water shows the same behavior as PNIPAM (Figure 5a). Radically cross-linking this polymer with 0.4 wt% DCP and 3.2 wt% TAIC results in a polymer network that is hardly swellable in water. This is due to the crystalline character of the material, which is preserved even in swollen state.\(^{[52,53]}\)

As found for the other hydrogels, the swelling curves of all differently cross-linked PiPropOx hydrogels converge at a temperature ($T_{3p}$), which corresponds to the LCST of the respective PiPropOx in water (Figure 5a). In contrast to the swelling curves of PETOx in aqueous salt solutions, lowly cross-linked PiPropOx shows a somewhat sigmoidal shape, indicating a more discrete thermal switching of the PiPropOx hydrogels near LCST. However, the crystalline character of the hydrogels prevents larger changes in swelling.

In order to create stronger swellable thermo-responsive hydrogels, amorphous statistical copolymers prepared with EtOx and ButOx in different compositions with molecular weights of 23 to 27 kg mol\(^{-1}\) were synthesized and cross-linked as described above. The $T_c$ versus temperature curves of the free polymers shown in Figure 6a indicate a near concentration-independence on $T_c$. The temperature-dependent swelling curves of the cross-linked polymers shown in Figure 6b all have a sigmoidal shape.

Particularly, the hydrogel with 43 mol% BuOx shows a strong shrinkage from $S = 3$ to $S = 1.57$ in a narrow temperature range of 5 K near the LCST of the linear polymer. This is close to the shrinkage found for a PNIPAM hydrogel and shows that the cross-linking strategy is generally suited to synthesize thermosensitive hydrogels with narrow phase transitions.
4. Conclusions

As shown in the present manuscript, salts of kosmotropic character are suited to diminish the concentration-dependence of $T_{cp}$ of an LCST polymer (PEtOx) in water resulting in $T_{cp}$-curves similar to PNiPAM. It was expected that this affords for a PEtOx hydrogel in the respective salt solution a PNiPAM hydrogel like thermally induced volume transition (Figure 7a).

Unfortunately, the salt solutions do not lead to a narrow phase transition of thermo-sensitive hydrogels prepared from PEtOx, as seen by the swelling curve not following the $T_{cp}$-curve (Figure 7b). The concentration-dependence of LCST polymers in aqueous solution is diminished by kosmotropic salts in suited concentrations, which is an observation not yet reported and may be of potential future use. We assume the salts ions form a corona (diffusion layer) around the polymer coil, which hinders
intermolecular interactions and, thus, precipitation. This would not work in a hydrogel, because the cross-linked polymers do not provide enough free volume for such a corona. The narrow transition of hydrogels prepared by cross-linking of concentration independent LCST polymers using the same cross-linking strategy shows that this argumentation is valid (Figure 7c). Interestingly, the salts still enable the same shift of $T_{\text{BP}}$ in the hydrogel as it affords a shift in LCST of the free polymer in aqueous salt solution. Altogether, the present study shows that it is mandatory for near discrete switching of thermo-responsive hydrogels to lowly cross-link high molecular weight LCST polymers that have no concentration dependence on $T_{\text{BP}}$.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

hydrogels, LCST, poly(2-oxazoline), thermoresponsiveness

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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