Investigation of the swelling behavior of hydrogels derived from high-molecular-weight poly(2-ethyl-2-oxazoline)

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Abstract
Thermoresponsive hydrogels are of great importance as smart materials. They are usually composed of cross-linked polymers with a lower critical solution temperature (LCST). Although much is known about networks of poly(N-isopropylacrylamide), all other polymers are somewhat neglected. In this work, the temperature-dependent swelling behavior of differently cross-linked thermoresponsive poly(2-ethyl-2-oxazoline) (PEtOx) hydrogels were investigated with regard to varying parameters of the network composition. It was found that the degrees of swelling of the hydrogels converge for a certain polymer/solvent system at a distinct temperature independent of its degree of cross-linking. Furthermore, this temperature correlates with the LCST of the respective starting PEtOx. Its net chain molecular weight $M_c$ only affects the maximum degree of swelling and thus, the swelling–deswelling rate of the hydrogel. The fundamental structure/property relations found in this study could be useful to predict the behavior of other thermoresponsive hydrogels.

KEYWORDS
hydrogel, LCST, thermoresponsive

1 | INTRODUCTION

Smart or responsive materials react to external stimuli by changing at least one of their properties, such as shape,[1,2] stiffness,[3,4] or optical properties.[5] One way to obtain stimuli-responsive materials is chemical cross-linking of linear polymers with high molecular weight. Performing an uncommonly light cross-linking at the borderline between elastomer and thermoplastic, referred to as critical cross-linking, offers the advantage that the initial properties of the thermoplastic are nearly preserved, while classically a shape-memory effect and often further new properties are obtained.[6–13] A suited approach for realizing new stimuli-responsive materials is to use thermoplastics, which are inherently thermoresponsive. Especially, polymers that undergo a temperature-triggered phase transition in aqueous solution are of great interest, for example, for medical applications in drug delivery,[14–20] artificial muscles,[21] and desalting/dewatering of proteins[22,23] or for actuators and sensors.[24–27] One class of such polymers is the lower critical solution temperature (LCST) polymers, which are fully soluble in water at low temperatures and phase-separate upon heating.[28] This phase separation is indicated by clouding appearing at the cloud point temperature ($T_{cp}$).

Popular thermoresponsive polymers include poly(N-isopropylacrylamide) (PNiPAM),[29,30] poly(vinyl caprolactame)s,[31] poly(vinyl methyl ether)s,[32] and poly(2-alkyl-2-oxazoline)s (POx).[28,33–35] POx polymers have
proven to be an interesting polymer class, as their LCST behavior can be influenced by chain length, side chains,[36] monomer composition,[34] end groups,[37] and copolymerization,[38] as well as external factors such as pH,[39] salt concentration,[40] or other additives.[41] POx with ethyl,[42] propyl,[34] cyclopropyl,[43] or iso-propyl[44] groups at the 2-position of the respective 2-alkyl-2-oxazoline exhibit an LCST in water.[45]

While, the phase transition of the free polymers in solution is usually rather sharp, being completed within 1–2 K, the phase transition of the cross-linked polymers is much broader. This is ascribed to the influence of molecular weight[46,47] and the nature of the end groups, but also to the concentration dependence of $T_{\text{cp}}$.[31,48–50] Numerous polymers have been cross-linked to obtain hydrogels that show a relatively sharp phase transition (transition range of 1–2 K).[31,46–48,50–52] However, POx-based hydrogels have been found to show no sharp phase transition, but to transit from a highly to a lowly swollen state due to a change of the swelling–deswelling rate $dS/dT$ over a broad temperature range.[46,48,53] Such POx-hydrogels are prepared by end-group linking,[48,54–56] simultaneous copolymerization of a monomer with a multifunctional cross-linker,[57–63] or only using a radical starter and a multifunctional cross-linker.[8]

Goal of this study was to find out if this broad transition stems from the inherent properties of the linear polymer used for hydrogel synthesis or if this is due to the used cross-linking approach. To achieve this, high-molecular-weight PEtOx was statistically cross-linked by using very low amounts of cross-linker. This approach offers the opportunity to be able to select a different degree of cross-linking without having to synthesize a new polymer or if this is due to the concentration of $C_p$.[31,48–50] The net chain molecular weight $M_c$ of the differently composed PEtOx networks was calculated from Young’s modulus determined by a dynamic thermomechanical analyzer (DMA2980). The respective Young’s modulus versus temperature curves are shown in Figures S1 and S2.

The $M_c$’s were calculated according to Flory’s theory of viscoelasticity[63] as

$$M_c = \frac{2(1+\theta)\cdot \rho(T) \cdot R \cdot T \cdot g^{1/3}}{E(T)},$$

where $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $\rho(T)$ is the density, $\varphi$ is the gel content, $T$ is the absolute temperature, and $E(T)$ is the equilibrium storage modulus. The equilibrium moduli were taken from the respective DMA measurements of dry PEtOx samples 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 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 (see Figure S3). The Poisson ratio $\nu$ is assumed as 0.4 as published in various papers.[66–68]

2.2 Network synthesis

PEtOx was cross-linked with a combination of DCP and TAIC as cross-linking agents. Various DCP/TAIC/PEtOx combinations ranging from 0.05 to 2.04 wt% DCP and a DCP to TAIC ratio of 1:8 were used.[8,64] DCP and TAIC were dissolved in approximately 30 ml of acetone. Subsequently, 10 g of powdered PEtOx was added and stirred until a high viscous liquid formed. Then, the acetone was completely removed by tempering in an oven at 80 °C for at least 24 hr. The remaining solid mixture of PEtOx, 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.

2.3 Network characterization

The following chemicals and solvents were obtained from various suppliers and used as received: acetone (laboratory grade); dicumyl peroxide (DCP) (98%), triallyl isocyanurate (TAIC) (98%), and poly(2-ethyl-2-oxazoline) (PEtOx) (Sigma Aldrich) with molecular weights $M_n$ labeled as 500 and 50 kg mol$^{-1}$. The $M_n$ was determined to be 122 kg mol$^{-1}$ with a polydispersity $D$ of 2.9 and 10 kg mol$^{-1}$ with a $D$ of 6.7, respectively, using SEC chromatography as described in a previous work.[8]

2.4 Measurement of the degree of swelling

The differently cross-linked hydrogels were swollen in water, ethanol, and a water/ethanol mixture (92/8 wt%).
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 hr in the respective solvent at temperatures ranging between \(-10\) and \(95^\circ\text{C}\) using a Lauda Eco Silver Thermostat. The equilibrium weight of the swollen samples \( m_{\text{swollen}} \) was measured at least in triplicate at the respective temperature after removal of excess water from the samples. The swelling temperature was decreased stepwise from \(95^\circ\text{C}\) to \(-10^\circ\text{C}\), depending on the used solvent, and increased again step-wise to \(95^\circ\text{C}\).

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

\[
S = \frac{m_{\text{swollen}}}{m_{\text{dry}}},
\]

### RESULTS AND DISCUSSION

The aim of this study was to investigate the temperature-dependent swelling behavior of hydrogels prepared from high-molecular-weight PE\(\text{O}_{x}\). PE\(\text{O}_{x}\) is the most common commercially available POx. It shows a Flory-Huggins Type I behavior in water, that is, its LCST shifts to lower concentration with increasing molecular weight. It further shows strongly increased \( T_{\text{cp}} \) with increasing polymer concentration.\(^{[31,48–50]} \) The whole curve shifts to lower \( T_{\text{cp}} \) values with higher molecular weight.\(^{[46,47]} \)

Two commercial PE\(\text{O}_{x}\) hydrogels with distinctly different average molecular weights \( M_{n} \) of 122 kg mol\(^{-1}\) \((M_{\text{w}} = 355 \text{ kg mol}^{-1}\)\) and 10 kg mol\(^{-1}\), \((M_{\text{w}} = 67 \text{ kg mol}^{-1}\)\), respectively, were used to prepare differently cross-linked PE\(\text{O}_{x}\) networks and to explore their degree of swelling \( S \) in dependence on the net chain molecular weight \( M_{c} \), temperature \( T \), and the kind of solvent used for swelling.

### 3.1 Network characterization

The two linear PE\(\text{O}_{x}\) starting polymers were cross-linked to different degrees using DCP as radical starter and TAIC as cross-linker in a ratio of 1:8 as reported elsewhere.\(^{[8,64]} \) The names of the obtained networks refer to the number average molecular weight of the respective starting polymer (e.g., PE\(\text{O}_{x10k}\) is a network based on PE\(\text{O}_{x}\) with an \( M_{n} \) of 10 kg mol\(^{-1}\)). Figure 1 shows the net chain molecular weights \( M_{c} \) of all prepared networks in dependence on the used starting polymer and applied cross-linker concentration \( w_{\text{DCP} + \text{TAIC}} \) (corresponding Young’s modulus vs. temperature plots are provided in Figures S1 and S2). The highest \( M_{c} \) of PE\(\text{O}_{x10k}\) and PE\(\text{O}_{x122k}\) corresponds to the respective critical degree of cross-linking, which is the degree of cross-linking right at the borderline between thermoplastic and elastomer where the viscosity of the polymer firstly becomes infinite.

The net chain molecular weights \( M_{c} \) of both networks decrease expectedly with increasing cross-linker concentration. Furthermore, as Figure 1 shows, PE\(\text{O}_{x10k}\) requires about 2.5 times more cross-linker compared to PE\(\text{O}_{x122k}\) to obtain a similar \( M_{c} \). This can be explained by the number of chains per unit volume, which is higher for PE\(\text{O}_{x10k}\) than for PE\(\text{O}_{x122k}\).

### 3.2 Swelling behavior

The swelling behavior of PE\(\text{O}_{x}\) networks was explored in dependence on the degree of cross-linking and temperature by immersing the respective samples in water until no change of the degree of swelling \( S \) was observable. To this end, the temperature was stepwise decreased from \(95^\circ\text{C}\) to up to \(-10^\circ\text{C}\), and increased again stepwise to \(95^\circ\text{C}\). To rule out kinetic effects, the sample was kept at the respective temperature for 48 hr before determining the degree of swelling. No hysteresis was found for degrees of swelling obtained upon heating or cooling.

Figure 2a shows the obtained degrees of swelling of differently cross-linked networks derived from PE\(\text{O}_{x122k}\) with a \( D \) of 2.9, in dependence on temperature. As seen in Figure 2a, the temperature dependence of \( S \) of the differently cross-linked PE\(\text{O}_{x122k}\) networks can be divided in two domains with different swelling–deswelling rates \( dS/dT \). The curves have different slopes on the left side and similar \( dS/dT \) values on the right side. The point where all the swelling curves converge is named break point, which is at a temperature of about

\[\text{FIGURE 1} \quad \text{Net chain molecular weight} \ M_{c} \ \text{in dependence on the used starting polymer and applied cross-linker concentration} \ w_{\text{DCP} + \text{TAIC}}. \]
66 °C. Below this break point temperature \( (T_{BP}) \), \( S \) of PEtOx\textsubscript{122k} is the higher the \( M_c \) of the network and it linearly decreases with increasing temperature.\[^{[69]}\] The network with the highest \( M_c \) shows the steepest slope of about 0.33 K\(^{-1}\). \( dS/dT \) abruptly changes at the \( T_{BP} \) and, above this temperature, all PEtOx\textsubscript{122k} samples exhibit nearly the same \( S \) values, which decrease with a \( T \) dependency (\( dS/dT \) of about 0.033 K\(^{-1}\)). A PEtOx\textsubscript{122k} network with an \( M_c \) of 1.5 kg mol\(^{-1}\) shows only the Flory–Huggins regime. In accordance with the literature, we assume that the swelling behavior below \( T_{BP} \) is solvation-induced amplified upon formation of hydration shells along the net chains of the PEtOx hydrogels.\[^{[42,70]}\]

Above \( T_{BP} \) and for hydrogels with critically low \( M_c \)'s also below \( T_{BP} \), this effect seems to play no role for the swelling behavior of PEtOx hydrogels. Wu et al. have investigated the temperature-dependent water content of single PNiPAM chains. They found that these chains still contain 66% of water above their LCST.\[^{[71]}\] It is likely that this is similar for PEtOx. This is in good agreement with the measured \( S \) of our PEtOx hydrogels above \( T_{BP} \). Thus, a hydrogel with a degree of swelling of less than 1.6 will not be thermoresponsive according to the LCST behavior.

The dependence of \( S \) on the temperature of the here described LCST hydrogel seems not typical for this kind of materials. Often, the swelling curves of hydrogels prepared from LCST polymers exhibit an S-shaped transition. The S-shaped transition can be separated in three domains. Before and after the transition from a high to a low degree of swelling \( S \), the change of \( S \) with temperature is low. The middle part shows a very high absolute value for \( dS/dT \), which reportedly occurs at a temperature around the LCST of the respective polymer. This holds true for hydrogels exhibiting a sharp transition range between the fully swollen and deswollen hydrogels. Here, however, the temperature-induced shrinking starts at a temperature supposedly near or below 0 °C and stops at the \( T_{BP} \) at 66 °C, which seems to coincide with the LCST of the linear polymer of 64 °C (see Figure S4).

This has also been reported for the PEtOx hydrogels, derived by cross-linking the polymers via their end groups.\[^{[48]}\] It is worth noting that the PEtOx hydrogels stay fully transparent over the whole swelling–deswelling cycle, indicating that the polymer chains do not aggregate as they do in solution (see Figure 2bc). This is most likely due to entropic reasons, because locally collapsing segments of the hydrogel would result in high stretching of the noncollapsed surrounding chains. Such a scenario would cause a great decrease in entropy and is therefore thermodynamically unfavorable.

In the described case here (Figure 2a),

1. the breaking point temperature \( T_{BP} \) seems to be related to the LCST of the linear polymer;
2. there is a very broad, nearly linear transition range; and
3. almost the whole temperature-induced fast shrinking occurs way below the LCST.

The following experiments are designed to get a better insight into this strange behavior.

First, it was explored, if the temperature-induced shrinking of the PEtOx hydrogel is indeed related to the LCST behavior of PEtOx. If this holds true, the temperature-dependent change of swelling of a PEtOx hydrogel in a solvent in which linear PEtOx shows no LCST should show a Flory–Huggins regime over the whole temperature range, that is, there will be no \( T_{BP} \). Because PEtOx is known to be fully soluble in ethanol at all temperatures,\[^{[35]}\] we carried out swelling experiments with the PEtOx\textsubscript{122k} hydrogels in ethanol to check this. The swelling curves of the PEtOx\textsubscript{122k} hydrogels with different \( M_c \)'s are shown in Figure 3.

\( S \) continuously decreases with increasing temperature with a \( M_c \)-dependent constant swelling–deswelling rate \( dS/dT \). In accordance with the Flory–Huggins solution theory, \( dS/dT \) ranges from 0.010 to 0.033 K\(^{-1}\) for hydrogels with \( M_c \)'s from 8.3 to 22.9 kg mol\(^{-1}\), respectively. These \( dS/dT \)s are nearly the same as found for PEtOx\textsubscript{122k} hydrogels swollen in water above \( T_{BP} \). Moreover, the
LCST behavior of a linear polymer is the prerequisite for the occurrence of a $T_{BP}$ in a hydrogel.

We assumed that the break point temperature $T_{BP}$ might be the LCST of the starting polymer of the cross-linked hydrogel. This is even more difficult to comprehend, since $T_{BP}$ is not dependent on the degree of cross-linking, as the molecular weight dependency of the LCST might suggest.\(^{[46,47]}\) In order to get more data for this assumption, the hydrogels based on the $10 \text{ kg mol}^{-1} \text{PEtOx}$ were investigated regarding their temperature-dependent swelling characteristics. This polymer has an LCST in water of $69{\degree C}$.\(^{[46,47]}\) As seen in Figure 4, the swelling curves of the differently cross-linked PEtOx10k hydrogels can be separated in two domains, similar to the hydrogels prepared from PEtOx122k. Again, the degree of swelling $S$ of the PEtOx10k hydrogels strongly depends on temperature and $M_c$ below the break point temperature $T_{BP}$. $dS/dT$ below $T_{BP}$ is the higher, the higher the $M_c$ of the hydrogel. The highest $dS/dT$ of $0.15 \text{ K}^{-1}$ was found for the PEtOx10k with a $M_c$ of $26.4 \text{ kg mol}^{-1}$. Above $T_{BP}$, the $dS/dT$s of all PEtOx10k hydrogels are nearly identical with approximately $0.012 \text{ K}^{-1}$. The difference of the $dS/dT$s of PEtOx10k networks above and below $T_{BP}$ is analog to the PEtOx122k hydrogels up to an order of magnitude. Compared to the PEtOx122k hydrogels (see Figure 2a), the $T_{BP}$ of the PEtOx10k hydrogels is at a higher temperature of about $72{\degree C}$. Analog to the hydrogels prepared from the PEtOx122k starting polymer, the $T_{BP}$ of $72{\degree C}$ found in the swelling curves of the PEtOx10k hydrogels also correlates well with the LCST of $69{\degree C}$ of the linear PEtOx10k starting polymer used for hydrogel synthesis. These findings support our hypothesis that the $T_{BP}$ is indeed related to LCST.

Another way to investigate this is to use a different solvent system to alter the LCST of the linear starting polymer and check if the $T_{BP}$ is altered, too. It is known that using binary water/ethanol mixtures with up to 12 wt% ethanol shifts the LCST of PEtOx to higher temperatures compared to pure water due to a better solution of the polymer chains.\(^{[35,72,73]}\) Before in a water/ethanol mixture containing more than 12 wt% ethanol the LCST behavior disappears, a mixture with only 8 wt% ethanol was chosen. Figure 5 shows the obtained equilibrium degrees of swelling of the differently cross-linked PEtOx122k networks in dependence on temperature in the water/ethanol mixture (92/8 wt%).

Similar to the swelling curves obtained for PEtOx122k hydrogels swollen in water, the swelling curves of the differently cross-linked PEtOx122k hydrogels (Figure 5) in a water/ethanol mixture (92/8 wt%) can be separated in two domains. Analog to the hydrogels swollen in pure water, $S$ again strongly depends on the temperature and $M_c$ below $T_{BP}$, with $dS/dT$ of up to $0.30 \text{ K}^{-1}$. Above $T_{BP}$,
the dependency of $S$ on temperature is less strong with $dS/dT$ of approximately 0.06 K$^{-1}$. $T_{BP}$, at which the swelling behavior changes, is also significantly higher at approximately 79 °C as seen in Figure 5. Moreover, the LCST of the linear PEtOx$_{122k}$ starting polymer in this water/ethanol mixture increases in accordance with the literature to about 75 °C (see Figure S6). Thus, both, the LCST of linear PEtOx$_{122k}$ and the $T_{BP}$ of the hydrogels shift by approximately 12 K to higher temperature upon adding 8 wt% ethanol. This also supports the aforementioned hypothesis of the correlation of $T_{BP}$ and the LCST.

According to our experiments, the location of the $T_{BP}$ correlation with the LCST of the linear polymer is, contrary to the usual expectation, independent of the net chain molecular weight and only depends on the initial molecular weight of the linear polymer and solvent used for swelling and thus, the increased molecular weight due to cross-linking offers no explanation to this behavior.

The found correlation of the break point temperature $T_{BP}$ of a PEtOx hydrogel with the LCST of the linear starting PEtOx used for network preparation can, however, be explained by the strong dependency of the LCST on the number and kind of end groups,[37] which is the higher, the lower the molecular weight of PEtOx. Because, due to the here applied cross-linking approach, the total amount of end groups of PEtOx is preserved in the hydrogel, it is reasonable that the LCST of the starting PEtOx and the $T_{BP}$ of the resulting hydrogel correlate. The kind of end group plays no role in this case.

Further indications that the break point temperature $T_{BP}$ truly correlates with the LCST independent of kind of end groups can already be found in the literature. For example, Christova et al. obtained swelling curves from hydrogels synthesized via end-group linking of PEtOx bis-macromonomers and other polymers.[48] The shown swelling curves exhibit a $T_{BP}$ at the LCST, independent of the hydrogel composition. Comparing the $T_{cp}$ curve$^{[30]}$ and the swelling curve$^{[74]}$ of the Flory–Huggins Type II polymer PNiPAM shows also that the LCST and the $T_{BP}$ of the swelling curves are both at about 32 °C. Moerkerke et al., who studied the swelling and phase behavior of cross-linked poly(vinyl methyl ether) with Flory–Huggins Type III behavior,[75] found a discontinuity of the swelling curve between 35 and 36 °C, while the $T_{cp}$ curve is bimodal with an estimated three phase line at 36 °C.$^{[75–77]}$

As described in other studies, the transition range below $T_{BP}$, in which $S$ of the hydrogel steeply decreases, is broader than the observed cloud point transition of the linear polymer.$^{[46,48,53]}$ While the transition range of hydrogels is very broad, spanning over at least 50 K in our case, the cloud point transition of the respective commercial linear polymer occurs within a range of 1–2 K (see Figures S4 and S6). Comparing the $T_{cp}$ curve of linear PEtOx$_{122k}$ (see Figure S4) and the swelling curves of PEtOx$_{122k}$-networks (Figure 6), it stands out that above the LCST, the swelling curves of the networks approximate the $T_{cp}$ curve. Looking at the $T_{cp}$ curve$^{[30]}$ and the swelling curve$^{[74]}$ of PNiPAM (Figure 7), this becomes clearer. Considering the correlation of the $T_{cp}$ curve and the swelling curves, it also supports the hypothesis of the correlation of $T_{BP}$ and LCST. This also shows that it is the characteristic of the $T_{cp}$ curve, which determines, whether a hydrogel shows a sharp or broad transition. Since the concentration-dependence of the $T_{cp}$’s of a polymer is related to its hydrophilicity,$^{[34]}$ the same would be expected for the respective hydrogel. PEtOx $T_{cp}$’s have a strong concentration-dependence leading to a continuous, broad transition in the hydrogel, while the $T_{cp}$’s of PNiPAM are up to a polymer concentration of about 30 wt% nearly independent of the concentration resulting in a sharp transition in the hydrogel.

This means, it is false to assume that a hydrogel prepared from a LCST polymer shows a sharp transition in general, even if the cloud point transition in solution is sharp.

Next, we address the question, why the majority of the transition of the hydrogel occurs below LCST of the linear polymer PEtOx. There is a number of possible explanations for the described discrepancy between the phase transition of the hydrogel and the linear polymer. One reason could be the hydrophobic cross-linker, which might act as comonomer lowering the cloud point temperature of chains with each cross-link$^{[38]}$ This would cause a gradual shrinking, starting at chains with a high cross-linker concentration and therefore low cloud point temperatures. Given the fact that the broad transition

![FIGURE 6 Phase diagram containing the cloud point temperatures $T_{cp}$ of the thermoplastic starting PEtOx$_{122k}$ and the swelling curves of differently cross-linked PEtOx networks prepared from PEtOx$_{122k}$ in water. $w_{PEtOx}$ was measured in triplicate and the error bars are the respective standard derivation. PEtOx, poly (2-ethyl-2-oxazoline)
range occurs in systems with already less than 0.4 wt% TAIC makes this scenario unlikely. Another possible explanation is based on the fact that LCST depends not only on a relatively weak binding of the solvent to the polymer chains, but on the entropy changes during heating. Since the entropy term in hydrogels is greater than in dissolved linear polymers, this could lead to a shift of the temperature-induced shrinking to lower temperatures. In this case, this shift should be strongly dependent on the cross-linking density. This, however, cannot be clearly seen, because the end of the linear region is below 0 °C and thus not measurable.

Another possible reason for the different transition range in the hydrogel compared to the polymer in solution is that the latter is supposedly shrinking as a hydrated coil over a broad temperature range below \( T_{cp} \), as nicely shown by Wu et al. on the example of PNiPAM.[71] Thus, the polymer chains partially dehydrate with increasing temperature since the entropy of the mixture increases when water molecules are released from polymer interaction due to weakening of the enthalpy hydrogen bond interactions.[42] Consequently, the polymer chains agglomerate, performing a coil-to-globule transition due to entropy driven conformational changes. The agglomeration will not occur in the hydrogel as discussed above. This would translate into a continuous shrinking of the respective hydrogel with increasing temperature below \( T_{cp} \). In the case of PNiPAM there is an abrupt loss of water at \( T_{cp} \), which will also result in a great change of \( S \) in the hydrogel at this temperature. Figure 8 confirms this assumption by showing the similar behavior of the degree of swelling \( S \) of a lightly cross-linked PNiPAM network and the hydrodynamic radius \( R_h \) of linear PNiPAM with changing temperature.

It stands to reason that PEtOx does not show the same behavior in solution as PNiPAM, but continuously shrinks until it forms aggregates. This is supported by the strong dependence of \( T_{cp} \) on the polymer concentration (see Figures S4 and S6). Such a behavior would lead to the observed swelling characteristics of the here presented hydrogels. Unfortunately, no light, X-ray, or neutron scattering experiments exist on a respective narrowly distributed high-molecular-weight PEtOx, which are required to clearly show such an effect.

4 | CONCLUSIONS

In this work, the temperature-dependent swelling behavior of differently cross-linked PEtOx hydrogels was investigated with regard to the molecular weight and, respectively, the LCST of the applied starting polymer, the net chain molecular weight of the synthesized hydrogel, the kind of solvent, and the cross-linker composition. We found that the degree of swelling \( S \) of the hydrogels converges in a break point temperature \( T_{BP} \) for a certain polymer/solvent system independent of its degree of cross-linking. While the \( T_{BP} \) of PEtOx hydrogels prepared from PEtOx10k was found at 72 °C, the \( T_{BP} \) of hydrogels prepared from PEtOx122k was found at 66 °C. The \( T_{BP} \) of PEtOx122k hydrogels increased to 79 °C when adding 8 wt% ethanol to the water. We were able to show that the \( T_{BP} \) of the synthesized PEtOx hydrogels correlates with the LCST of the respective starting PEtOx, 69 °C for PEtOx10k, 64 °C for PEtOx122k, and 75 °C for PEtOx122k swollen in a water/ethanol mixture (92/8 wt%).

The net chain molecular weight \( M_c \) only affects the maximum degree of swelling and, thus, the swelling–deswelling rate \( dS/dT \) of the hydrogel. It was found that

**FIGURE 7** Phase diagram containing the cloud point temperatures \( T_{cp} \) of the thermoplastic starting PNiPAM and the swelling curves of differently cross-linked PNiPAM networks in water. The hydrogel was obtained by irradiation with a \( ^{60} \text{Co} \) \( \gamma \) source with a dose of 20 kGy.[74] PNiPAM, poly(N-isopropylacrylamide)

**FIGURE 8** Comparison of the temperature dependence of the hydrodynamic radius \( R_h \) of linear PNiPAM and the degree of swelling \( S \) of cross-linked PNiPAM. The hydrogel was obtained by irradiation with a \( ^{60} \text{Co} \) \( \gamma \) source with a dose of 20 kGy.[74] PNiPAM, poly(N-isopropylacrylamide)
the full temperature-induced transition occurs below LCST and the transition range is broad and nearly linear in contrast to other reported LCST hydrogels.

Considering that due to entropic reasons polymer chains cannot aggregate in a polymer network as opposed to linear chains in a solution, it is reasonable to assume that the swelling behavior of a hydrogel correlates to the hydrodynamic radius $R_h$ of a polymer in solution measured via light scattering. Often $R_h$ is not accessible, especially above the cloud point temperature, due to the aforementioned aggregation of the chains. Wu et al. were able to monitor $R_h$ during the cloud point transition by a performing light scattering of highly diluted, narrowly distributed, high-molecular-weight PNIPAM. Comparing $R_h$ with the temperature-dependent swelling behavior of a lowly cross-linked PNIPAM network it becomes clear that the correlation of $S$ and $R_h$ holds true.

This means that, instead of performing light scattering experiments with not accessible polymers to obtain information about the coil-to-globule transition of a polymer in a solution, the degree of swelling over temperature curve can be considered as a substitute.

However, to estimate whether a polymer network might undergo a sharp transition like PNIPAM or a broad transition like PETOX, the concentration-dependent $T_{cp}$ curve should be considered. Only polymers that have practically no temperature-dependent $T_{cp}$ are promising candidates for LCST hydrogels with a sharp swelling transition.

Although the PETOX hydrogels show no sharp transition, they are still useful to create membranes with continuously adjustable permeability, shown in previous work on the example of thermosensitive amphiphilic polymer conetworks. Accordingly, $dS/dT$, the maximum degree of swelling $S$, as well as $T_{BP}$, below, which the thermoresponsiveness of a PETOX hydrogel is amplified by solvation, can be tailored as well as adapted to the requirements of a potential application.

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