ORIGINAL ARTICLE

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_{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 $\mathrm{d}S/\mathrm{d}T$ 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 with a different molecular weight and LCST characteristic for each degree of cross-linking. This way, we hoped to exclude the influence of the end groups and see the full potential of the LCST behavior on the thermal transition of the degree of swelling.

2 | EXPERIMENTAL

2.1 | Materials

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_{w} labeled as 500 and 50 kg mol^{-1}. The M_{n} was determined to be 122 kg mol^{-1} with a polydispersity Đ of 2.9 and 10 kg mol^{-1} with a Đ of 6.7, respectively, using SEC chromatography as described in a previous work.[8]

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 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[65] as

$$M_{\mathrm{c}} = \frac{2(1+\vartheta)\cdot\rho(T)\cdot R\cdot T\cdot g^{1/3}}{E(T)}, \qquad (1)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), $\rho(T)$ is the density, φ 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 υ is assumed as 0.4 as published in various papers.[66–68]

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_{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 °C using a Lauda Eco Silver Thermostat. The equilibrium weight of the swollen samples $m_{swollen}$ 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 °C to up to −10 °C, depending on the used solvent, and increased again stepwise to 95 °C.

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

$$S = \frac{m_{swollen}}{m_{dry}}. \tag{2}$$

3 | RESULTS AND DISCUSSION

The aim of this study was to investigate the temperature-dependent swelling behavior of hydrogels prepared from high-molecular-weight PEtOx. PEtOx 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_{cp} with increasing polymer concentration.[31,48–50] The whole curve shifts to lower T_{cp} values with higher molecular weight.[46,47]

Two commercial PEtOx hydrogels with distinctly different average molecular weights M_n of 122 kg mol^{-1} (M_W = 355 kg mol^{-1}) and 10 kg mol^{-1}, (M_W = 67 kg mol^{-1}), respectively, were used to prepare differently cross-linked PEtOx 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 PEtOx 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., PEtOx$_{10k}$ is a network based on PEtOx 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 $w_{DCP+TAIC}$ (corresponding

Figures S1 and S2). The highest M_c of PEtOx$_{10k}$ and PEtOx$_{122k}$ 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, PEtOx$_{10k}$ requires about 2.5 times more cross-linker compared to PEtOx$_{122k}$ to obtain a similar M_c. This can be explained by the number of chains per unit volume, which is higher for PEtOx$_{10k}$ than for PEtOx$_{122k}$.

3.2 | Swelling behavior

The swelling behavior of PEtOx 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 °C to up to −10 °C, and increased again stepwise to 95 °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 PEtOx$_{122k}$ with a Đ of 2.9, in dependence on temperature.

As seen in Figure 2a, the temperature dependence of S of the differently cross-linked PEtOx$_{122k}$ networks can be divided in two domains with different swelling–deswelling rates dS/dTs. 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
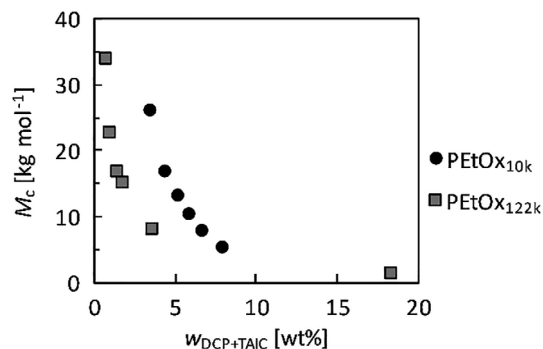

FIGURE 1   Net chain molecular weight M_c in dependence on the used starting polymer and applied cross-linker concentration $w_{DCP+TAIC}$. DCP, dicumyl peroxide; TAIC, triallyl isocyanurate

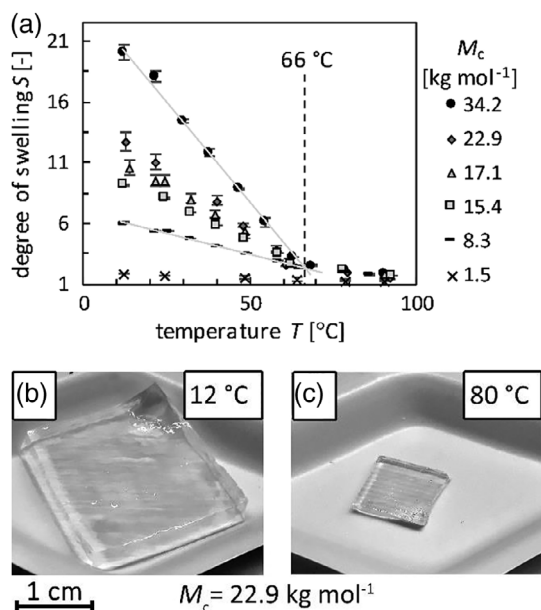**FIGURE 2** (a) Degree of swelling S of differently cross-linked PEtOx$_{122k}$ samples in dependence on temperature T in water. S was measured in triplicate and the error bars are the respective standard derivation. Swollen PEtOx$_{122k}$ sample with an M_c of 22.9 kg mol^{-1} at (b) 12 °C and (c) 80 °C. The scale bar is applicable for (b) and (c). PEtOx, poly(2-ethyl-2-oxazoline)

66 °C. Below this break point temperature (T_{BP}), S of PEtOx$_{122k}$ 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$_{122k}$ samples exhibit nearly the same S values, which decrease with a T dependency (dS/dT of about 0.033 K^{-1}). A PEtOx$_{122k}$ 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 2b,c). 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$_{122k}$ hydrogels in ethanol to check this. The swelling curves of the PEtOx$_{122k}$ 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/dTs range 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/dTs are nearly the same as found for PEtOx$_{122k}$ hydrogels swollen in water above T_{BP}. Moreover, the
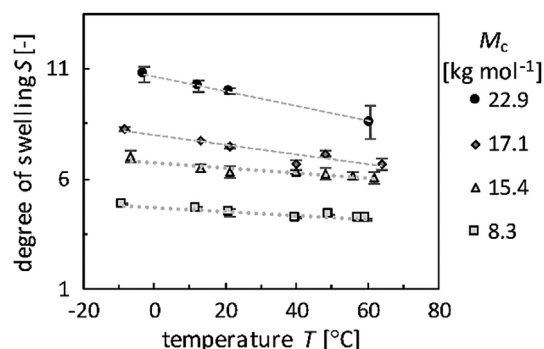
FIGURE 3 Degree of swelling S of differently cross-linked PEtOx$_{122k}$ samples in dependence on temperature T in ethanol. S was measured in triplicate and the error bars are the respective standard derivation. PEtOx, poly(2-ethyl-2-oxazoline)

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 kg mol^{-1} PEtOx were investigated regarding their temperature-dependent swelling characteristics. This polymer has an LCST in water of 69 °C (see Figure S5).

As seen in Figure 4, the swelling curves of the differently cross-linked PEtOx$_{10k}$ hydrogels can be separated in two domains, similar to the hydrogels prepared from PEt-Ox$_{122k}$. Again, the degree of swelling S of the PEtOx$_{10k}$ 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 K^{-1} was found for the PEtOx$_{10k}$ with a M_c of 26.4 kg mol^{-1}. Above T_{BP}, the dS/dTs of all PEtOx$_{10k}$ hydrogels are nearly identical with approximately 0.012 K^{-1}. The difference of the dS/dTs of PEtOx$_{10k}$ networks above and below T_{BP} is analog to the PEtOx$_{122k}$ hydrogels up to an order of magnitude. Compared to the PEtOx$_{122k}$ hydrogels (see Figure 2a), the T_{BP} of the PEtOx$_{10k}$ hydrogels is at a higher temperature of about 72 °C. Analog to the hydrogels prepared from the PEtOx$_{122k}$ starting polymer, the T_{BP} of 72 °C found in the swelling curves of the PEtOx$_{10k}$ hydrogels also correlates well with the LCST of 69 °C of the linear PEtOx$_{10k}$ 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 solvation 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 PEtOx$_{122k}$ networks in dependence on temperature in the water/ethanol mixture (92/8 wt%).

Similar to the swelling curves obtained for PEtOx$_{122k}$ hydrogels swollen in water, the swelling curves of the differently cross-linked PEtOx$_{122k}$ 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 K^{-1}. Above T_{BP},
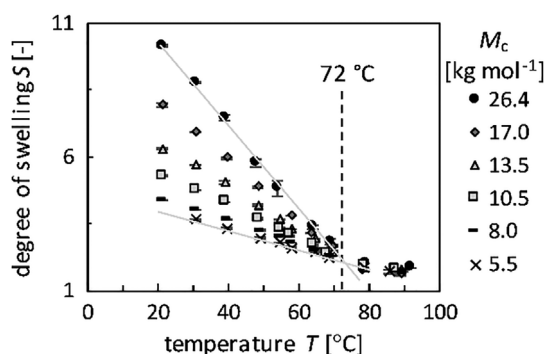

FIGURE 4 Degree of swelling S of differently cross-linked PEtOx$_{10k}$ samples in dependence on temperature T in water. S was measured in triplicate and the error bars are the respective standard derivation. PEtOx, poly(2-ethyl-2-oxazoline)
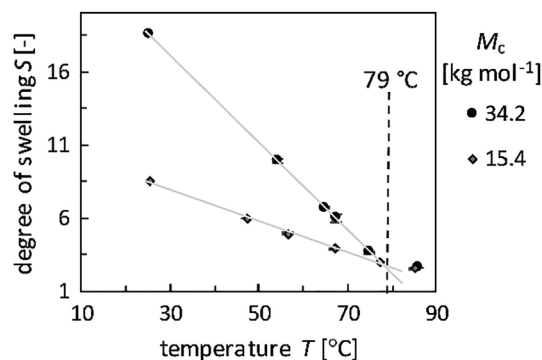

FIGURE 5 Degree of swelling S of differently cross-linked PEtOx$_{122k}$ samples in dependence on temperature T in a water/ethanol mixture (92/8 wt%). S was measured in triplicate and the error bars are the respective standard derivation. PEtOx, poly (2-ethyl-2-oxazoline)

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
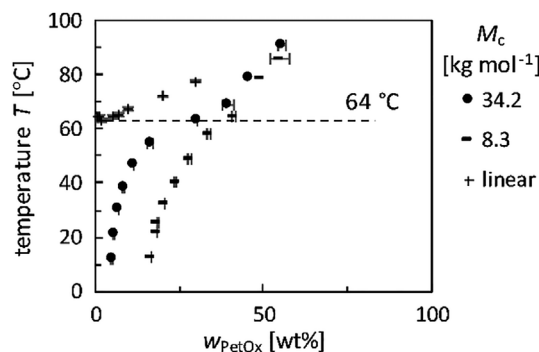

FIGURE 6 Phase diagram containing the cloud point temperatures T_{cp} of the thermoplastic starting PEtOx$_{122k}$ and the swelling curves of differently cross-linked PEtOx networks prepared from PEtOx$_{122k}$ in water. w_{PEtOx} was measured in triplicate and the error bars are the respective standard derivation. PEtOx, poly (2-ethyl-2-oxazoline)
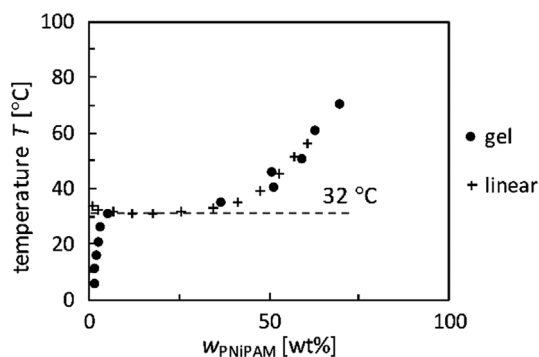
FIGURE 7 Phase diagram containing the cloud point temperatures T_{cp}[30] of the thermoplastic starting PNiPAM and the swelling curves[74] of differently cross-linked PNiPAM networks in water. The hydrogel was obtained by irradiation with a ^{60}Co γ source with a dose of 20 kGy.[74] PNiPAM, poly(N-isopropylacrylamide)
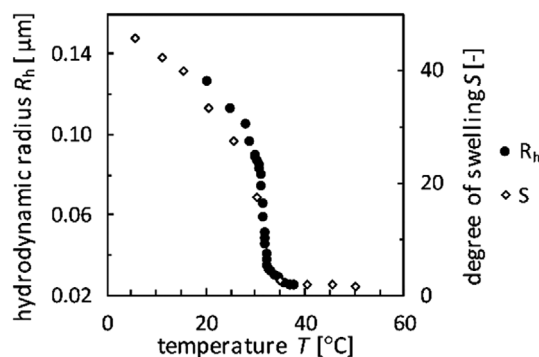

FIGURE 8 Comparison of the temperature dependence of the hydrodynamic radius R_h[71] of linear PNiPAM and the degree of swelling S[74] of cross-linked PNiPAM. The hydrogel was obtained by irradiation with a ^{60}Co γ source with a dose of 20 kGy.[74] PNiPAM, poly(N-isopropylacrylamide)

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 enthalpic 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[74] of a lightly cross-linked PNiPAM network and the hydrodynamic radius R_h[71] 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 hydrogels prepared from $PEtOx_{10k}$ was found at 72 °C, the T_{BP} of hydrogels prepared from $PEtOx_{122k}$ was found at 66 °C. The T_{BP} of $PEtOx_{122k}$ 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 $PEtOx_{10k}$, 64 °C for $PEtOx_{122k}$, and 75 °C for $PEtOx_{122k}$ 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

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.[71] Comparing R_h with the temperature-dependent swelling behavior of a lowly cross-linked PNiPAM network,[74] 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.[53,78–80] 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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