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New thermo-responsive polymer materials based on poly(2-ethyl-2-oxazoline) segments

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Abstract

First, the solution behavior of poly(2-ethyl-2-oxazoline) (PEtOx) in water has been investigated. The dependence of the cloud points on the molecular weight and concentration indicates a typical Flory–Huggins (Type I) demixing behavior with a lower critical solution temperature (LCST). Secondly, the synthesis and properties of temperature-responsive hydrogels and segmented polymer networks, based on PEtOx bis-macromonomers, are reported. PEtOx hydrogels have been prepared by UV-induced radical polymerization of the corresponding α,ω-bis-acrylates. The networks exhibited a continuous shrinkage with increasing temperature. Series of segmented networks with LCST-behavior have been obtained by free radical copolymerization of PEtOx bis-macromonomer with the comonomers 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl acrylate (HPA) or methyl methacrylate (MMA). The LCST-behavior of the materials is controlled by varying the philicity of the comonomer and the fraction of PEtOx in the networks. PHEMA–PEtOx and PHPA–PEtOx hydrogels exhibited a large and reversible swelling–deswelling process, whereas the volume changes in PMMA–PEtOx swollen networks were small and occurred in a broad temperature interval.

Keywords: Poly(ethyl oxazoline); Thermo-responsive hydrogels; Segmented polymer networks

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1. Introduction

Polymer materials that respond to external stimuli such as temperature, pH, solvent quality, pressure, light etc. by changing their physical or chemical properties have become a topic of major interest in the last few decades [1–3]. Among them, temperature-responsive polymers were most comprehensively studied due to the possible applications in fields such as drug delivery [4,5], enzyme activity control [6,7] and membrane separation [8]. Three types of so-called lower critical solution temperature (LCST) behavior have been distinguished recently by a phenomenological analysis of the critical miscibility behavior. The critical points of the corresponding polymer solutions in water differ in their dependence on concentration and polymer chain length [9]. Furthermore, it was shown that the swelling behavior of the corresponding cross-linked polymers could be directly related to the type of demixing. While the classical Type I demixing results in a temperature induced continuous swelling–deswelling behavior of the networks, the Type II and Type III demixing results in a discontinuous swelling behavior. Representatives of each class respectively, are poly(*N*-vinyl caprolactam) (Type I), poly(*N*-isopropyl acrylamide) (Type II) and poly(methyl vinyl ether) (Type III).

PEtOx is an amorphous non-ionic tertiary polyamide, soluble in water as well as in a wide range of organic solvents. It possesses a unique combination of properties, leading to the proposal of several applications [10–12]. Chiu et al. reported that aqueous PEtOx solutions exhibit a cloud point temperature around 62–65 °C depending on the molecular weight [12]. In subsequent studies by Lin et al. the influence of the nature of the solvent and added salts on the cloud point temperatures of PEtOx was studied [13]. In a light scattering investigation of water solutions by Chen et al. the second virial coefficient of PEtOx was found to decrease with increasing temperature, indicating LCST behavior due to hydrogen bonding [14]. Only very recently, PEtOx has been used for the first time to design

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temperature-sensitive polymer materials with reasonable potential for use in biomaterials and specific drug delivery [15].

The objectives of this work were to synthesize thermo-responsive polymers comprising PEtOx segments and to study the LCST behavior of these materials, as well as to investigate the possibilities to control the temperature range of the LCST behavior. For this purpose PEtOx-bis-macromonomers, i.e. macromolecules bearing polymerizable groups at both chain ends, were synthesized by terminating the living polymerization of PEtOx with acrylic acid [16]. PEtOx hydrogels have been prepared by UV-induced radical polymerization of these bis-macromonomers. Series of segmented networks with LCST behavior, in which PEtOx acts as a macromolecular cross-linker for other polymers, have been obtained by copolymerization of PEtOx-bis-macromonomers with 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl acrylate (HPA) or methyl methacrylate (MMA). In a recent paper, the synthesis, amphiphilic and solid state properties of segmented networks based on poly(2-alkyl-2-oxazoline) and poly(methyl methacrylate) have been reported [17].

The responses of the obtained water swollen materials to temperature changes were investigated and compared with those of aqueous solutions of the linear polymers.

2. Experimental

2.1. Materials

2-Ethyl-2-oxazoline (EtOx) (Aldrich, 99 + %) was twice refluxed over CaH_2/KOH and distilled. 1,4-Dibromo-2-butene (DBB) (Aldrich, 99%) was dried in vacuum before use. Acetonitrile (Aldrich, 99.9 + %, HPLC grade) was purified by distillation over calcium hydride. HEMA (Aldrich, 99 + %), HPA (Aldrich, 95%) and MMA (Aldrich, 99%) have been purified by distillation in the presence of a radical inhibitor, phenothiazine (Aldrich). Other reagents and solvents were purified as usual. All purification operations were performed under nitrogen.

PEtOx-bis-macromonomers and PEtOx homopolymer networks were synthesized as described previously [17]. The main characteristics of the PEtOx-α,ω-bis-acrylate used in this work are as follows: the theoretical degree of polymerization, calculated from the monomer-to-initiator ratio, is equal to 100; ^{1}H NMR measurements: $\bar{M}_n = 10.7 \times 10^3$ g/mol, end-group functionality (i.e. average number of acrylate end groups per macromolecule) $f = 1.97$; GPC analysis (eluent chloroform): $\bar{M}_n = 11.2 \times 10^3$ g/mol, polydispersity equal to 1.3.

High molecular weight linear PEtOx was obtained in bulk polymerization by dissolving the chosen amount of the initiator DBB (monomer-to-initiator ratios 20–200) in the carefully purified monomer. The reaction mixture was then placed in a well-dried glass tube. The air was replaced by nitrogen within three freeze–thaw cycles under vacuum and the tube was finally sealed. The polymerizations were carried out at 120 °C for 24 h. The solid polymers obtained were dissolved in chloroform, precipitated in diethyl ether and dried in vacuum (yield 95–97%).

Segmented polymer networks were prepared by UV-polymerization as follows: a chosen amount of a bis-macromonomer was dissolved in the comonomer (MMA, HEMA or HPA) under nitrogen. In the case of MMA, methanol was added dropwise until a homogeneous solution was obtained. Then, 0.5 mol% of the initiator 1-methanesulfonic ester of methylbenzoine (MSMB) with respect to the comonomer was added. The reaction mixture was stirred until homogeneity was reached and finally transferred by means of a syringe in a mould composed of two glass plates separated by a 1 mm silicon spacer. The mould was irradiated with UV light (360 nm; 10 mW/cm^2) for 30 min from both sides. After the removal of the glass plates, the film obtained was dried at 70 °C under vacuum for 24 h.

2.2. Measurements

^{1}H NMR spectra were recorded on a Bruker AM 500 spectrometer in $CDCl_3$ with tetramethylsilane as a standard.

The viscosity average molar masses M_v were determined employing the Mark–Houwink relation $[\eta] = KM_v^\alpha$ with $K = 6.5 \times 10^{-4}$ *mL/g* and $\alpha = 0.56$ [12]. The intrinsic viscosities $[\eta]$ were measured with an Ubbelode-type viscometer Schott Geräte CT1150 at 20 °C in water.

GPC analyses of PEtOx bis-macromonomers were performed in chloroform by using a PL-gel $(5\mu)10^3$ Å column and a Waters Differential Refractometer R 401, calibrated with polystyrene standards.

Differential scanning calorimetry (DSC) analyses were carried out on a Perkin–Elmer 7 equipment provided with a TAC 7/DX thermal controller at a scanning rate of 10 °C/min.

Soluble fractions were measured as follows: a sample of the dry network was extracted with water in a Soxhlet extraction apparatus for 8 h and then dried at 70 °C under vacuum until constant weight. The soluble fractions, S, have been calculated from Eq. (1), where w_0 is the initial weight of the dry sample and w is the weight of the dry sample after the extraction.

$$S = 100\frac{w_0 - w}{w_0}\% \tag{1}$$

Swelling studies for all prepared networks were done gravimetrically. In a typical case, a disc cut from the network film was weighed, transferred into a test tube with distilled water and placed in a thermostat at a desired temperature. At regular intervals, the disc was taken out, the excess solvent was removed from the surface with tissue paper, the disc was weighed and then returned to the medium. The swelling was continued until a constant weight was attained. The equilibrium degree of swelling, Q, has been calculated from Eq. (2), where w_0 is the initial weight of the dry sample and w_e is the final weight of the swollen sample.

$$Q = 100\frac{w_e - w_0}{w_0}\% \tag{2}$$

For the cloud point measurements, PEtOx solutions of known concentrations were transferred in closed test tubes and placed in a water bath, which was heated at a rate of 1 °C/min. The temperature at which the first change in the intensity of the scattered light appeared in the solution was recorded. The solutions were also cooled from above this temperature at a rate of 1 °C/min and the temperature at which the finest opalescence disappeared was recorded. The average of these two temperatures was reported as cloud point temperature (T_{cp}).

3. Results and discussion

3.1. Synthesis and LCST behavior of linear PEtOx

Benzyl or allyl halides are highly reactive electrophiles capable of initiating cationic ring-opening polymerization of 2-alkyl-2-oxazolines [10,11]. Benzyl bromide is often used as a monofunctional initiator for polymerization of EtOx, as the initiation rate is much faster than that of propagation. Although the equilibrium between the cationic and covalent active centers in this case is shifted to the last ones at higher temperatures, it has been proved that the propagation proceeds almost exclusively on the ionic ones [18]. Polymerization initiated by allyl-type dihalides, such as DBB, was reported to be a ‘fast initiation-slow propagation living system’ providing good control over the molecular weight of the polymer by the monomer-to-initiator ratio [19]. Because of its high stability toward moisture and air, DBB was applied in this study, not only for the synthesis of telechelic PEtOx-α,ω-bis-acrylate, but also for the preparation of high molecular weight samples of linear PEtOx by bulk polymerization. Molar masses of these samples were determined from the Mark–Houwink Eq. (3) by using data from the intrinsic viscosity measurements in water solutions (Table 1) [12].

$$[\eta] = (6.5 \times 10^{-4})M_v^{0.56} \tag{3}$$

GPC measurements of the samples, performed with different eluents such as THF, chloroform or water, gave no relevant data for the molar masses. Similar discrepancies between the expected molecular weights and the values calculated from the GPC elugrams have been reported earlier and ascribed to the adsorption of the polymer onto the immobile phase of the column [20]. Although the values of the molecular weight distributions (MWD) might also be affected by these adsorption effects, they could be compared to the MWD-values obtained under the same conditions in this and earlier [16] reports for lower molecular weight PEtOx bis-macromonomers. For molecular weights up to 10,000 g/mol, MWD’s have been reported between 1.1 and 1.3. MWD-data from the GPC measurements on higher molecular weight PEtOx-samples, listed in Table 1, show that the MWD’s are considerably broader. This observation could be assigned to a number of factors. The ^{13}C NMR analysis showed a singlet at 170 ppm for the N–C=O group, giving no evidences for long chain branches in the macromolecules. Therefore, it is believed that the broad MWD could be ascribed to viscosity problems during the synthesis, which influences the equilibrium between different active species, and/or to termination reactions with impurities in the reaction system.

Table 1
Characterization of high molecular weight PEtOx

Sample	$M_{\mathrm{th}} \times 10^{-3}$[a] (g/mol)	$\bar{M}_{\mathrm{vis}} \times 10^{-3}$[b] (g/mol)	$\bar{M}_{\mathrm{n}} \times 10^{-3}$[c] (g/mol)	MWD[d]
PEtOx1	20	22	9.2	1.7
PEtOx2	50	52	18	1.7
PEtOx3	100	85	26	2.1
PEtOx4	200	136	39	2.1
PEtOx5	210	170	40	3.2

[a] Theoretical molecular weight calculated from the monomer-to-initiator ratio.

[b] Viscosity average molecular weight calculated from the data of the viscosimetric measurements.

[c] Number average molecular weight measured by GPC.

[d] Molecular weight distribution measured by GPC.

A LCST demixing curve of PEtOx (M_v equal to 1.7×10^5 g/mol, PEtOx5), constructed by turbidimetric observations, is plotted in Fig. 1 to show the concentration dependence of the cloud points. This curve only shows one minimum at about 62 °C, which is situated close to the solvent axis. The shape of this temperature-composition diagram is similar to that obtained for poly(*N*-vinyl caprolactam), which was the first described example of a Type I demixing behavior [21]. All these observations

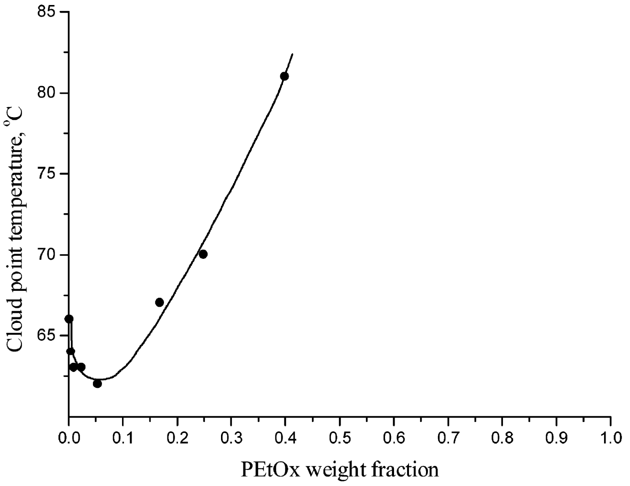

Fig. 1. Dependence of the cloud point of PEtOx water solutions on the weight fraction. Molecular weight 1.7×10^5 g/mol.

strongly indicate that the demixing behavior of the PEtOx/water system is also described by a classical Type I Flory–Huggins behavior. The cloud point measurements of the PEtOx/water solutions as a function of molecular weight are presented in Fig. 2 for a constant concentration of 5 g/L. It can be observed that the cloud point temperature (T_{cp}) decreases considerably (from 78 to 66 °C) with increasing molecular weight of the polymer. This is the consequence of the fact that a Type I behavior is characterized by a shift of the LCST towards lower polymer concentration with increasing polymer chain length. PEtOx samples with molecular weight of 10^4 or lower do not demix from water below 100 °C.

3.2. Synthesis and LCST behavior of PEtOx homopolymer networks

PEtOx bis-macromonomers, bearing acrylate groups at both chain ends, have been synthesized upon terminating the living species with acrylic acid as described previously [16]. Homopolymer networks were prepared by UV-initiated radical polymerization of the bis-macromonomers. However, as can be seen in Table 2, polymerization of pure bis-macromonomer leads to networks with high soluble fraction. Therefore, an equimolar amount of ethyleneglycol dimethacrylate (EGDM), with respect to the polymerizable groups of the macromonomer, was added to the reaction mixture in order to decrease the soluble fraction and to improve the mechanical strength of the final product in the swollen state. From Table 2, it can be observed that the soluble fraction indeed decreased considerably upon addition of EGDM.

The PEtOx hydrogel exhibits a T_{cp} of 68 °C, which is lower than the T_{cp} of the linear polymer with comparable molecular weight (Table 1, PEtOx1: $T_{cp} = 73$ °C). A similar impact of cross-links on cloud points has been described earlier [22]. The addition of EGDM leads to a dramatic decrease in T_{cp} from 68 to 46 °C. This phenomenon is attributed to the increase of the cross-linking degree and to the inclusion of the more hydrophobic EGDM moiety in the network structure.

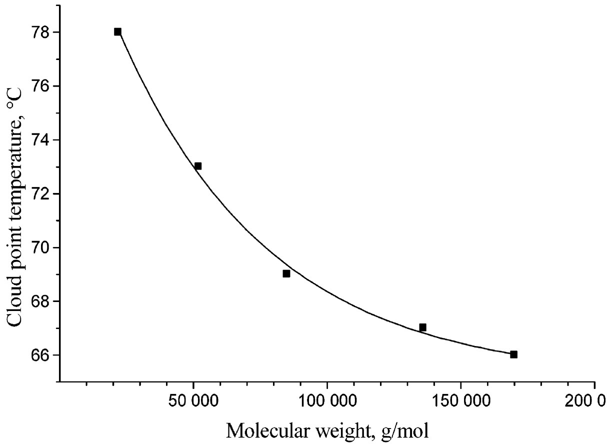

Fig. 2. Dependence of the cloud point of PEtOx water solutions on the molecular weight. Concentration 5 g/L.

Table 2
Soluble fractions, glass and cloud point temperatures of cross-linked PEtOx

Sample	Soluble fraction in water (wt%)	T_g[a] (°C)	T_{cp}[b] (°C)
PEtOx-net	28	51	68
PEtOx–EGDM-net	4	58	46

[a] T_g-values of dry samples measured by DSC.
[b] Sample swollen in water to equilibrium at room temperature.

The equilibrium swelling degree of the hydrogels was followed as a function of temperature. As can be seen in Fig. 3, PEtOx hydrogels show S-shaped deswelling curves, typical for a cross-linked material prepared from a system with Type I LCST-behavior. In this case, the network gradually contracts in the temperature region where less polymer/solvent interactions occur.

PEtOx–EGDM-net showed a completely different swelling–deswelling behavior. The initial swelling degree of this hydrogel was quite lower compared to that of the 'pure' PEtOx gel. With increasing temperature, it abruptly collapsed around 40 °C, squeezing out about 20% of the water, but further increase in the temperature had no effect on the swelling equilibrium.

3.3. Synthesis and LCST-behavior of PEtOx-containing segmented polymer networks

In order to have a control on the cloud point behavior of the hydrogels, PEtOx has been combined with other polymers in the form of segmented polymer networks. In such materials, PEtOx is applied as a macromolecular cross-linker for the other segments [17]. It has been shown by us and by other research groups that segmented networks demonstrate interesting multi-component topologies for a variety of applications [23–25].

Three series of segmented networks were synthesized by

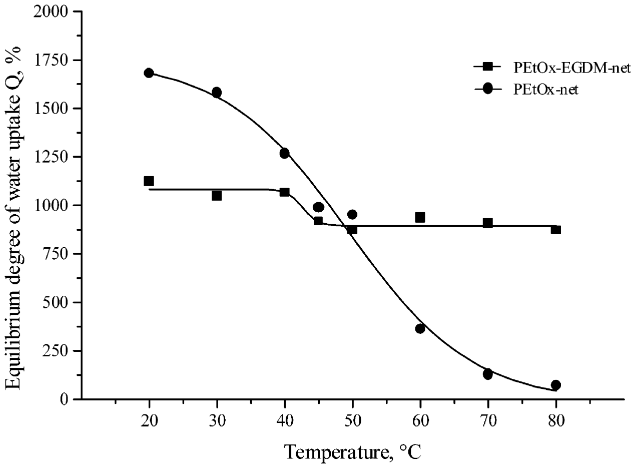

Fig. 3. Equilibrium degree of water uptake of polyoxazoline hydrogels as a function of the temperature.

co-polymerizing a PEtOx bis-macromonomer with the co-monomers HEMA, HPA and MMA in different compositions. Again, UV-initiated radical polymerization was performed, using a small amount of methanol in order to obtain homogeneous initial reaction mixtures. The main characteristics of the final materials are presented in Table 3. For all networks prepared, the low soluble fractions demonstrate the efficiency of the bis-macromonomer in the cross-linking reactions with the comonomers. DSC-measurements performed on dry samples show one T_g for the PHEMA and PHPA-containing networks, suggesting that there is no pronounced phase separation in these materials. This could be ascribed to strong hydrogen interactions between the amide groups of PEtOx and the alcohol groups of PHEMA or PHPA. On the other hand, PMMA-containing networks clearly show two T_gs indicating the presence of PEtOx-rich and PMMA-rich domains.

The hydrogels containing PHEMA or PHPA segments are both transparent at room temperature and show a cloud point at temperatures lower than those of the linear and cross-linked PEtOx-homopolymers. In the case of the PHPA–PEtOx hydrogels, this decrease could be assigned to the fact that PHPA itself has an LCST-behavior with reported T_{cp} of 16 °C [13]. Another possible explanation, which also holds for the PHEMA-containing hydrogels, is the fact that there might be a competition between PEtOx and PHEMA/PHPA to interact with water, resulting in a weakening of the interactions of PEtOx with water. This phenomenon has been described recently for similar poly(*N*-vinyl caprolactam)/poly(ethylene oxide) hydrogel systems [26].

The changes in the swelling behavior of the segmented polymer networks as a function of temperature are summarized in Figs. 4–6. Both the highly hydrophilic PHPA–PEtOx and PHEMA–PEtOx hydrogels exhibit considerable volume shrinkage in the temperature range of 40–60 °C. The shrinkage is more abrupt in the case of PHEMA-containing gels. PHPA-based products show almost the same final equilibrium water uptake independent of the copolymer composition. In both series, the networks with higher PEtOx content display a higher equilibrium water uptake at room temperature and the most spectacular volume change. On the other hand, PMMA–PEtOx swollen networks are opaque at any temperature in the studied temperature interval. In these series, the volume changes take place over a higher temperature interval of 40 to 70 °C. For PMMA contents over 60 wt%, the thermo-responsive behavior disappears completely. It is obvious that this observation should be attributed to the presence of a hydrophobic PMMA matrix which does not allow PEtOx segments, even long enough, to display their LCST-features.

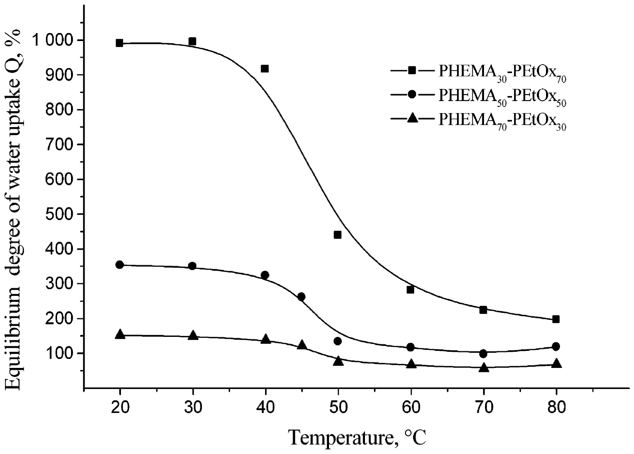

Fig. 4. Equilibrium degree of water uptake of PHEMA–PEtOx segmented polymer networks as a function of temperature.

The swelling–deswelling kinetics of several PHPA–PEtOx hydrogels (when immersed in a large amount of water) in response to stepwise changes in temperature, respectively at 20 and 70 °C, was followed. A typical example has been shown in Fig. 7. As the time between every step is only 5 min, the experimental data are not equilibrium values. However, kinetic data show that the biggest changes in the swelling and deswelling process already happen in the first 5 min. More detailed kinetic experiments as a function of network composition, film thickness, temperature and pH are currently under

Table 3
Characterization of PEtOx-containing copolymer networks

Sample	Soluble fraction in water (wt%)	T_g[a] (°C) (DSC)	T_{cp}[b] (°C) (visual observation)
$PHEMA_{30}–PEtOx_{70}$	5	48	56
$PHEMA_{50}–PEtOx_{50}$	6	43	49
$PHEMA_{70}–PEtOx_{30}$	6	41	53
$PHPA_{30}–PEtOx_{70}$	3	41	55
$PHPA_{50}–PEtOx_{50}$	9	37	53
$PHPA_{70}–PEtOx_{30}$	8	28	46
$PMMA_{30}–PEtOx_{70}$	4	37; 109	–[c]
$PMMA_{50}–PEtOx_{50}$	9	37; 102	–[c]
$PMMA_{70}–PEtOx_{30}$	11	53	–[c]

[a] Dry sample.

[b] Sample swollen in water to the equilibrium at room temperature.

[c] Opaque in the investigated temperature interval.

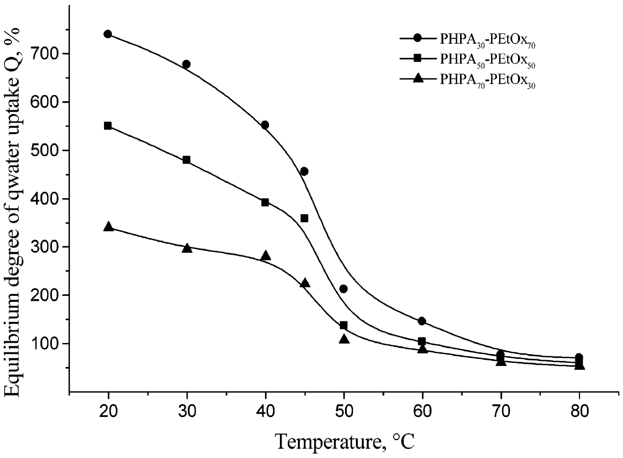

Fig. 5. Equilibrium degree of water uptake of PHPA–PEtOx segmented polymer networks as a function of temperature.

investigation and will be subject to forthcoming paper. The example shown in Fig. 7 already demonstrates the reversibility of the swelling–deswelling process and the mechanical stability of such hydrogels. It has been found that, by increasing the PEtOx-fraction or the step time, it is possible to get stable swollen and shrunken gels for many cycles. These properties make these water-swollen segmented polymer networks promising materials for applications as actuators and on–off switches.

4. Conclusions

The molecular weight and concentration dependence of the cloud points of poly(2-ethyl-2-oxazoline) give strong indications for a Flory–Huggins (Type I) demixing behavior in water.

Novel temperature-responsive hydrogels have been prepared based on poly(2-ethyl-2-oxazoline) segments. In these hydrogels, PEtOx has been combined with several polymers by making use of the macromonomer method. It has been demonstrated that the LCST behavior of the water swollen segmented networks can be tailored by varying the fraction of the poly(ethyl oxazoline) precursor and the philicity of the comonomer used. By this approach, new polymer materials with temperature-induced swelling and optical transitions, designed for specific applications, are made available.

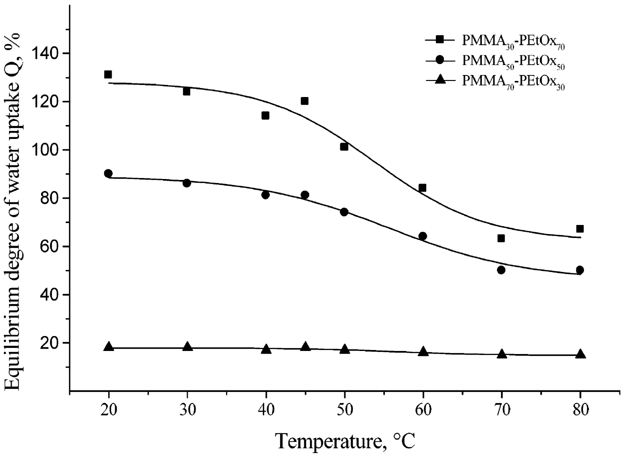

Fig. 6. Equilibrium degree of water uptake of PMMA–PEtOx segmented polymer networks as a function of temperature.

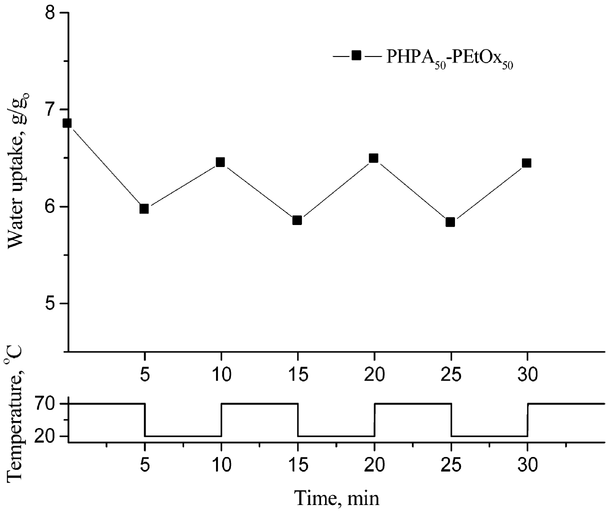

Fig. 7. Five-minute swelling–deswelling cycles for PHPA–PEtOx segmented polymer networks.

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