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Thermoresponsive hydrogels of hydrophobically modified polyglycidol

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Abstract: Synthesis, swelling properties and thermoresponsive behavior of a new class of hydrogels based on high molar mass polyglycidol are presented. High molar mass polyglycidol was synthesized by coordination polymerization. Thermosensitive poly(glycidol-co-glycidyl ethyl carbamate)s were obtained via a simple chemical modification of the polyglycidol with ethyl isocyanate. Polyglycidol and poly(glycidol-co-glycidyl ethyl carbamate)s were chemically crosslinked in DMF solution using oligomeric poly(ethylene glycol)-bis-(carboxymethyl ether chloride) as crosslinking agent. The hydrogels of degree of swelling of over 1000% were obtained. Thermoresponsive properties of the networks and the swelling-deswelling behavior of hydrogels in response to cyclic changes of the temperature were studied.

Introduction

Hydrogels are three-dimensional networks, which can absorb and retain large amount of water while maintaining their structural integrity. Hydrogels resemble the natural living tissue more than any other class of synthetic biomaterials. Thus hydrogels have found widespread application in different areas, e.g. as materials for contact lenses and artificial skin, wound dressing, protein separation, membranes for biosensors and devices for the controlled release of drugs [1-4].

In recent years great interest has been focused on stimuli responsive hydrogels – where the network can change considerably but reversibly its swelling properties in response to small changes of the external environment [5-7]. Due to the crosslinking, various properties of individual polymers become visible on a macroscopic scale.

Among stimuli responsive gels, temperature sensitive hydrogels are most widely investigated. Their behavior in water was described in many reviews [8-12]. These hydrogels undergo volume changes in the vicinity of a certain temperature during heating or cooling. Below the volume phase transition temperature the gel is swollen, hydrated and hydrophilic. Above this temperature the gel shrinks and forms a collapsed, dehydrated and hydrophobic material. The precise control over the temperature at which hydrogels change its swelling behavior is essential for all possible applications. Usually the thermoresponsive properties of the hydrogels originate from polymers, which exhibit a lower critical solution temperature in water before crosslinking [9, 13]. The balance between the hydrophilic and hydrophobic groups in the network and its distribution in the polymer chain, type of crosslinker used, the crosslinking density and hydrogel preparation method have great influence on the behavior and application of the corresponding hydrogels [14-17].

It was previously shown that the networks based upon polyglycidol exhibit thermoresponsive behavior, if hydrophobic elements were introduced into their structures. Thermoresponsive gels were obtained when polyglycidol-*block*-poly(ethylene oxide)-*block*-polyglycidol were crosslinked with glutaraldehyde [18], thus introducing hydrophobic methylene units. The acetal bonds of the networks prone to acidic hydrolysis made gels unstable in acidic media. Thermoresponsive networks result also when a part of the hydroxyl groups of polyglycidol was esterified with acetic anhydride and the chains crosslinked [19].

This paper reports the synthesis and behavior in water of thermoresponsive hydrogels based on high molar mass polyglycidol and random copolymers of glycidol and glycidyl ethyl carbamate. Poly(ethylene glycol)-bis-(carboxymethyl ether chloride) was used as a crosslinker. The influence of the copolymer composition and network density on the response of swollen polymer materials to the temperature changes and the swelling-deswelling behavior is described.

Results and discussion

Synthesis of high molar mass linear polyglycidol

It was shown before that the coordination polymerization of glycidol with protected hydroxyl groups with different organometallic catalysts and then acidic hydrolysis of the protective groups lead to polyglycidol with high molar masses [20-22].

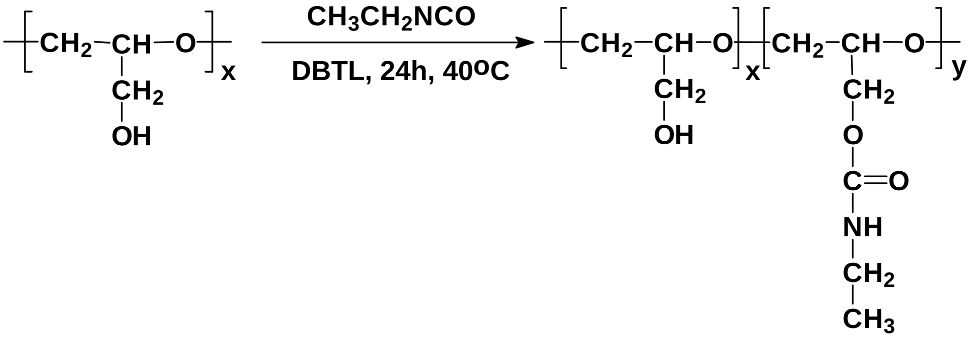
In this work, coordination polymerization of ethoxyethyl glycidyl ether using partially hydrolyzed diethyl zinc ($ZnEt_2/H_2O$ equal to 1:0.8) was applied. After deprotection of ethoxyethyl groups in HCl solution, the polyglycidol of molar mass M_n=800 000 g/mol and dispersity of 1.46, checked by GPC with multiangle light scattering detection, was obtained. The detailed synthesis and characteristics of obtained high molar mass polyglycidol is reported in our previous work [23].

Chemical modification of high molar mass polyglycidol

The controlled modification of functional hydroxyl groups of derivatives of polyacrylamides or polymethacrylamide [24], poly(vinyl alcohol) [25] and polyglycidol [23, 26] has been already applied and thermoresponsive polymers exhibiting cloud point in a wide range of temperature have been obtained.

The polyglycidol is a water soluble, highly hydrophilic polymer. Its hydroxyl groups may be hydrophobically modified and used to control the equilibrium of the hydrophilic/hydrophobic properties and to influence the behavior of final polymers in aqueous solution.

To obtain thermosensitive polyglycidol, simple chemical reaction (Scheme 1) was used for introducing hydrophobic groups into polymer chain as previously described in [23]. Hydroxyl groups of polyglycidol were reacted with ethyl isocyanate yielding poly(glycidol-co-glycidyl ethyl carbamate)s. The presence of a catalyst – dibutyltin dilaurate was necessary to carry out the urethanization reactions of polyglycidol.



Scheme 1. Synthesis of poly(glycidol-co-glycidyl ethyl carbamate)s.

It has been already shown [23] that the proper choice of stoichiometry yields a series of copolymers containing various amounts of hydrophobic ethyl carbamate groups. The extent of modification was controlled by the molar ratio of the reagents employed. All copolymers were characterized by ^{1}H NMR spectroscopy. The integration of the spectra signals provided the copolymer composition and the degree of modification.

The main characteristics of the linear polymers used in this work for networks synthesis are summarized in Table 1. The cloud points of the aqueous polymer solutions were measured with UV-VIS spectroscopy as described in the Experimental Part. Both polyglycidol (PG) and the copolymer containing 10 % of glycidyl ethyl carbamate groups ($P(G_{0.9}$-co-$EGC_{0.1}))$ are water soluble in the whole temperature range. For the copolymer containing 34 % of glycidyl ethyl carbamate units ($P(G_{0.66}$-co-$EGC_{0.34}))$ transition point is registered at 42 °C, whereas a cloud point at 30 °C is observed for the copolymer with 37 % hydrophobic groups ($P(G_{0.63}$-co-$EGC_{0.37}))$.

Tab. 1. Characterization of the polymers used to obtain networks.

Sample	Degree of modification [%]	Cloud point [^{o}C]
PG	0	soluble
$P(G_{0.9}$-co-$EGC_{0.1})$	10	soluble
$P(G_{0.66}$-co-$EGC_{0.34})$	34	42
$P(G_{0.63}$-co-$EGC_{0.37})$	37	30

The synthesis of temperature responsive hydrogels

In chemically crosslinked stimuli responsive gels covalent bonds between different polymer chains ensure a good mechanical stability of obtained materials.

In this work the chemically crosslinked gels were prepared by a reaction between hydroxyl groups of polyglycidol or between residual hydroxyl groups of poly(glycidol-co-glycidyl ethyl carbamate)s with poly(ethylene glycol)-bis-(carboxymethyl ether chloride).

-Synthesis of crosslinking agent

Poly(ethylene glycol)-bis-(carboxymethyl ether chloride) was synthesized by reacting poly(ethylene glycol)-bis-(carboxymethyl ether) with thionyl chloride as shown in Scheme 2.

$$HO-\overset{O}{\overset{\|}{C}}-CH_2-O-(EO)_{12}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} Cl-\overset{O}{\overset{\|}{C}}-CH_2-O-(EO)_{12}-CH_2-\overset{O}{\overset{\|}{C}}-Cl$$

Scheme 2. The synthesis of poly(ethylene glycol)-bis-(carboxymethyl ether chloride).

The structure of the synthesized crosslinking agent was confirmed by the ^1H NMR spectroscopy (Figure 1).

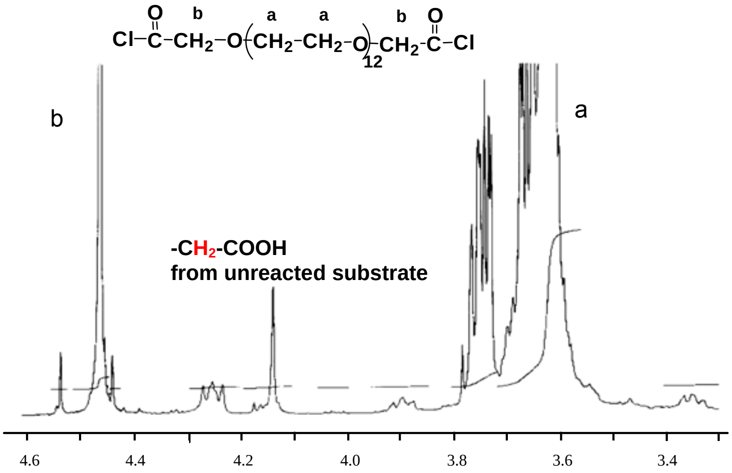


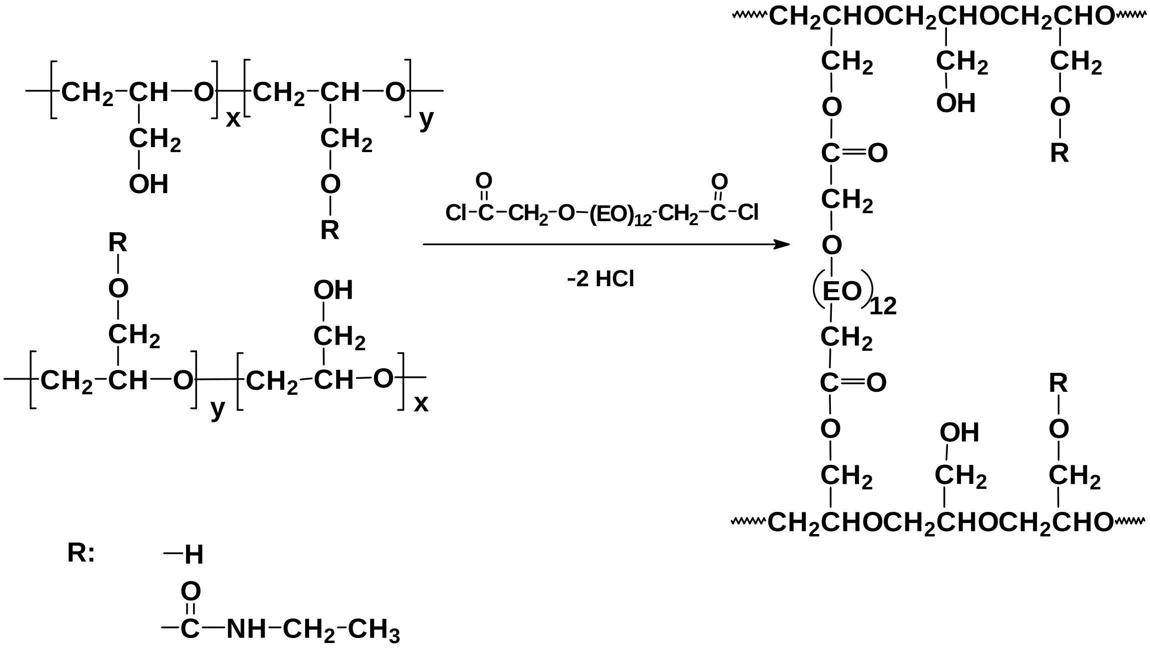
Fig. 1. ^1H NMR of the poly(ethylene glycol)-bis-(carboxymethyl ether chloride), (300 MHz, $CDCl_3$).

The signals of the protons of the methylene groups next to the acyl chloride end groups appear at δ=4.5 ppm (Figure 1, signal b) and confirm the acylation reaction. Signals of the protons of the carboxymethylene groups are also present, although of low intensity. From the integrals of the signals it has been estimated that 90 % of the carboxyl groups were converted to acyl chlorides. As the -COOH groups are less reactive than -COCl groups it can be expected that along with bridging of the crosslinker chains the gel contain “dangling” crosslinker chains with -COOH end groups.

-Crosslinking reaction

The acyl chloride groups of the obtained crosslinker are of high reactivity towards the hydroxyl groups of the synthesized polymers. The reaction was carried out for 24 to 30 hours. The crosslinking reaction of high molar mass polyglycidol and its hydrophobically modified derivatives was carried out in DMF as a solvent to ensure homogeneous reaction conditions. The amount of the solvent was kept as low as possible. In order to gain the control over the network density, the amount of crosslinking agent was varied.

The crosslinking reaction proceeded with the formation of the ester linkages between the glycidol units and the crosslinker and is shown in Scheme 3.



Scheme 3. The crosslinking of PG and P(G_x-co-EGC_y) with poly(ethylene glycol)-bis-(carboxymethyl ether chloride).

The main characteristics of the networks including soluble fractions and fraction of hydroxyl groups reacted with the poly(ethylene glycol)-bis-(carboxymethyl ether chloride) are presented in Table 2.

Tab. 2. Characteristics of crosslinked PG and P(G_x-co-EGC_y).

No	Precursor	Polymer to crosslinker ratio [g/g]	SF [%]	fraction of OH groups reacted with crosslinker [%] *⁾	
				assuming full crosslinker conversion	accounting for the amount of soluble fraction
1	PG	1:1	16	19	13
2		1:0.75	9	15	12
3	P($G_{0.9}$-co-$EGC_{0.1}$)	1:1	6	19	17
4		1:3	13	58	43
5	P($G_{0.66}$-co-$EGC_{0.34}$)	1:1	7	19	16
6	P($G_{0.63}$-co-$EGC_{0.37}$)	1:0.75	35	15	5

*⁾ the amount of OH groups before hydrophobization with ethyl isocyanate was assumed to 100%.

The amount of the soluble fraction of a network washed out during its swelling provides information about the efficiency of the crosslinking and allows the estimation of the fraction of hydroxyl groups reacted with crosslinker. The soluble fractions of the developed networks calculated according to equation 2 (see Experimental Part) are listed in Table 2.

The substances extracted from the networks have been subjected to ^1H NMR analysis. A spectrum of the solubles washed out from the hydrogel 3 (Table 2) is presented in Figure 2.

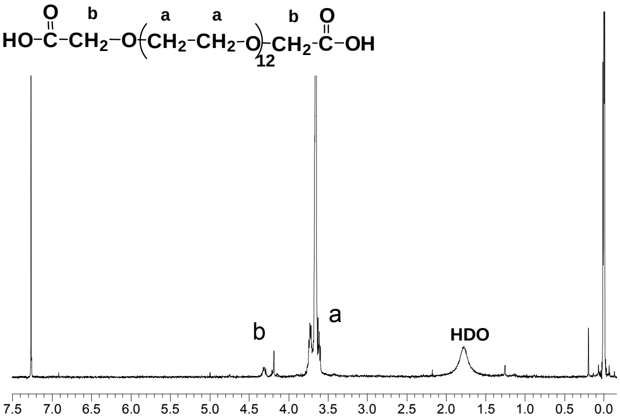


Fig. 2. ^1H NMR of the soluble fraction of the $P(G_{0.9}\text{-co-}EGC_{0.1})$ hydrogel (entry 3, Table 2) (300 MHz, $CDCl_3$).

It evidences that all chains of the starting copolymer are crosslinked as no signals derived from the glycidyl ethyl carbamate groups are observed. The sharp peak at $\delta=3.6$ ppm is assigned to protons of the methylene groups of poly(ethylene glycol) crosslinker. The signals at $\delta=4.2$ ppm are assigned to the protons of the $–CH_2$ group next to the terminal –COOH groups. This confirms that the soluble fraction consists only of unreacted crosslinker.

The fraction of hydroxyl groups reacted with the crosslinker (columns 5 and 6 in Table 2) was calculated taking into account the polymer to crosslinker ratio used for the reaction, soluble fraction measured after crosslinking and the fact that the soluble fraction consists of unreacted crosslinker only. In order to compare samples of different composition but of the same degree of polymerization, the initial OH content of copolymer before hydrophobic modification with ethyl isocyanate was taken as 100%.

An increase of the crosslinker to polymer ratio caused a higher degree of crosslinking. The results indicate that the degree of crosslinking of poly(glycidol-co-glycidyl ethyl carbamate)s with poly(ethylene glycol)-bis-(carboxymethyl ether chloride) can be controlled.

Swelling behavior of temperature responsive hydrogels

The swelling behavior of obtained networks in aqueous medium was measured as a function of time at room temperature and is presented in Figure 3. The equilibrium swelling degrees of obtained networks were reached in a relative short time – within one hour.

The equilibrium swelling degrees (SD) of investigated hydrogels were calculated according to equation 1 (see Experimental part). In Table 3 the data concerning the swelling of the studied hydrogels are summarized.

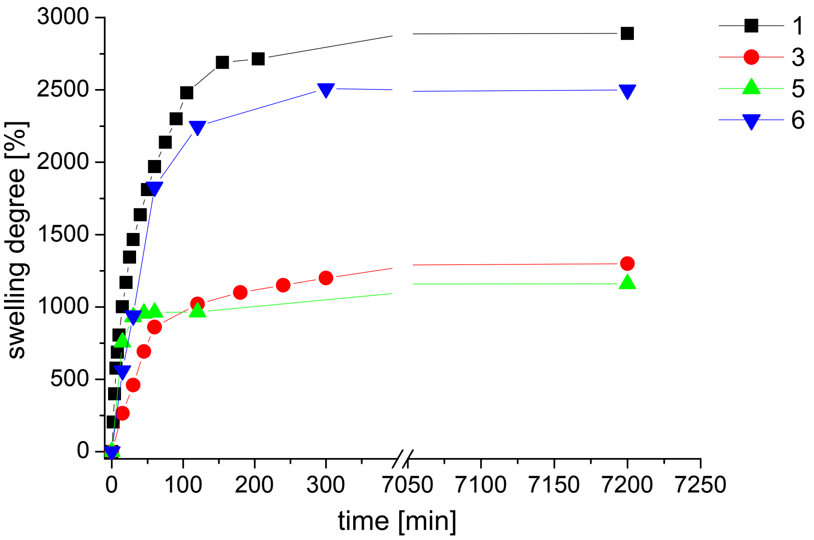


Fig. 3. Swelling of the networks of PG and P(G_x-co-EGC_y) (hydrogels 1, 3, 5 and 6) as a function of time.

Tab. 3. Swelling characteristics of obtained hydrogels.

No	Precursor	Polymer to crosslinker ratio [g/g]	SD [%]
1	PG	1:1	2900
2		1:0.75	2500
3	P($G_{0.9}$-co-$EGC_{0.1}$)	1:1	1300
4		1:3	800
5	P($G_{0.66}$-co-$EGC_{0.34}$)	1:1	1200
6	P($G_{0.63}$-co-$EGC_{0.37}$)	1:0.75	2300

All synthesized networks exhibit high water absorbing capacity. The equilibrium swelling degrees of hydrogels are higher than 1000 %.

The equilibrium swelling degrees in water of all obtained hydrogels were much higher than those of hydrogels previously prepared from polyglycidol and its block copolymers with ethylene oxide crosslinked with glutaraldehyde [18, 27]. This higher water uptake of the polymers described in this paper can be attributed to the introduction of the hydrophilic, long spacers of the poly(ethylene glycol)-bis-(carboxymethyl ether chloride) in the network. The use of poly(ethylene glycol) chains with DP=12 as a crosslinking spacer yields a better ability to bind water molecules between the hydrophilic segments of the network than the shorter, hydrophobic glutaraldehyde spacers [18]. The improved swelling capacity can be also assigned to the addition of solvent during the crosslinking reaction, which favors formation of loose networks containing probably a fraction of dangling (grafted) crosslinker chains.

The equilibrium swelling degrees at room temperature are dependent on the network density (the amount of crosslinker used) and can also be controlled by composition of the copolymer precursor. At the same copolymer composition (series P($G_{0.9}$-co-$EGC_{0.1}$), hydrogels 2-4 in Table 3) the swelling of the networks decreases considerably with the increasing amount of the crosslinker used. Comparing the networks prepared from copolymers with different composition (hydrogel pair 3 and 5 in Table 3) and having the same fraction of OH groups reacted with crosslinker, it is observed that the higher amount of hydrophobic glycidyl ethyl carbamate groups reduces the swelling ability of the gels.

The hydrogel prepared from crosslinking of pure polyglycidol swells much more than crosslinked poly(glycidol-co-glycidyl ethyl carbamate)s of approximately the same degree of crosslinking (Table 3) because of the stronger hydrophilic interaction between the chain elements of polyglycidol and water molecules.

Temperature response of hydrogels

The response of the hydrogels to the changes in the temperature of the aqueous media is shown in Figure 4 and 5.

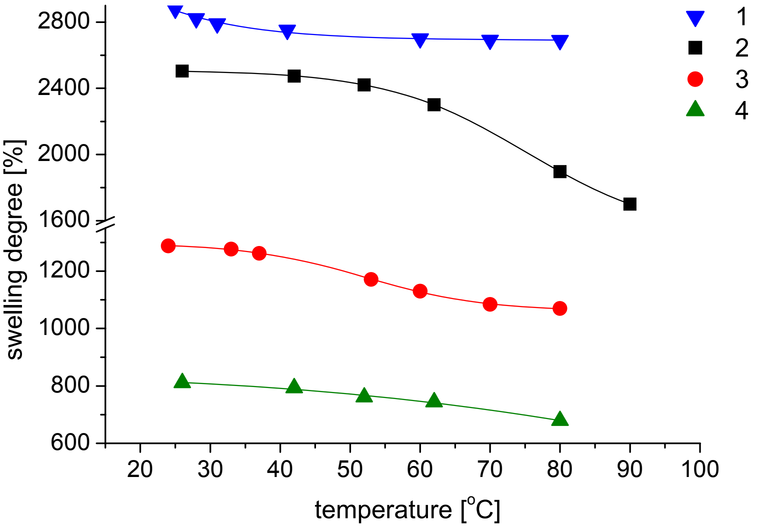


Fig. 4. Swelling degree of hydrogels of PG and of P($G_{0.9}$-co-$EGC_{0.1}$) with different degree of crosslinking, as a function of temperature.

Hydrogel prepared by crosslinking of pure polyglycidol (Figure 4, sample 1) does not exhibit considerable volume changes even at temperatures exceeding 80 °C. The swelling degree of this polymer at 25 °C is almost 2900 % and at 80 °C it drops only slightly to 2750 %. Here, the hydroxyl groups present in every chain unit form hydrogen bonds with water molecules. The energy that is supplied to the system by raising the temperature is not sufficient to break these bonds and to induce the shrinking of the hydrogels.

When hydrophobic groups are introduced into the polymer chain, the system behaves differently. At lower temperatures, hydrogen bonds between hydrophilic segments of the polymer chains and water molecules dominate which causes swelling of the hydrogels. When the temperature is increased, the interactions of the polymer chains with water are broken resulting in a decrease of the hydration capability of the gels. The state of the water molecules in the gel changes from bound to free water. This causes in network shrinking and the absorbed water is expelled.

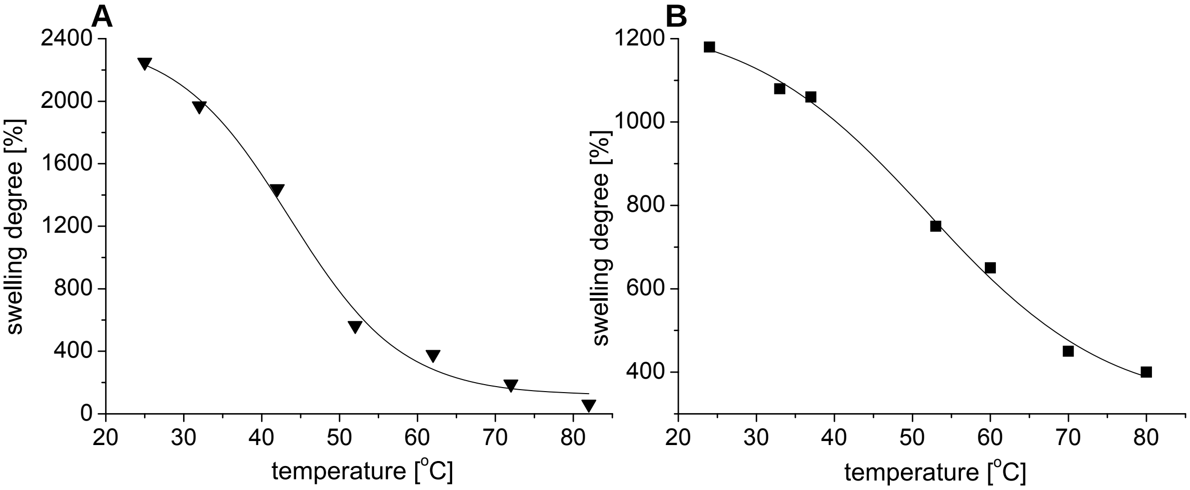


Fig. 5. Swelling degree of hydrogels of (P($G_{0.63}$-co-$EGC_{0.37}$) copolymer (A) and P($G_{0.66}$-co-$EGC_{0.34}$) copolymer (B) as a function of temperature.

All studied hydrogels prepared from the hydrophobically modified polyglycidol show a decrease in swelling degree with the increasing temperature, independent of the presence or absence of cloud point behavior of their linear precursors. The temperature response of those hydrogels is caused by the presence of additional junction point in the network structure. For example 10 % of substitution of hydroxyl groups by hydrophobic ones, as for P($G_{0.9}$-co-$EGC_{0.1}$) copolymer, does not induce thermosensitivity of copolymer itself, but creates sensitivity to temperature changes when polymer is crosslinked.

Volume shrinkage of the investigated hydrogels takes part in a broad temperature range from 25 °C to 80 °C. Similar broad volume transitions were observed for PEO-PNIPAM [28], PEtOx-PHEMA, PEtOx-PHPA [29] or poly(vinyl ether)s hydrogels [30]. The dispersity of the copolymer precursor and the distribution of the copolymer composition contribute to the broadening of the volume phase transition range of their hydrogels.

The magnitude of shrinking depends on the degree of crosslinking and on the copolymer composition of the precursor. Hydrogels with lower degree of crosslinking and higher amount of hydrophobic groups display the most pronounced volume change with temperature. When the ratio of polymer to crosslinker is equal or lower than 1:1 (low crosslinking degree) the hydrogels exhibit a volume transition showing typical S-shaped curves (Figure 4 and 5, hydrogel 2, 3, 5 and 6). For these hydrogels volume phase transition temperature (T_V) was estimated as the maximum on the curve of the first derivative of swelling degree ($\frac{d(SD)}{dT}$). The values of the volume phase transition temperatures for hydrogels are listed in Table 4. The hydrogel prepared from the highly crosslinked P($G_{0.9}$-co-$EGC_{0.1}$) copolymer (at 1:3 polymer to crosslinker ratio) decrease their volume linearly without any significant inflection of volume transition temperature curve.

Tab. 4. Transition temperatures of hydrogels and their linear precursors.

No	Precursor	Polymer to crosslinker ratio [g/g]	T_{CP} [°C] of linear precursor	T_V [°C]
1	PG	1:1	soluble	*
2	$P(G_{0.9}\text{-co-}EGC_{0.1})$	1:0.75	soluble	80
3		1:1	soluble	60
4		1:3	soluble	*
5	$P(G_{0.66}\text{-co-}EGC_{0.34})$	1:1	42	53
6	$P(G_{0.63}\text{-co-}EGC_{0.37})$	1:0.75	30	42

*) swelling degree decreases linearly with temperature

When the content of the hydrophobic glycidyl ethyl carbamate groups in the copolymer precursor chain is increased (for $P(G_{0.9}\text{-co-}EGC_{0.1})$, $P(G_{0.66}\text{-co-}EGC_{0.34})$ and $P(G_{0.63}\text{-co-}EGC_{0.37})$) the volume phase transition temperature of hydrogel decreased. An increase of the degree of crosslinking induced the same effect. Similar behavior was observed for many hydrogels [29, 31].

Hydrogels obtained from copolymer with LCST behavior (sample 5 and 6 in Table 4) show volume phase transition temperature higher than the cloud point of uncrosslinked linear precursor.

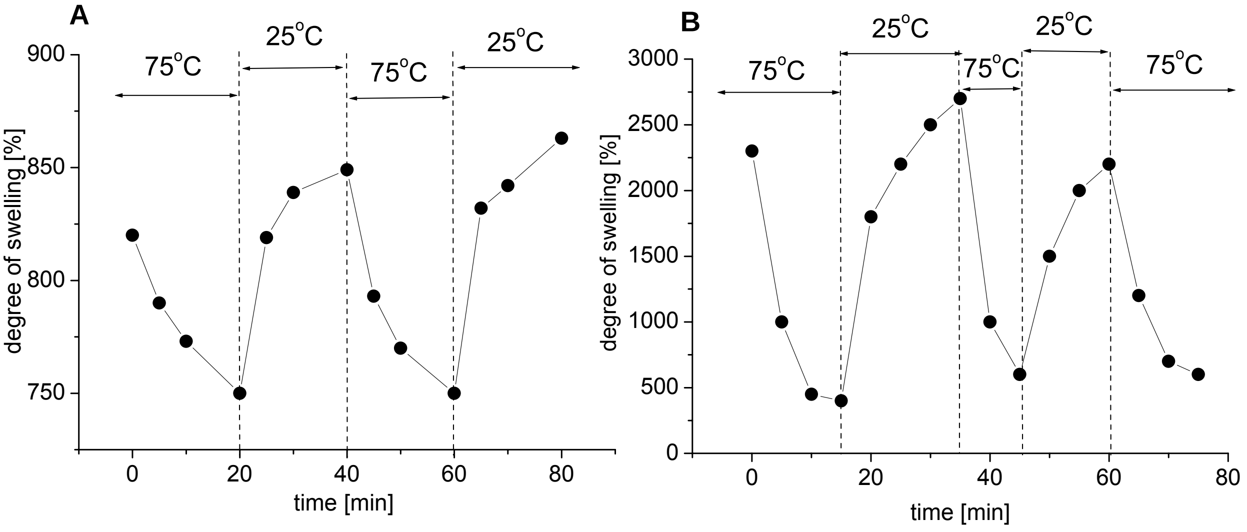


Fig. 6. Swelling-deswelling cycles of hydrogels of (A) $P(G_{0.9}\text{-co-}EGC_{0.1})$ crosslinked with polymer to crosslinker ratio 1:3; (B) $P(G_{0.63}\text{-co-}EGC_{0.37})$ crosslinked with polymer to crosslinker ratio 1:0.75.

The swelling-deswelling properties of the studied hydrogels in response to stepwise changes of temperature were also followed. The temperatures 25 °C and 75 °C have been chosen to cover the expected transition temperatures for all investigated hydrogels. Samples swollen to the equilibrium at room temperature were heated up to 75 °C and cooled back in short intervals. A typical example of swelling-deswelling curves is shown in Figure 6. These multiple swelling-deswelling experiments revealed that the obtained hydrogels respond relatively fast to the changes of temperature, showing stable swollen and shrunk levels. A similar behavior was reported for hydrogels based upon poly(N-isopropylacrylamide) [3], poly(propylene oxide) [20] or poly(2-ethyl-2-oxazoline) [29].

The investigated hydrogels were transparent at 25 °C, but started to become opaque at the end of the cycle at 75 °C, indicating formation of large (> 1μm) inhomogeneities in the network due to the formation of hydrophobic domains. These experiments have demonstrated the reversibility of the swelling-deswelling behavior of investigated hydrogels and proved indirectly their mechanical stability.

Conclusions

Polyglycidol and poly(glycidol–co–glycidyl ethyl carbamate) were crosslinked with functionalized ethylene oxide oligomers. Hydrogels with high swelling capacity were obtained.

Some of the hydrogels were responding to changes of temperature and shrink when a certain range of temperatures is exceeded. By changing the network composition and the crosslinking density the control of the volume transition temperature was possible. Crosslinking of thermosensitive polymers, i.e. those exhibiting T_{CP}, resulted in hydrogels with the most pronounced volume shrinkage with increasing temperature.

The obtained thermosensitive hydrogels undergo several swelling/deswelling cycles in response to stepwise changes of temperature which makes them interesting for potential application.

Experimental part

Materials

Ethoxyethyl glycidyl ether was synthesized in an acid-catalyzed reaction of 2,3-epoxypropanol-1 (glycidol) (Aldrich) with ethyl vinyl ether (Fluka) according to Fitton *et al.* [32] and distilled under reduced pressure to obtain fraction with purity exceeding 99.8 % (checked by GC). Diethyl ether (POCh Gliwice) for polymerization experiment was dried over Na/K alloy and distilled under dry nitrogen atmosphere. Ethyl isocyanate 98 % (Aldrich) was purified by distillation under dry nitrogen atmosphere. DMF (POCh Gliwice) was initially dried over molecular sieves type 4 Å and then over CaH_2 and distilled under reduced pressure. 1 M solution of diethyl zinc in hexane ($ZnEt_2$) (Aldrich), dibutyltin dilaurate 95 % (DBTL) (Aldrich), thionyl chloride ($SOCl_2$) (Aldrich) and poly(ethylene glycol)-bis-(carboxymethyl ether) of M_n=600 g/mol (Aldrich) were used as received.

Synthesis of high molar mass linear polyglycidol

Ethoxyethyl glycidyl ether was polymerized using $ZnEt_2/H_2O$ (1:0.8) as a catalyst according to procedure described previously [23]. After polymerization the poly(ethoxyethyl glycidyl ether) was hydrolyzed by dissolving in 3 M HCl and the high molar mass homopolymer of glycidol was obtained (PG).

Chemical modification of high molar mass polyglycidol

Polyglycidol was hydrophobically modified in a reaction with ethyl isocyanate in the presence of dibutyltin dilaurate as a catalyst, using DMF as a solvent. The amount of the reagents used was varied depending on the desired degree of modification. The detailed procedure was described previously in [23].

The obtained copolymers were denoted as P(G_x-co-EGC_y) for modified linear, high molar mass polyglycidol where x and y indicate the mole fractions of glycidol (G) and glycidyl ethyl carbamate (EGC), respectively.

Synthesis of crosslinking agent - poly(ethylene glycol)-bis-(carboxymethyl ether chloride)

Poly(ethylene glycol)-bis-(carboxymethyl ether chloride) was synthesized in the acylation reaction of poly(ethylene glycol)-bis-(carboxymethyl ether) with thionyl chloride, similar to the procedure described by Chacon *et al.* [33]. Poly(ethylene glycol)-bis-(carboxymethyl ether) (4 g, $6.6 \cdot 10^{-3}$ mol) was reacted with 3 mL of thionyl chloride. The mixture was stirred for about 24 hours at room temperature. The excess of thionyl chloride was removed by vacuum evaporation at 40 °C.

Crosslinking with poly(ethylene glycol)-bis-(carboxymethyl ether chloride)

Polyglycidol or hydrophobically modified polyglycidols were dissolved in dry DMF (100 g/L). Next the solution of poly(ethylene glycol)-bis-(carboxymethyl ether chloride) in DMF was added to the polymer solution. The concentration of the crosslinker in the solution was varied between 25 and 100 g/L. After stirring, the mixture of polymer and crosslinker in DMF was cast onto a Teflon dish. The reaction was left to proceed at room temperature in dry atmosphere for at least a day. After reaction DMF was removed from the polymer film under reduced pressure to constant weight. Alternatively, it was washed out with water via swelling of the network. The films were then dried at atmospheric pressure.

Measurements

The molar mass and the dispersity of obtained polyglycidol were determined by GPC system equipped with a multiangle light scattering detector (λ=690 nm) DAWN EOS of Wyatt Technology, using DMF as an eluent. The details are given in [23].

The ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or D_2O at 300 MHz on Unity-Inova spectrometer (Varian).

The cloud point temperatures of hydrophobically modified polyglycidol were determined on Jasco V-530 UV-VIS spectrophotometer with a cuvette thermostated by Medson MTC-P1 Peltier thermocontroller. The transmittance of the aqueous polymer solutions (5 g/L) were monitored by spectrophotometer at λ=500 nm as a function of temperature. The sample solutions were heated step-wise. Once the desired temperature was reached, the samples were equilibrated for 5 min before measuring the transmittance. Then the solutions were heated to the next temperature with a heating rate of 0.2 °C/min. The cloud points were determined as maximum on the first derivative of the transmittance in temperature function.

The degree of swelling (SD) of polymer films was measured gravimetrically in distilled water in a temperature range from 25 to 80 °C. A disc cut from the film was weighed and put into a vial with distilled water. At regular intervals the disc was taken out, the excess solvent from the surface was removed with tissue paper; the disc was weighed and then returned to water. At elevated temperature the process was carried out in oven. The samples were equilibrated at the given temperature until the swelling degree remained constant. All manipulations were carried out inside the oven to minimize the changes of swelling with temperature.

The degree of swelling was calculated from equation 1:

$$SD = \frac{w - w_o}{w_o} \cdot 100\% \qquad (1)$$

where w_o is the initial weight of the dry sample and w is the weight of the swollen sample.

Soluble fractions (SF) were measured as follows: a sample of the dry network was washed 10 times with water at room temperature, every time for one hour. The extracts were combined. No residuals were detected in last fraction. Then the gels were dried first at the room temperature and then at 50 °C under vacuum until constant weight. The soluble fractions were calculated from equation 2:

$$SF = \frac{w_o - w_e}{w_o} \cdot 100\% \qquad (2)$$

where w_o is the initial weight of the dry sample and w_e is the weight of the dry sample after the extraction.

Acknowledgements

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