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Hydrophobically modified polyglycidol – the control of lower critical solution temperature

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Summary

Polymers of glycidol (2,3-epoxypropanol-1) of different molar masses (between $2 \cdot 10^4$ and $2 \cdot 10^5$) and chain topology (linear and comb-like) were synthesised and used to obtain a series of temperature responsive water-soluble poly(glycidol-co-glycidol acetate)s. The degree of the substitution of the hydroxyl groups with the acetate groups influences the solution behaviour of the obtained copolymers, the cloud point may be controlled between +4°C and +100°C.

Introduction

Polymers which exhibit in aqueous solution large changes of properties in response to small external stimuli e.g. temperature, light, pH or presence of electrolytes have attracted a great attention (for review, see [1, 2]), also because of their potential applications in such areas, as controlled release [2, 3, 4], selectively permeable membranes [2, 5] or sensors and actuators [6].
These polymers are water-soluble at low temperature but become insoluble as the temperature rises above the lower critical solution temperature (LCST). The control of the transition temperature is important for any application. To achieve this control, a carefully chosen balance of the hydrophobic and hydrophilic segments of the macromolecule is necessary.
Poly(ethylene oxide) (PEO), a water-soluble polyether, was frequently used as the building block for LCST polymers. However, PEO itself has an LCST of over 100°C [7, 8]. To influence the temperature behaviour of PEO macromolecules hydrophobic elements have to be introduced, which may not be easy, as the PEO itself does not contain any reactive functional groups (except for the end groups). The control of the LCST was achieved by the block copolymerisation of EO with different hydrophobic monomers [9-12], by the introduction

of the hydrophobic elements into the core of the PEO stars [13] or by attachment of the hydrophilic PEO side chains to the hydrophobic backbones [14, 15]. In most cases, considerable synthetic efforts were necessary to achieve control of the transition point.
Here we want to report the results of the screening of the properties of an analogue of the PEO, the hydrophobically modified poly(2,3-epoxypropanol-1) – the polyglycidol. Polyglycidol itself is water soluble from almost 0°C to the boiling point of water. Unlike the PEO however it contains reactive hydroxyl groups which may be hydrophobically modified and used to control the equilibrium of the hydrophilic – hydrophobic properties and to influence the LCST.

Experimental

Materials

Ethoxy ethyl glycidyl ether(further referred to as glycidol acetal) was synthesised from 2,3-epoxypropanol-1 (glycidol) and ethyl vinyl ether according to Fitton et al [20] and fractionated under reduced pressure. A fraction with purity exceeding 99.8% (GC) was used.
THF and diethyl ether were refluxed over Na/K alloy.
Dimethyl sulfoxide (DMSO) was dried over CaH_2 and distilled.
Potassium t-butoxide (Aldrich) and diethyl zink (1 M solution in hexane, Aldrich) were used as received.
DMF, acetic anhydride and pyridine were distilled before use.

Polymer synthesis

Synthesis of polyglycidol – high molar mass
The polymerisation of glycidol acetal was initiated with $ZnEt_2/H_2O$ (1:0.8) in bulk according to Spassky [16]. The poly(ethoxy ethyl glycidol ether) was hydrolysed using 3M HCl.

Synthesis of polyglycidol – low molar mass
The anionic polymerisation of glycidol acetal was carried out using potassium tert-butoxide as an initiator at 60°C in THF to full conversion of the monomer as described earlier [17]. To remove the protecting groups the polymer was hydrolysed with oxalic acid.

Synthesis of polyglycidol-graft-polyglycidol
Linear polyglycidol was ionized by potassium tert-butoxide and used to initiate the anionic polymerisation of glycidol acetal. The polymerisation was carried out at 70°C for 24 h in DMSO. Details are given in [18]. The solvent was evaporated under vacuum and the protecting groups were removed using formic acid as described earlier [19].

Esterification of polyglycidol
Polyglycidol was esterified with acetic anhydride in DMF using pyridine as proton acceptor, as described by Laschewsky [21]. The degree of esterification

was controlled varying the ratio of the acetic anhydride to the hydroxyl groups in the polymer. A typical procedure is as follows: Polymers were reacted with acetic anhydride and pyridine in DMF at 60°C for about 20h. The concentration of polymers was 50g/L. After cooling, the mixtures were precipitated into diethyl ether cooled to –30°C. The differently acetylated poly(glycidol-co-glycidol acetate)s were obtained by varying the amounts of acetic anhydride and pyridine.
The obtained copolymers were denoted H for high molar mass polyglycidol, L – for low molar mass and G – for graft polymer. The degree of esterification (the percentage content of acetate groups) was denoted as x, e.g. H_x.

Measurements

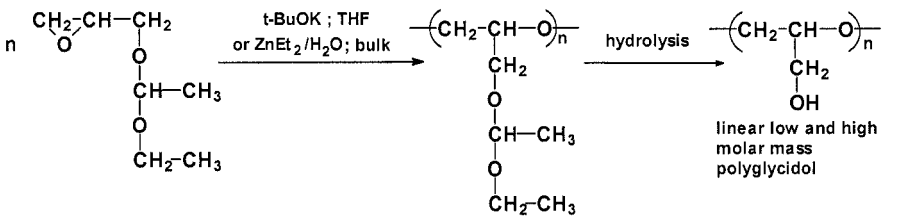
NMR
The ^{1}H NMR spectra were recorded at 300 MHz in D_2O using Varian Unity spectrometer.

Size exclusion chromatography
The molar masses of obtained polyglycidols were determined by SEC using 2 x PlGel Mixed D 30 cm and guard columns with a refractive index detector Δn-1000 (WGE Dr. Bures) and a multiangle light scattering detector DAWN EOS of Wyatt Technologies. Measurements were performed in DMF containing 5 mmol/L LiBr at 30°C with a nominal flow rate of 1 mL/min. Results were evaluated using the ASTRA software from Wyatt Technologies.
Refractive index increment of polyglycidol in DMF was determined independently to 0.054 mL/g in DMF at 30°C and 620 nm.

Cloud point measurements
The cloud points of poly(glycidol-co-glycidol acetate) copolymers in aqueous solution were determined visually by following the variation of the turbidity with temperature. A water bath was heated just below the cloud point and the sample was immersed into the bath, the temperature was than raised slowly until the sample became turbid and than the temperature was lowered until the sample became clear. The cloud point was estimated as average of both measurements.

Results and discussion

Linear polyglycidol was obtained using the living anionic polymerisation of poly(glycidol acetal) under the previously estimated conditions [17]. Narrowly dispersed polymer of M_n=20000 and M_w/M_n=1.21 was obtained.
Anionic polymerisation however cannot be used to obtain polyglycidol of a much higher molar mass. To achieve this, the Vandenberg initiator, a partially



hydrolysed $ZnEt_2$ was used. This leads to a much higher molar mass (table 1) and broader molar mass distribution.
Linear polyglycidol of M_n=10000 was chosen to synthesise the grafted polyglycidol, as described in [18]. Some of the hydroxyl groups were transformed into alcoholate anions and the obtained polyanion was used to initiate the polymerisation of 1-ethoxyethyl glycidyl ether. Removal of the protecting groups yielded polyglycidol-graft-polyglycidol. The analysis of the NMR spectra of this polymer makes the determination of the grafting density possible [18]. It turned out that 75% of the main chain units have been grafted and the average length of the side chain is 9 units. The molar masses and the polydispersities of the obtained polymers are shown in table 1.

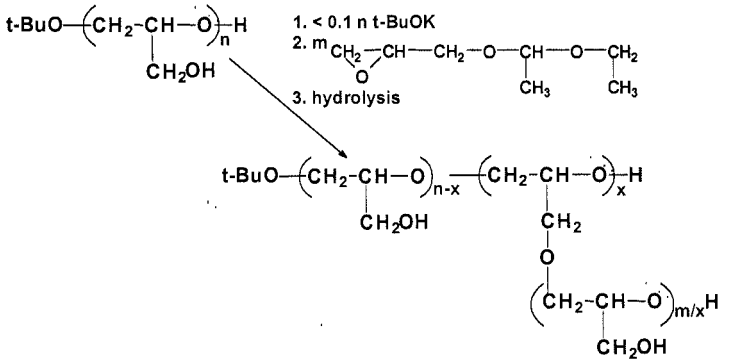
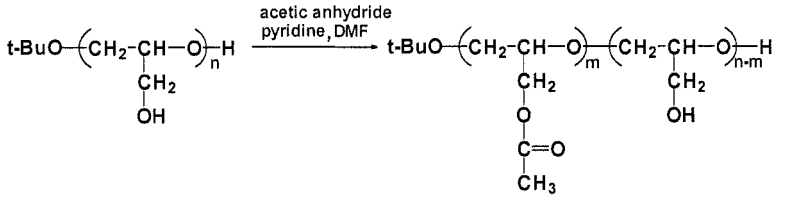


Table 1. Molar masses of obtained polymers

Polyglycidol	M_n	M_w/M_n
Low molecular (L)	20 000	1.21
High molecular (H)	186 000	1.67
Graft (G)	82 000	1.25

Modification of polyglycidols

Laschewsky [21] has polymerised a hydroxyl groups containing derivative of NIPAM and has shown that the esterification causes strong and controllable changes of the cloud point of the obtained polymers. We applied a similar approach to obtain poly(glycidol-co-glycidol acetate)s.



The esterification yields randomly substituted polyglycidol. The proper choice of the stoichiometry (amount of the esterifying agent) allows to obtain copolymers containing from 30 to 90% of ester groups. The degree of esterification may easily be determined from the NMR spectra (fig.1). The signals of the methyl groups at δ=2.1 ppm and methylene groups at δ=4.1 ppm and 4.4 ppm yield the degree of esterification.

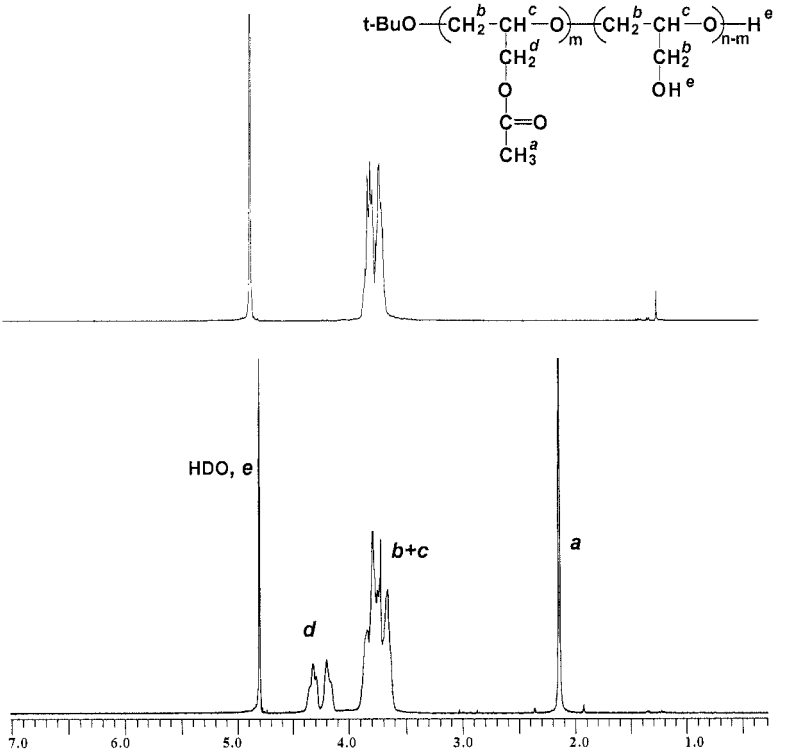


Fig. 1. ^{1}H NMR spectrum (300 MHz, D_2O) of (a) polyglycidol, (b) acetylated polyglycidol with 66% of ester groups (H_66)

Thermosensivity of the modified polyglycidol

Polyglycidol is very well soluble in water. The replacement of a part of the hydroxyl groups with the hydrophobic ester groups leads to copolymers which exhibit a cloud point in water solutions varying from +4°C÷+100°C. Fig 2 shows the dependence of the cloud point upon the degree of esterification.
The solubility of the modified glycidol polymers depends upon the degree of the esterification. When more than ca. 80% of the hydroxyl groups are esterified, the polymers become insoluble in water. When the degree of the esterification is lower than ca. 40%, both the high and the low molar mass linear copolymers become water soluble up to 100°C.

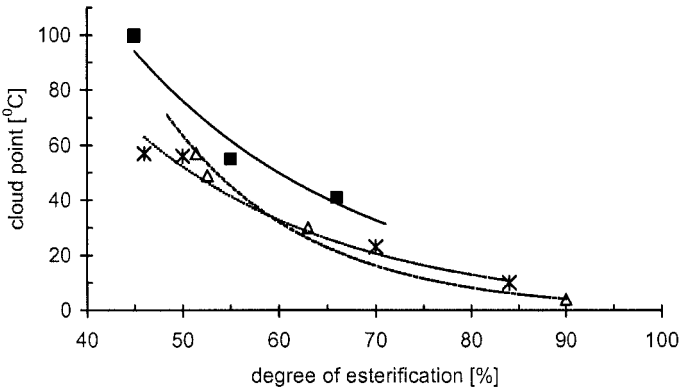


Fig. 2. The cloud point of poly(glycidol-co-glycidol acetate) as a function of the copolymer composition (polymer concentration 5g/L): (■) – H; (Δ) – L; (*) – G, see table 1. The lines are drawn as visualization aid only, the approximation functions have no physical meaning.

At the same degree of the esterification, the higher the molar mass, the higher the cloud point. In fig. 2, the curve for the high molar mass poly(glycidol - co - glycidol acetate) lies substantially above the curve for the lower molar mass polymer.

Also the chain topology influences the dependence of the cloud point upon the degree of the esterification. The curve for the comb-like polymer of M_n=80000 is almost identical with the curve for the linear chain of M_n=20000 and lies significantly below the curve for the linear chain of M_n=186000. Several factors may account for this. A possible explanation has to take into account that the structure of the comb-like chain with a rather high grafting density is much more compact then the structure of the linear chain. Therefore the outer units of the grafted chains are more accessible to the esterification, so that the hydrophobic units are likely to be concentrated on the outer sphere. It is however the outer sphere which interacts with the solvent and with other macromolecules, so that the macromolecule appears to be more hydrophobic then the linear one, even if the overall content of the ester groups is the same.

The cloud point depends on the concentration of the polymer in water solution. (fig. 3). When the concentration of the dissolved macromolecules increases, the intermolecular hydrophobic interaction start prevailing, which lowers the cloud point. At higher concentrations, this influence is higher for the grafted chain then for the linear polymer.

The addition of water soluble salts to the solution of LCST polymers facilitates the formation of aggregates and lowers the cloud point. In fig. 4 the influence of the NaCl concentration upon the cloud point of the obtained polymers is shown. For all studied polymers the cloud point decreases with increasing salt concentration.

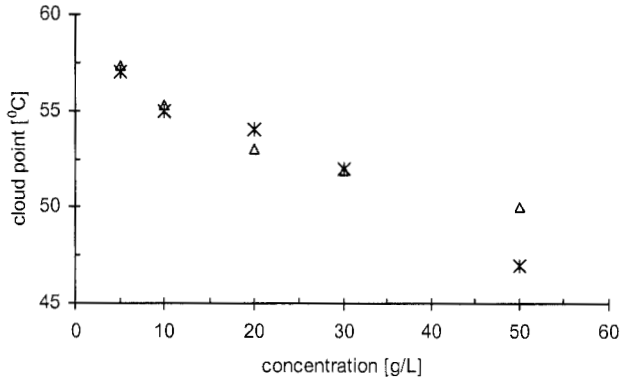


Fig. 3. The cloud point of poly(glycidol-co-glycidol acetate) as a function of polymer concentration: (Δ) L_51; (*) G_50

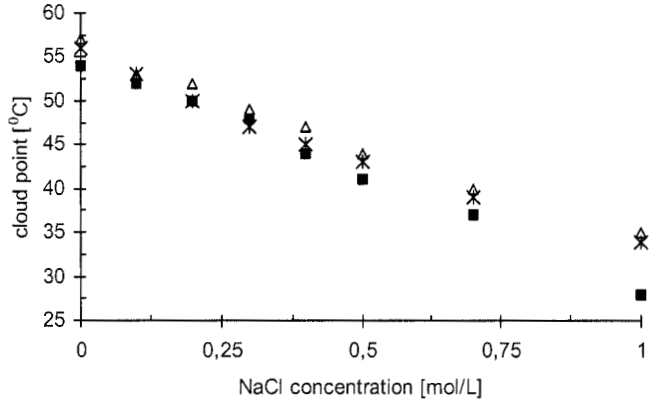


Fig. 4. NaCl effects on the cloud point of poly(glycidol-co-glycidol acetate) with different molar masses: (■) H_55; (Δ) L_51; (*) G_50

Conclusions

The hydrophobic modification of poly(2,3-epoxypopanol-1), the polyglycidol, opens an easy route to the LCST polymers. The structure of the starting polymers may easily be controlled using the living polymerisation techniques. Relatively little synthetic effort necessary to esterify a part of the hydroxyl groups makes polyethers of LCST varying between 0 and 100^{0}C available. The obtained LCST polymers contain reactive hydroxyl groups, which may be used to obtain stimuli sensitive hydrogels or nanoparticles.

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