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Novel Reactive Thermosensitive Polyethers – Control of Transition Point

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Summary: A new class of thermosensitive polymers based on polyethers is discussed. Using living anionic polymerisation techniques a series of homo- and block copolymers of 2,3-epoxypropanol-1 (the glycidol), ethoxy ethyl glycidol ether, its hydrophobic derivative, and ethylene oxide of different molar masses and topology (linear and comb-like) was obtained. By simple chemical modification of hydroxyl groups in polyglycidol segments hydrophobic elements were introduced into polymer chains, which allowed to control the transition point related to the lower critical solution temperature between 0 to 100°C. The relation between the transition temperature and the structure of obtained polymers is discussed.

Keywords: anionic polymerisation; cloud point; polyethers; polyglycidol; temperature sensitive polymers

Introduction

Stimuli sensitive polymers are structures, which exhibit distinct and reversible change of properties in response to the action of external stimuli. Different stimuli may be applied to invoke the change of properties, temperature being one of the most frequently studied[1-3]. Many polymers exhibit the so called lower critical solution temperature: a temperature above which the polymer precipitates from the solution, in most studied cases from water solution. The control of the transition temperature is important for all actual or envisaged application of such polymers[4-6]. This temperature is the function of the balance of hydrophobic and hydrophilic groups of the macromolecules undergoing transition and of polymer architecture.

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The aim of this work is to present a new group of temperature sensitive polymers based upon reactive polyethers, the transition point of which may be easily controlled within wide limits.

Experimental

Synthesis of linear polyglycidol

Polyglycidol of moderate molar mass (below 20 000), further referred to as PGl_L was obtained by the anionic polymerisation of ethoxy ethyl glycidyl ether using potassium tert-butoxide as initiator. The subsequent removal of the acetal group, as described previously[7] is necessary to obtain the desired polyglycidol. In order to obtain high molar mass polyglycidol the initiator of Vandenberg[8], the partially hydrolysed diethyl zinc ($ZnEt_2/H_2O$ 1:0.8) was used[9]. This high molar mass linear polyglycidol is further referred to as PGl_H.

Synthesis of polyglycidol-graft-polyglycidol

Linear polyglycidol was ionised by potassium tert-butoxide and used to initiate the anionic polymerisation of glycidol acetal. The acetal groups were removed using formic acid. Details are given in[10]. This comb-like polyglycidol is further referred to as PGl_G.

Synthesis of block copolymers of PEO and glycidol

The polyoxyethylene glycol cesium dialcoholates (M_n=10000, M_n=6000) and monoalcoholate (M_n=5000) were used as the initiators of the polymerisation of glycidol acetal. Details are given in[11]. The block copolymers are denoted as PGl_x-b-PEO_y-b-PGl_x or PEO_y-b-PGl_x; x, y denotes the number average degree of polymerisation of the polyglycidol and PEO blocks, respectively.

Esterification of hydroxyl group of polyglycidol

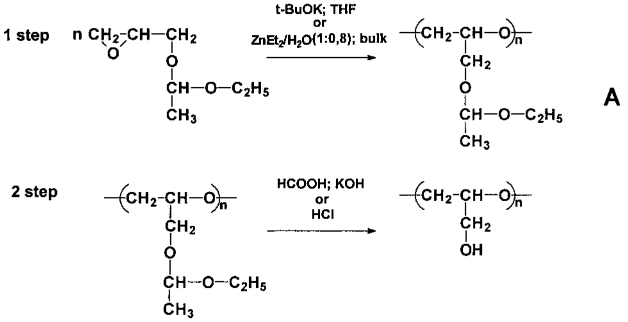
Obtained linear, graft and block polymers of glycidol were reacted with acetic anhydride in pyridine/DMF. The degree of esterification was controlled by varying the amount of acetic anhydride. The details of esterification are given in[12]. Ester groups are denoted by Ate.

Results and Discussion

The synthesis of the linear homopolymer of glycidol and its block copolymers with PEO

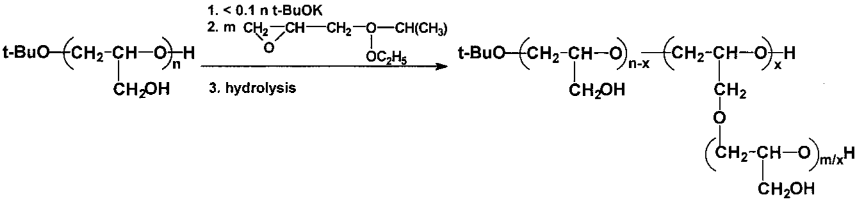
It is known that the cationic and anionic polymerisation of 2,3-epoxypropanol-1 (glycidol) are difficult to control and lead to branched products with not well defined structure. That is why the hydroxyl group of this monomer has to be protected before the polymerisation if linear chains of controlled DP are aimed at. In all our experiments with glycidol we applied the acetalization of the hydroxyl group, a protection method proposed by Spassky[13].

Low molar mass polyglycidol (PGl$_L$) was obtained by the anionic polymerisation of ethoxy ethyl glycidyl ether and subsequent removal of the protecting group under acidic conditions[7] (scheme 1). When degree of polymerisation of ca. 300 is not exceeded, the system is close to living, allowing to control the molar masses and yielding polymers with narrow molar mass distribution.



Scheme 1. Synthesis of linear polyglycidol.

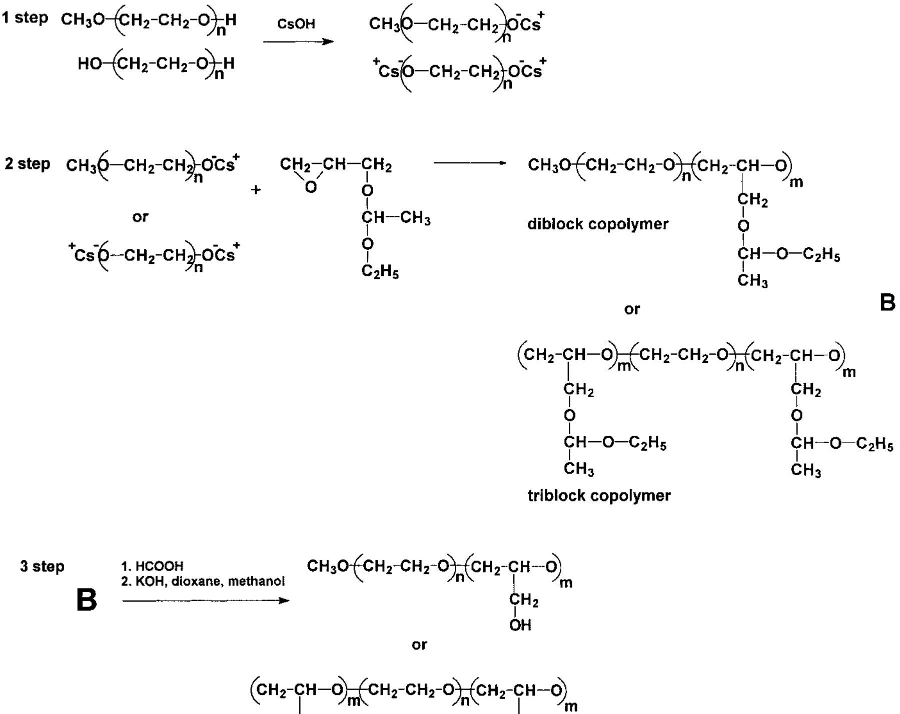
Higher molar masses are difficult to be achieved using the anionic polymerisation, probably because of the influence of adventitious electrophilic impurities. However, the use of the Vandenberg catalyst[8], the partially hydrolysed diethylzink ($ZnEt_2/H_2O=1:0.8$) leads to polymers of high molar masses (PGl$_H$) (up to 800 000), however, at the expense of lost control and broader molar mass distribution.



Scheme 2. Synthesis of comb-like polyglycidol.

The comb-like polyglycidol (PGl$_G$) was obtained[10] using an anionic „grafting from” polymerisation. Linear polyglycidol, obtained as described below, was partially transformed into its cesium alcoholate. This macroinitiator was used to initiate the polymerisation of protected glycidol. After deprotection, polyglycidol–graft–polyglycidol was obtained (scheme 2).

The living character of the polymerisation of protected glycidol makes the synthesis of block copolymers possible. Mono- or dialcoholates of polyethylene glycols were used as the initiators of the polymerisation of ethoxy ethyl glycidyl ether. A number of di- and triblock copolymers with poly(ethylene oxide) block, flanked on both or one side with polyglycidol chains were obtained (PGl_x-b-PEO_y, PGl_x-b-PEO_y-b-PGl_x) (scheme 3).



Scheme 3. Synthesis of di- and triblock copolymers of glycidol and ethylene oxide.

Due to the living character of the polymerisation the length of blocks was well defined and the molar mass distribution (therefore the block length distribution) remained narrow (table 1).

Table 1. Studied polymers of glycidol.

Sample	Molar mass[1)]	M_w/M_n
Homopolymers of glycidol		
PGl_L (linear)	20 000	1.21
PGl_H (linear)	186 000	1.67
PGl_G (graft)	82 000	1.25
Triblock copolymers PGl_x-PEO_y-PGl_x[2)]		
PGl_{68}-b-PEO_{227}-b-PGl_{68}	21 000	1.06
PGl_{44}-b-PEO_{227}-b-PGl_{44}	15 500	1.04
PGl_{28}-b-PEO_{227}-b-PGl_{28}	14 000	1.04
PGl_{80}-b-PEO_{136}-b-PGl_{80}	25 600	1.07
PGl_{34}-b-PEO_{136}-b-PGl_{34}	11 400	1.03
PGl_{17}-b-PEO_{136}-b-PGl_{17}	8 300	1.03
Diblock copolymers PEO_y-PGl_x[2)]		
PEO_{113}-b-PGl_{40}	8 000	1.02
PEO_{113}-b-PGl_{72}	11 100	1.02
PEO_{113}-b-PGl_{110}	12 600	1.10
PEO_{113}-b-PGl_{220}	20 800	1.16

(1) From GPC with refractive index and multiangle laser light scattering detectors

(2) Indices denote the number average degree of polymerisation of the polyglycidol blocks (x) and poly(ethylene oxide) blocks (y)

Temperature sensitivity of the studied polymers

Hydrophobic modification of the homopolymers

The polyglycidol is a water soluble, highly hydrophilic polymer. It is a close analogue of poly(ethylene oxide). However, unlike the PEO, it has reactive hydroxyl groups in the chain units, which in case of their hydrophobic modification may open the route to induce the lower critical solution temperature behaviour and allowing to control the transition point.

Already the intermediate product of the synthesis of linear glycidol polymers, the poly(ethoxy ethyl glycidyl ether) (polymer A in scheme 1) is water soluble below +10°C and precipitates when this temperature is exceeded[14, 15]. Following the route of Laschewsky[16] we have chosen the simplest hydrophobic modification of the hydroxyl group, the esterification of the polymers with acetic acid.

In the case of the homopolymers of glycidol, the degree of substitution between 30 and almost 100% was obtained (table 2) The aim was to study the relationship between the degree of substitution, the molar mass and the chain topology (linear and comb-like) and the lower critical solution temperature, for which the cloud temperature was taken as a measure.

Table 2. Thermosensivity of hydrophobically substituted homopolymers of glycidol.

Sample	Degree of esterification [%]	Cloud point [°C]
Esterified linear polyglycidol of molar mass 20 000 (PGl_L, table 1)	90	4
	63	33
	53	49
	51	57
Esterified linear polyglycidol of molar mass 186 000 (PGl_H, table 1)	66	41
	55	55
	45	>100
Esterified comb-like polyglycidol (PGl_G, table 1)	84	10
	70	23
	50	56
	46	57

For all studied samples, the cloud point depends upon the degree of esterification. The higher the degree of substitution with the hydrophobic ester groups, the lower the transition temperature.

The degree of substitution influences the transition temperature most significantly, but the molar mass and the topology of the macromolecules is also important. For the linear samples of higher molar mass PGl_H, the cloud point at the same degree of esterification is higher then for the sample of lower molar mass PGl_L.

Although the molar mass of the comb-like polyglycidol PGl_G is four times higher than of the linear polyglycidol PGl_L, its cloud point is almost identical with the cloud point of the latter for every degree of esterification, but much lower then for the esterified high molar mass polyglycidol PGl_H. This indicates that at the same degree of esterification the comb-like macromolecules appears more hydrophobic, then the linear chains of comparable molar mass. Most likely reason is that during the esterification of the comb-like polyglycidol the outer hydroxyl groups of the branched macromolecules are esterified preferably, causing an increased concentration of the hydrophobic groups in the outer sphere. The outer sphere decides about the interaction with water.

Hydrophobic modification of the block copolymers of ethylene oxide and glycidol

The hydrophobic ester groups were introduced into the di- and triblock copolymers by esterification (tables 3 and 4).

Table 3. Composition of block copolymers of glycidol acetate (PAte) and ethylene oxide (PEO). Numbers denote number average degree of polymerisation of the blocks.

Sample	Degree of esterification [%]
PAte$_{68}$-b-PEO$_{227}$-b-PAte$_{68}$	100
PAte$_{44}$-b-PEO$_{227}$-b-PAte$_{44}$	100
PAte$_{28}$-b-PEO$_{227}$-b-PAte$_{28}$	85
PAte$_{80}$-b-PEO$_{136}$-b-PAte$_{80}$	96
PAte$_{34}$-b-PEO$_{136}$-b-PAte$_{34}$	95
PAte$_{17}$-b-PEO$_{136}$-b-PAte$_{17}$	100

The cloud point of the hydrophobically modified triblock copolymers poly(glycidol acetate)–block–poly(ethylene oxide)–block–poly(glycidol acetate) may be varied within wide limits (Figure 1) and depends upon both the ratio of the hydrophilic (poly(ethylene oxide)) and hydrophobic (poly(glycidol acetate)) units and upon the length of the central hydrophilic PEO block (Figure 1). The shorter hydrophilic central block makes the cloud point of the copolymer less sensitive to the hydrophobic modifications: the cloud point vs degree of esterification curve for the copolymer with the longer central block lies significantly below the curve for the copolymer with shorter PEO sequences.

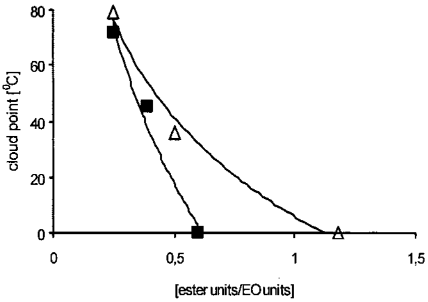


Figure 1. Cloud point vs content of acetate groups to EO units in PAte-b-PEO-b-PAte with DP$_{PEO}$=227 (■) and DP$_{PEO}$=136 (Δ).

Table 4. Polymer composition and cloud point of water solutions (5 wt%) of the diblock copolymers poly(glycidol acetate)–block–poly(ethylene oxide).

Sample	Degree of esterification [%]	Cloud point [°C]
PEO$_{113}$-b-PAte$_{40}$	100	95
PEO$_{113}$-b-PAte$_{72}$	100	95
PEO$_{113}$-b-PAte$_{110}$	95	87
PEO$_{113}$-b-PAte$_{220}$	98	Insoluble

Also the diblock copolymers, consisting of a hydrophilic poly(ethylene oxide) block and a hydrophobic poly(glycidol acetate) block are thermosensitive, their solution exhibit a cloud point due to the lower critical solution temperature (table 4). If the hydrophilic and the hydrophobic blocks are of similar length or if the hydrophilic block is longer then the hydrophobic one, the cloud point does not depend upon the copolymer composition and the cloud point is rather high, between 87 and 95°C. The probable reason is the micelle formation in water solution, which is conformed by the preliminary results of the fluorescence spectroscopy study with pyrene probe. The organization of the diblock copolymers in water solutions will be the subject of a separate study.

Conclusions

Polyglycidol, an itself highly hydrophilic polymer, may easily be transformed into a polymer exhibiting lower critical transition temperature by simple hydrophobic modification of the hydroxyl groups. After the modification temperature sensitive homo- and copolymers of glycidol are obtained. The transition point may easily be controlled within wide limits. The presence of reactive hydroxyl groups in the temperature sensitive macromolecules obtained makes further modifications possible and prospective applications possible.

Acknowledgment

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