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Hydrophilic and Amphiphilic Copolymers of 2,3-Epoxypropanol-1

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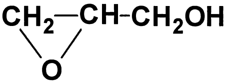
SUMMARY: Conditions for living or controlled polymerization of glycidol (2,3-epoxypropanol-1) with hydroxyl group protected via acetalization are described. Based upon these findings hydrophilic di- and triblock copolymers of glycidol and ethylene oxide were synthesized and their swelling behavior after crosslinking investigated. Initiation of the polymerization of protected glycidol with polystyrene dianion leads to amphiphilic polyglycidol-block-polystyrene-block-polyglycidol, which forms micelles in selected solvents. Termination of the living polymerization of protected glycidol with p-chloromethylstyrene yields a reactive surfactant, which stabilizes water emulsion of styrene and allows the synthesis of polystyrene microspheres.

Introduction

2,3-Epoxypropanol-1 (glycidol) **(1)** takes a special position amongst the oxiranes, as its molecule contains a hydroxyl group next to the oxirane ring. The bifunctionality of this monomer influences its behavior in the polymerization processes and the properties of obtained materials.



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Polymerization of glycidol was subject of several studies (for review, see$^{1)}$). Both the cationic$^{2)}$ and anionic$^{2)}$ polymerization of this monomer yields highly branched products of limited molecular mass and poorly defined structure, the processes are far from living and may not be properly controlled. The reason that branched products are obtained in the cationic polymerization of glycidol is the prevailing participation of the activated monomer mechanism in the chain growth$^{3,4)}$. In the anionic polymerization of glycidol the fast exchange between the alcoholates and the hydroxyl groups in the polymer chain causes strong chain branching.

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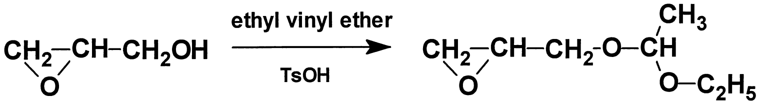
In order to obtain linear polyglycidol chains the hydroxyl group of the monomer has to be protected. Vandenberg2) used silylation or etherification of the hydroxyl group of the monomer. Spassky5) polymerized 1-ethoxy ethoxy glycidyl ether **(2)**, in this paper further referred to as glycidol acetal, obtained in the reaction of glycidol with ethyl vinyl ether:



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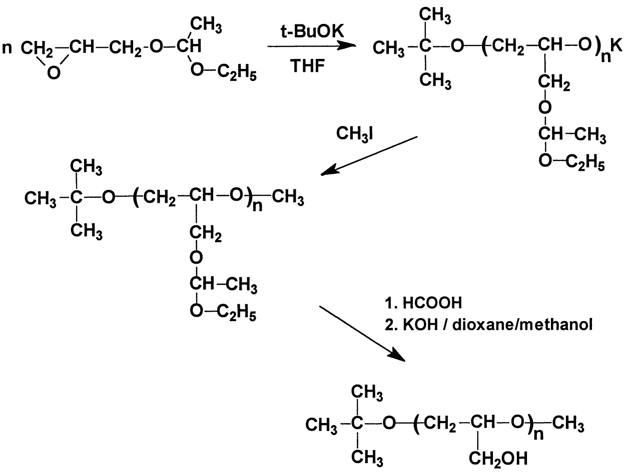
For removing the protecting group after the polymerization, he first reacted the poly(glycidol acetal) with formic acid, obtaining poly(glycidol formate) and removed the formate groups in an alkaline medium. In this way, he minimized the degradation of the polyether chains, otherwise prone to degradation under acidic condition. His method of protection and deprotection we applied in all our experiments.

The aim of this work is to find ways to polymerize protected glycidol under conditions close to living, to use such conditions for the synthesis of well defined hydrophilic and amphiphilic block copolymers containing polyglycidol blocks and for the synthesis of polyglicydol containing macromonomers.

Anionic polymerization of protected glycidol

Spassky5) described the anionic polymerization of glycidol acetal. He obtained linear polyglycidol with M_n up to 30 000. The used initiators (CsOH, KC_{24}) were not soluble in the reaction medium, which made the control of the process difficult and broadened the molecular mass distribution.

We were able to show that the initiation of the polymerization of glycidol acetal with potassium (or cesium) alcoholates in THF proceeds in a homogenous medium and may easily be controlled. After removal of the acetal group it leads to linear polyglycidol **(3)** (Fig. 1 and Table 1).



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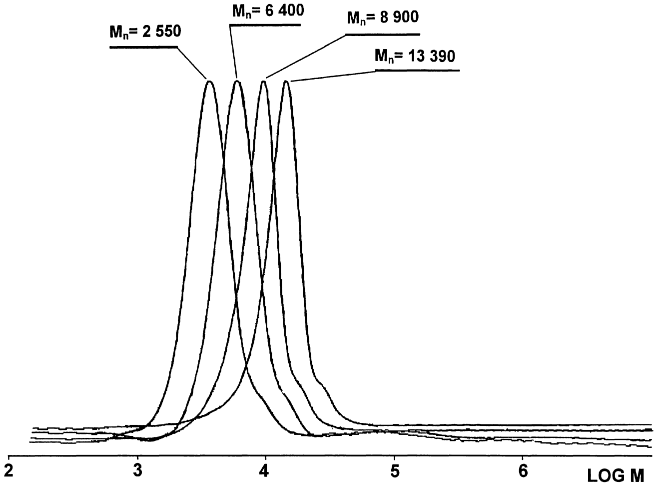


Fig. 1: GPC of poly(glycidol acetal) obtained according to (3) at different initial monomer to initiator concentrations ratio (THF, polystyrene calibration)

Table 1. Polymerization of glycidol acetal initiated with potassium t-butoxide in tetrahydrofurane. $[M]_0$, $[I]_0$ initial monomer or initiator concentrations, M_m is the molar mass of the constitutional chain unit.

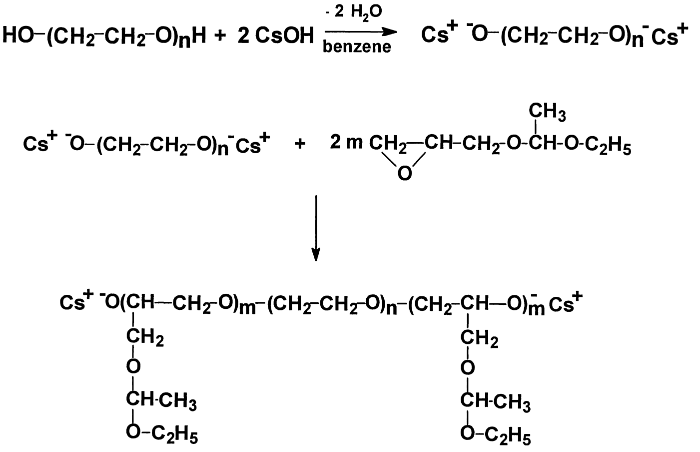
$\frac{[M]_0}{[I]_0} \times M_m$	M_n* (GPC)	M_w * (GPC)	M_w/M_n *
3 000	2 550	3 040	1.19
5 000	6 400	7 630	1.20
10 000	8 900	10 480	1.18
20 000	13 390	15 850	1.18

*) Polystyrene calibration was used for GPC.

The degree of polymerization corresponds well to the initial monomer to initiator ratio. Initiator is quantitatively incorporated into polymer chains and the molecular mass distribution is rather narrow. The process may be quantitatively terminated through addition of e.g. methyl iodide.

Hydrophilic block copolymers of glycidol and ethylene oxide

The initiation of the polymerization of glycidol acetal with alkali metal alcoholates opens the route to the synthesis of amphiphilic di- and triblock copolymers of glycidol and ethylene oxide. For this purpose, we synthesized alcoholates of poly(oxyethylene) diols **(4)** and used them to initiate the polymerization of glycidol acetal[6]:



$$HO{-}(CH_2{-}CH_2{-}O)_nH + 2\,CsOH \xrightarrow[\text{benzene}]{-2\,H_2O} Cs^+\,{}^-O{-}(CH_2{-}CH_2{-}O)_n^-\,Cs^+$$

4

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When alcoholates of monomethyl ethers of glycols are used to initiate the polymerization, diblock copolymers are obtained.

After removing the acetal group, we obtained di- and triblock copolymers containing poly(oxyethylene) blocks from 45 to 230 units and polyglycidol blocks from 25 to 150 units. These polymers are strongly hydrophilic. The hydroxyl side groups in these chains may be used for crosslinking, yielding gels. After crosslinking with glutaric aldehyde gels swell strongly in water and in lower alcohols (see Table 2, for comparison, data on swelling of poly(vinyl alcohol) crosslinked under the same conditions are also shown). The degree of swelling in water is significantly higher than in methanol, which indicates that such materials may be of potential use for water – alcohol separation.

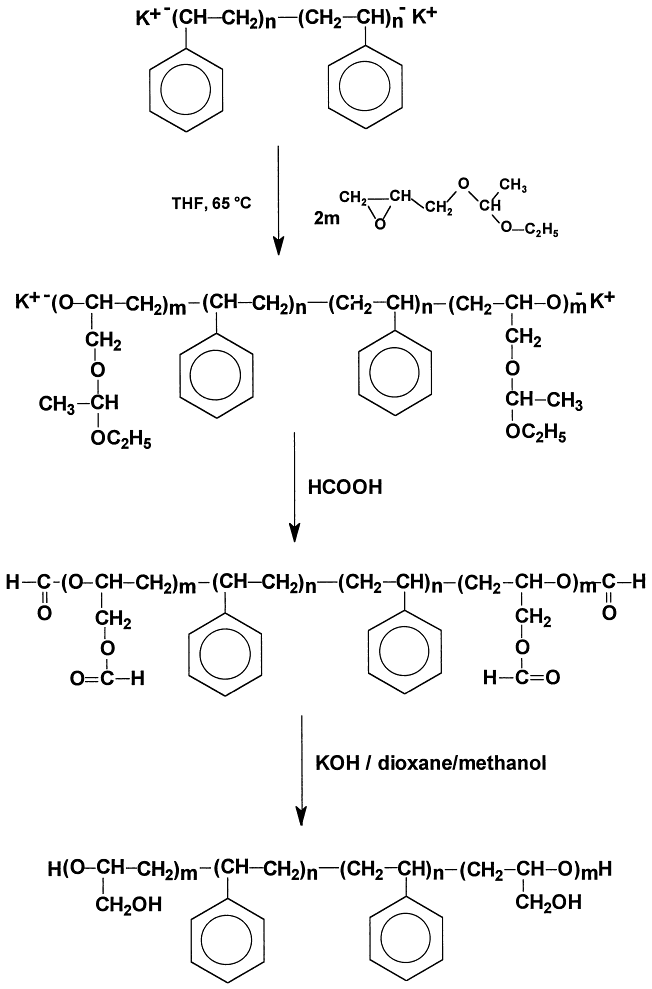
Table 2. Equilibrium swelling degree of polyglycidol – block – poly(ethylene oxide) – block – polyglycidol in water and in methanol[6)]

Block copolymer	Equilibrium swelling degree [%]	
$DP_{glycidol}$-DP_{EO}-$DP_{glycidol}$*)	In water	In methanol
27-227-27	3,084	860
27-136-27	1,152	415
68-227-68	990	305
27-45-27	731	210
Polyglycidol	664	173
68-45-68	425	140
68-136-68	433	112
Poly(vinyl alcohol)	39	28

[*)] Number average degree of polymerization of individual blocks in the block copolymer

Amphiphilic block copolymers of styrene and glycidol

It is known that the anionic polymerization of styrene approaches very well the living conditions. When the polymerization is initiated with potassium naphthalenide, a macromolecular polystyrene dianion is generated[7)]. Carbanions are capable to initiate the polymerization of oxiranes. This makes possible to synthesize triblock copolymers of glycidol and styrene**(6)**.



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The polymerization of styrene is first initiated at -80 °C with potassium naphthalenide. To the living system glycidol acetal is added, which leads to the formation of triblock copolymers. After deprotection block copolymers **(7)** are obtained, containing the middle polystyrene block of DP from 280 to 770, flanked with two hydroxypolyether chains of DP from 80 to 250.

These block copolymers contain a lipophilic central block and two strongly hydrophilic polyglycidol side chains. The amphiphilic character of such copolymers causes their micellization in some solvents, observed both for polyglycidol copolymers and its much better soluble formates, as evidenced by the ^1H NMR spectra (Fig. 6).

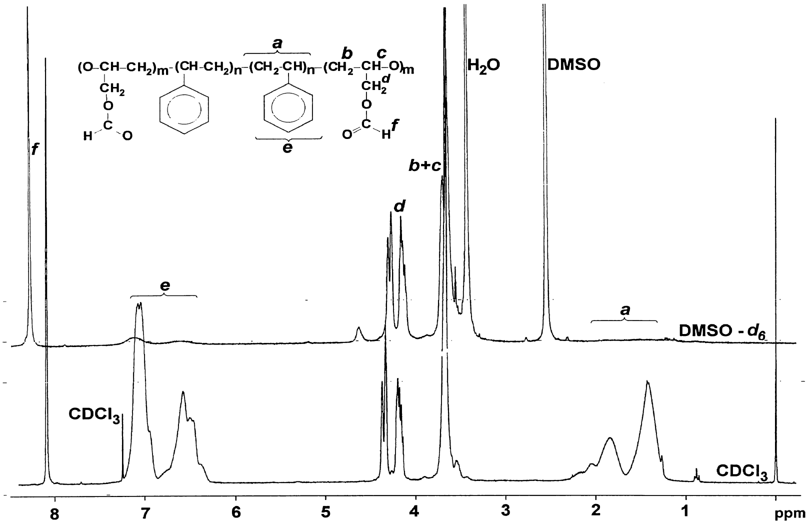
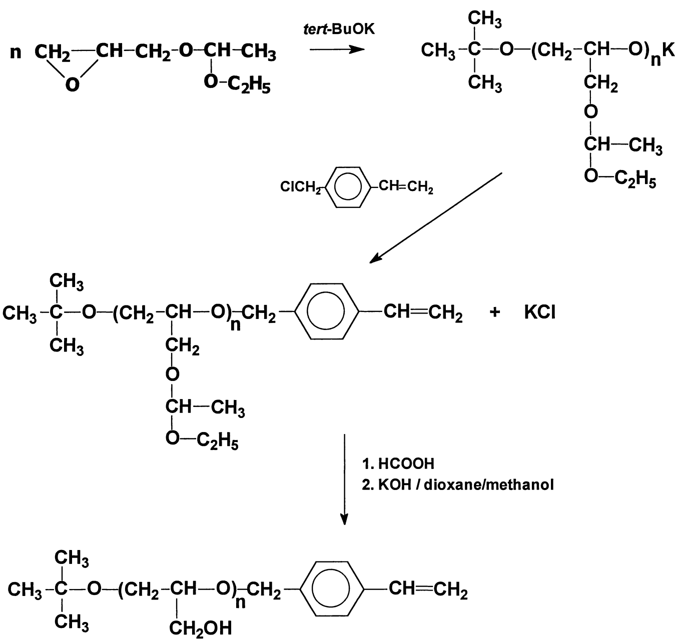


Fig. 2: ^{1}H NMR spectra of block copolymers **(6)** in DMSO and in $CDCl_3$.

Chloroform is a good solvent for both polyether and polystyrene blocks. In the ^{1}H NMR spectra of block copolymers in this solvent the signals originating from both blocks are observed. DMSO however is a good solvent only for the polyether blocks, not for the polystyrene. Although the solution appears homogeneous, in the ^{1}H NMR spectra of block copolymers in these solvent the signals of the polystyrene blocks disappear. This is due to the formation of micelles. The central polystyrene blocks aggregate inside of micelles, which are kept in solution by the polyether chains in the outer sphere of micelles. The crowding of the polystyrene blocks in the micelles shortens the spin-lattice relaxation times of protons and broadens the lines so that they almost cannot be observed by high resolution NMR.

Reactive surfactant based upon polyglycidol

The living character of the polymerization of glycidol acetal initiated with alkali metal alcoholates makes the synthesis of a reactive macromonomer via the termination method possible. To achieve this, the polymerization of glycidol acetal was initiated with potassium butoxide and the active centers were reacted with p-chloromethyl styrene$^{8)}$:



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After removal of the protecting group, the structure of the products was documented by GPC, ^{1}H NMR and MALDI-TOF. Styrene terminated polyglycidol chains with the degree of polymerization from 10 to 50 and M_w/M_n not exceeding 1.2 were obtained.

These macromonomers contain strongly hydrophilic polyglycidol chains, terminated with lipophilic, polymerizable styrene unit. The homopolymerization of these macromonomers was not attempted, however, they stabilize water emulsion of styrene and are built into the polystyrene chains under the conditions of emulsion copolymerization (Table 3).

The radical emulsion copolymerization of poly(α-t-butoxy-ω-styryl-glycidol) with styrene leads to high molecular weight copolymers of rather broad molecular mass distribution. The titration according to ASTM 2880 allows to determine the hydroxyl group content in the copolymers and evidences that most of the macromonomer is incorporated into the copolymer chains.

Table 3. Copolymerization of the macromonomer **(8)** with styrene (water emulsion, $Na_2S_2O_8$)[8)]

Macromonomer			Copolymer		
M_n	Concentration in feed [weight-%]	Yield [%]	M_n	M_w/M_n	Macromonomer conversion [%]
2 800	10	89	730 000	3.8	62
2 800	5	70	810 000	3.6	75
2 800	1	80	590 000	4.1	80
2 800	0.6	65	720 000	3.7	**
3 400	5	80	810 000	3.7	81
3 400	1	75	645 000	3.7	85
3 400	0.6	60	740 000	4.1	**

**) not determined

Reactive surfactants (surfmers) are useful stabilizers for the emulsion polymerization systems, as they do not need to be removed from the obtained material. The amphiphilic character of the described macromonomer allows to apply it for the synthesis of the polystyrene microspheres. Under proper conditions, the copolymerization of this macromonomer with styrene leads to microspheres (Fig. 3) of the diameter in the micron range and rather uniform size distribution*).

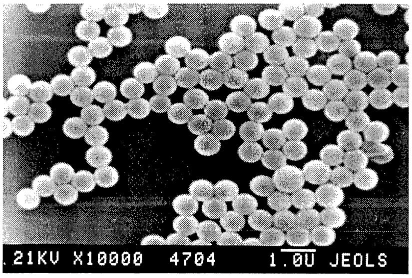

Fig. 3: SEM of styrene microspeheres obtained with polyglycidol surfmer, M_n surfmer 3000, weight ratio surfmer : styrene 1 : 100

The macromonomer stabilizes the styrene micelles in the emulsion polymerization. The macromonomer chains are due to their hydrophilic character expelled from the inside of the styrene micelles and accumulate on the outer surface. This causes that the microspheres obtained are enriched with OH groups on the surface, as evidenced by the ESCA measurements. The hydroxyl enriched surface may be used for modification reactions (medical diagnostics).

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*) The study of the microspheres was carried out together with T. Basizska and S. Slomkowski, Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Lódz, Poland

Conclusions

Proper choice of conditions makes the synthesis of homo- and block copolymers of 2,3-epoxypropanol of well controlled structure possible and opens the route to new hydrophilic and amphiphilic materials.

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