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Title: Anionic ring-opening copolymerization of styrene oxide with monosubstituted oxiranes: analysis of composition of prepared new copolyether-diols by MALDI-TOF mass spectrometry

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Introduction

Polyether-polyols are the most important group of polyols for synthesis of polyurethanes, which represent about 80% of the total oligo-polyols production [1, 2]. The functionality of an oligo-polyol for elastic polyurethane is 2–3 hydroxyl groups/mol. Polyether-polyols are obtained by the polymerization of oxiranes, such as ethylene oxide (EO), propylene oxide (PO) and 1,2-butylene oxide (BO). Polymerization is carried out in bulk at elevated temperature and pressure in the presence of starter/catalyst systems. The most important starters used for the synthesis of oligo-polyols for elastic polyurethanes are water, ethylene glycol, diethylene glycol, 1,2-propylene glycol, dipropylene glycol and glycerol [1]. The catalysts utilized for polymerization belong to anionic (alkali metal hydroxides) [3], cationic (Lewis acids and Brønsted super acids) [4–6], coordinative groups (aluminum and zinc alkyls and alkoxides, titanium alkoxides [7–9] and also dimetallic catalysts (DMC) can be used [10].

The most important system used industrially for the synthesis of polyether-diols with high molar masses is KOH and 1,2-propylene glycol [1]. The second system is the group of dimetallic catalysts based on a nonstoichiometric complex of $Zn_3[Co(CN)_6]_3 \cdot ZnCl_2$ with various ligands [10], which are 100 times more active than KOH. The polyether-diols are used especially for polyurethane elastomers, coating adhesives and sealants [11, 12]. The most popular classes of such polymers are PPO-diols ($M_n=400-4000$), block copolymers PO-EO with terminal PEO blocks ($M_n=2000-4000$), block copolymers PO-EO with internal PEO block ($M_n=2000-4000$) and random copolymers PO-EO ($M_n=2000-4000$). ^{13}C NMR spectra of homopolymers and block and random linear copolymers PO-EO have been studied [13, 14]. In the earlier studies [11] the monomer sequence was elucidated at the diad level. Then, triad sequence has been unequivocally identified, including the effects of stereoisomerism [14]. The second commonly used class of polyether-polyols are the polyether-triols which are applied in flexible polyurethane foams fabrication. The majority of technologically important polyether-triols are copolymers PO-EO. Random copolymers are used in continuous slabstock flexible foams and block copolymers PO-EO with terminal PEO block used in molded foams [1]. The high M_n polyether-triols, i.e., PO-EO copolymers, being the largest part of industrial production, are synthesized by polymerization of PO and/or EO initiated by eluent [1]. To modify the properties of the polyol component, copolymers are widely synthesized using anionic ring-opening copolymerization for propylene oxide and glycidol [15, 16], propylene oxide and N,N-diethyl glycidyl amine [17], ethylene oxide and sulfonamide-activated aziridines [18] or ethylene oxide or butylene oxide with glycerol [19]. Also cationic ring-opening copolymerization can be performed [20]. In the literature, there are reports concerning performing of ROP of other oxirane-ring-based monomers like styrene oxide [21], cyclohexane oxide [22] or ethoxyethyl glycidyl ether (EEGE) and isopropylidene glyceryl glycidyl ether (IGG) [23]. It is known that homopolymerization of styrene oxide in ROP either cationic or anionic leads to low molecular mass oligomers, accompanied by higher temperature and longer polymerization time [21].

In the present work, we decided to synthesize new copolymers, i.e., random SO-oxirane copolyether-diols [where SO denotes styrene oxide and oxirane was PO, isopropyl glycidyl ether (IPGE) or allyl glycidyl ether (AGE)] and analyze their composition. The novelty of the work is the use of monopotassium salt of dipropylene glycol activated by 18-crown-6 complexing agent as initiator. Also new copolymers are synthesized, which can be interesting as substrates for synthesis of new thermoplastic polyurethanes. All reactions, i.e., synthesis of initiator and copolymerization, were carried out in tetrahydrofuran solution at room temperature and normal pressure. The products obtained were characterized by use of SEC, ^{13}C NMR and MALDI-TOF techniques.

Experimental

Materials

Monomers, i.e., propylene oxide, styrene oxide, isopropyl glycidyl ether and allyl glycidyl ether (all from Aldrich), were dried over CaH_2 and distilled at 306 K (33 °C), 467 K (194 °C), 414 K (131 °C), 427 K (154 °C), respectively. Anhydrous tetrahydrofuran (THF) (Acros Organics) was kept over CaH_2 and distilled at 339 K (66 °C) prior to use. Potassium hydride (KH) (Aldrich) was purified according to the procedure described by Brown [24]. Dipropylene glycol (Aldrich) and 18-crown-6 (18C6) (Merck) and were used without purification.

Synthesis

All syntheses were carried out at room temperature in a 50 cm³ reactor equipped with a magnetic stirrer and a Teflon valve enabling substrates delivery and sampling under argon atmosphere. Monopotassium salt of dipropylene glycol was obtained in the reaction of KH with dipropylene glycol dissolved in THF. For example, potassium hydride (0.08 g, 2.0 mmol) and tetrahydrofuran (6.2 cm³) containing 18C6 (0.53 g, 2.0 mmol) were introduced into the reactor and then 0.5 mol/dm³ solution of dipropylene glycol in tetrahydrofuran (4.0 cm³) was added. The reaction mixture was then stirred during 20 min until all hydrogen (44.7 cm³) was evolved. It resulted in solution of monopotassium salt of dipropylene glycol activated by 18C6 complexing agent. That system was then used as the initiator, when the mixture of styrene oxide (4.6 cm³, 4.8 g, 40 mmol) and equimolar amount of IPGE (4.7 cm³) was introduced into the reactor and stirred to the end of copolymerization. Then, the reaction mixture was neutralized with HCl/H₂O system (0.1 mol/dm³, 50 cm³) and transferred to the separator containing chloroform (70 cm³). After 5-min shaking, two layers were obtained, i.e., inferior copolyether layer and superior layer containing water and the potassium salt. These layers were separated, and the superior layer was removed. After triple washing with distilled water, copolyether was obtained by evaporating of chloroform and water in vacuum. In the next experiments SO-PO and SO-AGE copolyethers were prepared in similar way. The concentration

of monomers during the polymerization was monitored by the 1,4-dioxane method [25]. The final conversion of monomers was ~99%, while the yields of the products were 97–99%.

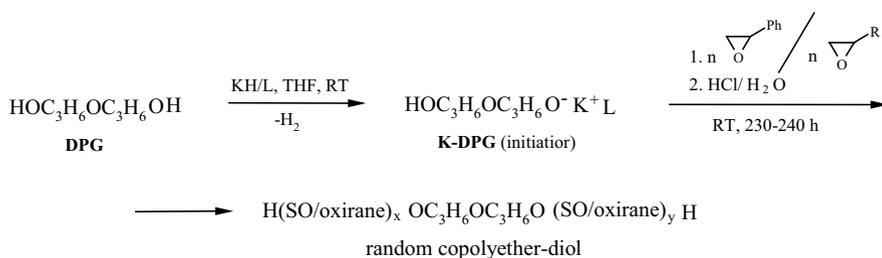
Measurements

100 MHz ^{13}C NMR spectra were recorded in CDCl_3 at 25 °C on a Bruker Avance 400 pulsed spectrometer equipped with 5 mm broad band probe and applying Waltz16 decoupling sequence. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. In order to obtain a good spectrum of the copolymer main chain exhibiting its microstructural details, about 3000 scans were satisfactory, but in order to observe the signals of the polymer chain ends more than 10,000 scans were necessary. Molar masses and dispersities of copolymers were obtained by means of size exclusion chromatography (SEC) on a Shimadzu Prominence UFLC instrument at 40 °C on a Shodex 300 mm \times 8 mm OHpac column using tetrahydrofuran as a solvent. Polystyrenes were used as calibration standards. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectra were recorded on a Shimadzu AXIMA Performance instrument. The mass spectrometer operated in linear mode. The laser power was optimized to obtain a good signal-to-noise ratio after averaging 250 single-shot spectra. Dithranol was used as a matrix (10.0 mg/mL) and polymer samples were dissolved in tetrahydrofuran (2.0 mg/mL) producing clear, homogenous solutions. By using a pipette 0.5 μL of sample solution and 0.5 μL of matrix solution were applied onto a stainless-steel target plate then air dried at room temperature for several minutes. Data were acquired in continuum mode until acceptable averaged data were obtained and were analyzed using Shimadzu Biotech Launchpad program. Resolution and accuracy of the registered spectra were 1000 and 0.5, respectively. The spectrometer mass calibration was performed upon 4 calibration points derived for peptides standards within mass range between 757.40 (standard₁: Bradykinin fragment 1–7, $M_{\text{calc}}(\text{M} + \text{H})^+ = 757.40$ Da) up to 3657.93 (standard₄: Adrenocorticotrophic Hormone Fragment 7–38 human, $M_{\text{calc}}(\text{M} + \text{H})^+ = 3657.93$ Da).

Results and discussion

Three new copolymers were prepared in this work by use of monopotassium salt of dipropylene glycol as initiator which was activated by macrocyclic ligand 18-crown-6 (K-DPG/L). In each experiment, SO was mixed with other oxirane as comonomer and introduced to initiator solution in tetrahydrofuran. It starts anionic ring-opening copolymerization, which results in random copolyether-diols (Scheme 1).

The role of ligand was activation of alkoxide center of growing chain by the formation of separated ion pairs and free ions. It resulted in increasing of the reactions rate and yield. The products obtained were analyzed by several techniques. SEC



where R: CH₃, CH₂OCH(CH₂)₂ or CH₂OCH₂CH=CH₂ and L:18C6

Scheme 1 Synthesis of initiator and copolyether-diols by ring-opening copolymerization of styrene oxide with monosubstituted oxiranes

method indicated that all copolymers are unimodal. Their characterization is presented in Table 1.

¹³C NMR analysis of copolymers reveals strong signals of carbons present in polymer chains (CH₂ and CH) and substituents as well as weak signals of terminal carbons. Spectrum of exemplary copolymer (1) is shown in Fig. 1. For SO/PO copolyether-diol (1) the chemical shift of signals corresponding to end group carbon (δ_{CH(R)OH}) is at 73.0, 65.0 and 67.1. The chemical shifts of respective signals for SO/IPGE copolyether-diol (2) and SO/AGE copolyether-diol (3) are at 73.0; 69.8 and 73.0; 70.1.

Additionally weak signals in unsaturated region (at 136.2 and 159.7 ppm) were found for the copolymers (1)–(3). They indicated that chain transfer with SO occurred during the propagation, observed recently by us in anionic homopolymerization of SO [26], but this reaction is strongly limited. On the other hand, similar reaction with comonomers did not take place. For example, signals at 116.7 and 134.9 ppm characteristic for allyloxy group were not observed in the spectrum of copolymer (1). It is also worth noting that in the spectra of copolymers (2) and (3) weak signal of CH₃ group derived from initiator is shown at 17.3 ppm (Fig. 2). Other weak signals of terminal carbons in CH(R)OH groups derived from comonomers. It clearly indicated that propagation occurred in two directions due to cation exchange reaction (Scheme 2).

In order to determine the composition of macromolecules MALDI-TOF mass spectrometry was applied. Spectra of copolymers (1)–(3) were shown below.

Table 1 Characterization of copolyether-diols by SEC technique

No.	Copolymer	Yield (%)	Time of reaction (h)	M _{calc} ^a	M _n (sec)	M _w /M _n (sec)
1	SO/PO	99.5	240	3698.8	3500	1.18
2	SO/IPGE	99.1	230	4860.4	4500	1.19
3	SO/AGE	99.3	236	4820.0	4600	1.16

^aM_{calc} = ([SO]₀/[I]₀) · M_{SO} + ([comon.]₀/[I]₀) · M_{comon.} + M_{DPG}

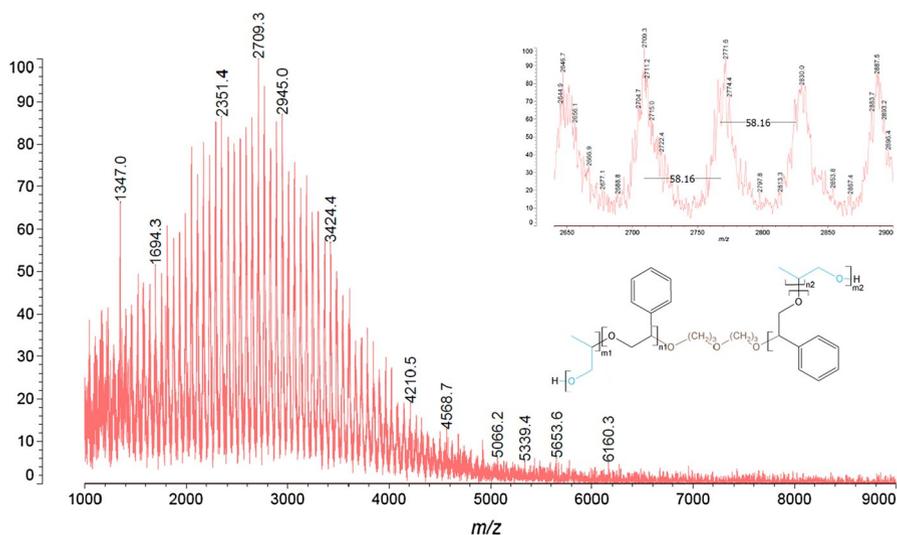


Fig. 3 MALDI-TOF spectrum of SO/PO copolyether-diol (1)

the macromolecules composition was described as $H-(PO)_{m_1}-(SO)_{n_1}-INI-(SO)_{n_2}-(PO)_{m_2}-H$, where $n_1 \neq n_2$ and $m_1 \neq m_2$.

Several signals were observed in the spectrum at m/z 1000 to 5000. Among them there are scarce signals corresponding to PSO-diols and PPO-diols homopolymers. The signal represent macromolecules containing different numbers of SO and PO mers. All macromolecules contain central part derived from initiator and form adducts with sodium ions. The main characterization data of SO/PO copolyether-diol (1) involving composition of macromolecules are presented in Table 2.

In the range of m/z 1694.3 to 3428.6, several kinds of macromolecules were identified, which contain 7 ÷ 19 mers of SO and different PO mers (9 ÷ 20), for example, macromolecules containing 10 mers of SO and 10 ÷ 16 mers of PO (no4, Table 2), macromolecules with 18 mers of SO and 10 ÷ 18 mers of PO (no12, Table 2). In general, in analyzed m/z range with increasing number of SO mers in the macromolecules chains numbers of PO mers decreased. The most abundant signals represent sodium adducts of macromolecules with following composition: $SO_{14}PO_{15}$ (no8, Table 2), SO_9PO_{16} and SO_9PO_{13} (no3, Table 2).

Similar results were obtained for other systems (Figs. 4, 5 and Table 4, respectively). Next to the spectrum of each copolymers, one of the possible structure of the macromolecules chains is presented, which originates from incorporation of both SO ($M_{mer}=120.1$) and either IPGE ($M_{mer}=116.1$) (Fig. 4) or AGE ($M_{mer}=114.1$) (Fig. 5) mers. The general scheme of the macromolecules composition was described as $H-(IPGE)_{m_1}-(SO)_{n_1}-INI-(SO)_{n_2}-(IPGE)_{m_2}-H$ for SO/IPGE copolyether-diol (2) and $H-(AGE)_{m_1}-(SO)_{n_1}-INI-(SO)_{n_2}-(AGE)_{m_2}-H$ for SO/AGE copolyether-diol (3).

In the spectrum of SO/IPGE copolyether-diol (2) at m/z 1000 to 5500, no signals of homopolymers, i.e., PSO-diols or PIPGE-diols were observed. The signals

Table 2 Composition of copolyether-diols formed in SO/PO copolymerization initiated with K-DPG/18C6

No.	Formula ^a	Number of PO mers (n) and intensities of the main signals (> 40%) ^b	Signals of highest intensity (> 40%) ^c		
			<i>m/z</i> (MALDI-TOF)	<i>m/z</i> (calc)	SO/PO (mol-%/ mol-%)
1	SO ₇ PO _n	12 (46.9),	1694.3	1695.2	37/63
		14 (68.8)	1811.1	1811.3	33/67
2	SO ₈ PO _n	15, 16			
3	SO ₉ PO _n	11, 12, 13 (88.4),	1992.8	1993.5	41/59
		14 (42.0),	2051.3	2051.6	39/61
		16 (98.0), 19	2166.4	2167.8	36/64
4	SO ₁₀ PO _n	10, 12 (59.8),	2055.2	2055.6	45/55
		13 (44.5), 15, 16	2113.0	2113.7	43/57
5	SO ₁₁ PO _n	10, 12 (61.5), 13–16	2175.1	2175.2	48/52
6	SO ₁₂ PO _n	12, 13, 16 (70.5), 17, 18, 19	2527.6	2528.3	43/57
7	SO ₁₃ PO _n	9, 11–13, 15–17,	2765.8	2764.6	42/58
		18 (64.0), 19, 20			
8	SO ₁₄ PO _n	11, 14, 15 (100), 16–19	2709.3	2709.8	48/52
9	SO ₁₅ PO _n	10, 12–14, 16, 17	2945.0	2946.8	
10	SO ₁₆ PO _n	10, 11, 15, 16 (85.1), 17 (68.3), 20	2945.0	2946.3	50/50
			3066.5	3066.9	48/52
11	SO ₁₇ PO _n	14–19 (80.4)	3303.8	3303.2	47/53
12	SO ₁₈ PO _n	10 (58.8), 13–18	2890.1	2890.7	64/36
13	SO ₁₉ PO _n	10, 14, 17 (45.7)	3428.6	3428.0	53/47

^aCentral fragment –OC₃H₆OC₃H₆O– derived from initiator as well as two end H–atoms and Na⁺ were omitted

^bSignals intensities of other macromolecules are 10 ÷ 40%

^cFor most abundant signal in the group

represent copolyether-diols which form adducts with sodium ions. Characterization data of macromolecules describing their composition are shown in Table 3. In the range of *m/z* 983.4 to 5016.1, a number of macromolecules were identified, which contain 4 ÷ 17 mers of SO and 3 ÷ 17 mers of IPGE.

In general, in analyzed *m/z* range with increasing number of SO mers in the macromolecules chains numbers of IPGE mers decreased. For instance, macromolecules with 6 mers of SO contain 6 ÷ 12 mers of IPGE (no3, Table 3), whereas macromolecules with 17 mers of SO contain 10 ÷ 14 mers of IPGE (no14, Table 3). Signals of the most intensities represent sodium adducts of SO₁₂IPGE₁₃ (no9, Table 3), SO₁₄IPGE₁₄ (no11, Table 3) and SO₁₅IPGE₁₃ (no12, Table 3) macromolecules.

Several signals were shown in the spectrum of SO/AGE copolyether-diol (3) in the range of *m/z* from 1500 to 5500. Most signals represent copolyether-diols, which form adducts with sodium ions. Sare signals of homopolymers, i.e.,

Table 3 Composition of copolyether –diols formed in SO/IPGE copolymerization initiated with K-DPG/18C6

No.	Formula ^a	Number of PO mers (n) and intensities of the main signals (> 40%) ^b	Signals of highest intensity (> 40%) ^c		
			<i>m/z</i> (MALDI-TOF)	<i>m/z</i> (calc)	SO/IPGE (mol-%/ mol-%)
1	SO ₄ IPGE _n	3, 9			
2	SO ₅ IPGE _n	7–11			
3	SO ₆ IPGE _n	6, 7, 9, 11, 12			
4	SO ₇ IPGE _n	3, 10 (48.2), 12 (42.3), 14	2160.0 2392.2	2159.8 2392.2	41/59 37/63
5	SO ₈ IPGE _n	7, 8, 9, 10 (44.3), 12, 13, 15	2279.4	2280.1	44/56
6	SO ₉ IPGE _n	9, 10 (41.7), 11, 13, 14 (41.9), 15	2400.1 2864.4	2400.1 2864.8	47/53 39/61
7	SO ₁₀ IPGE _n	7, 8, 10 (51.8), 12 (70.0) 13, 15 (64.6)	2520.2 3100.3 2753.5	2520.3 3101.1 2752.3	50/50 40/60 45/55
8	SO ₁₁ IPGE _n	9, 10, 11, 12 (51.0), 13 (71.8), 14 (48.3), 16 (55.2), 17	2872.5 2989.9 3104.8 3337.5	2872.1 2988.6 3105.1 3337.4	48/52 46/54 44/56 41/59
9	SO ₁₂ IPGE _n	8–12, 13 (100) 14, 15, 17	3109.1	3110.1	48/52
10	SO ₁₃ IPGE _n	8, 12, 13, 16, 17 (42.1)	3694.1	3693.9	43/57
11	SO ₁₄ IPGE _n	9, 13, 14 (68.8), 17 (52.6)	3465.0 3815.5	3465.5 3814.0	50/50 45/55
12	SO ₁₅ IPGE _n	11, 12, 13 (79.2)	3471.3	3469.0	53/47
13	SO ₁₆ IPGE _n	9, 16 (45.2)	3938.8	3939.6	50/50
14	SO ₁₇ IPGE _n	10, 11 (60.0), 14	3477.1	3477.4	61/39

^aCentral fragment –OC₃H₆OC₃H₆O– derived from initiator as well as two end H-atoms and Na⁺ were omitted

^bSignals intensities of other macromolecules are 10 ÷ 40%

^cFor most abundant signal in the group

Table 4), whereas macromolecules with 17 mers of SO contain 11 and 13 mers of AGE (no11, Table 4). The most abundant signals represent sodium adducts of macromolecules with the following formulas SO₁₃AGE₁₅, SO₁₁AGE₁₄ and SO₁₆AGE₁₇.

Summarizing, styrene oxide easily polymerizes with other oxiranes, as propylene oxide, isopropyl glycidyl ether or allyl glycidyl ether giving random copolyether-diols after protonation. The product consists of macromolecules with various composition. They could be useful for synthesis of new thermoplastic polyurethanes.

Table 4 Composition of copolyether –diols formed in SO/AGE copolymerization initiated with K-DPG/18C6

No.	Formula ^a	Number of PO mers (n) and intensities of the main signals (>40%) ^b	Signals of highest intensity (>40%) ^c		
			<i>m/z</i> (MALDI-TOF)	<i>m/z</i> (calc)	SO/IPGE (mol-%/mol-%)
1	SO ₇ AGE _n	12, 13, 16			
2	SO ₈ AGE _n	10–16, 18			
3	SO ₉ AGE _n	9, 12, 14–17			
4	SO ₁₀ AGE _n	12, 14 (66.6),	2955.3	2956.6	42/58
		15 (48.3), 16–18	3068.3	3069.4	40/60
5	SO ₁₁ AGE _n	9, 10, 12, 14 (71.3),	3075.6	3076.8	44/56
		15 (60.2), 16–18	3189.6	3189.5	42/58
6	SO ₁₂ AGE _n	11 (56.6)	2852.9	2854.5	52/48
		13 (65.0),	3081.7	3082.8	48/52
		14 (72.7), 15, 16, 18, 19	3195.2	3196.9	46/54
7	SO ₁₃ AGE _n	11, 12, 14, 15 (100) 19	3428.7	3429.5	46/54
8	SO ₁₄ AGE _n	10–12, 13 (50.5), 15	3322.0	3323.1	52/48
		19 (45.6)	4006.5	4007.9	42/58
9	SO ₁₅ AGE _n	10, 12, 15, 16 (80.5) 17	3782.4	3783.1	50/50
10	SO ₁₆ AGE _n	12, 17 (65.3), 19	4016.6	4017.2	48/52
11	SO ₁₇ AGE _n	11, 13			
12	SO ₁₈ AGE _n	13, 14			

^aCentral fragment –OC₃H₆OC₃H₆O– derived from initiator as well as two end H–atoms and Na⁺ were omitted

^bSignals intensities of other macromolecules are 10 ÷ 40%

^cFor most abundant signal in the group

Conclusions

Monopotassium salt of dipropylene glycol activated by coronand 18C6 in THF solution at room temperature effectively initiates random copolymerization of styrene oxide and propylene oxide, isopropyl glycidyl ether or allyl glycidyl ether. The main features of these processes are:

- All synthesized copolyether-diols are unimodal and have relatively low dispersity ($M_w/M_n = 1.16–1.19$). This value is close to the dispersities derived for catalyzed ring-opening homopolymerization of SO (1.06–1.14) [21].
- Mainly copolymers were synthesized in the reaction course with spare homopolymers chains formed during the studied processes.
- Chain transfer reaction with monomer occurs exclusively for styrene oxide, leading to very low unsaturation.
- Propagation occurs in two directions due to cation exchange reaction.

- MALDI-TOF technique allows to determine composition of copolyether-diols obtained; exemplary SO/AGE system contain several macromolecules with 7–18 mers of SO and 9–19 mers of AGE; in general, with increasing number of SO mers in the macromolecules chains numbers of AGE mers decreased.
- The products obtained could be interesting as substrates for synthesis of new thermoplastic polyurethanes.

Compliance with ethical standards

Conflict of Interest The authors declare that there is no known conflict of interest concerning the given work.

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