

Ring opening polymerization of styrene oxide initiated with potassium alkoxides and hydroxyalkoxides activated by 18-crown-6: determination of mechanism and preparation of new polyether-polyols

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Abstract It was stated that initiation in ring opening polymerization of styrene oxide depends on the kind of potassium alkoxide activated by 18-crown-6 used. In the presence of potassium methoxide the oxirane ring opening occurs exclusively in the β -position and not in the β or α position, i.e., contrary to the previous data. A similar result was obtained in the systems initiated with potassium *t*-butoxide, 2-methylpropoxide and 1-phenylethoxide. Unexpectedly, potassium *i*-propoxide and 1-methylpropoxide open the oxirane ring in the β or α position. In all polymerizations, deprotonation of methine group in the monomer takes place under the influence of the initiator and in chain transfer reaction to the monomer. It leads to the formation of macromolecules with unsaturated starting group. However, deprotonation of methylene group in the monomer does not occur. Applying of potassium hydroxyalkoxides, i.e., monopotassium salt of dipropylene glycol or tripotassium salt of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol it was possible to synthesize PSO-diols and PSO-pentols without unsaturation. Molar masses of polymers ($M_n = 1700\text{--}4800$ Da) are much higher than reported in literature for other anionic systems. Dispersity of polymers is rather low ($M_w/M_n = 1.07\text{--}1.15$) indicating relatively high rate of initiation and cation exchange reaction.

Keywords ROP · Oxiranes anionic polymerization · Styrene oxide · Potassium alkoxides · Polyether-polyols

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Introduction

The literature data dedicated to anionic ring opening polymerization of styrene oxide (SO) are rather scarce [1–6]. The papers present the course of the process mediated with sodium [4] or potassium methoxide [2, 3]. It was reported that these compounds open the oxirane ring in the SO molecule in two positions, i.e., α or β , the latter even prevails ($\sim 67\%$) during initiation of the polymerization. However, during propagation the oxirane ring opens exclusively in the β -position. The side reactions, i.e., chain transfer to the monomer involving deprotonation of methylene and methine groups in SO molecule lead to the formation of two kinds of potassium enolates [2]. Potassium hydride was then used for SO polymerization [5]; however, the course of the process was not proposed. Molar masses of PSOs obtained with mentioned initiators were relatively low, i.e., $M_n = 980\text{--}2900$ Da. Finally, cyclic oligo(potassium glycidoxide)s with three or six alkoxide groups activated by coronand 18-crown-6 (18C6) were also applied as macroinitiators for the ROP of SO [6]. Star-shaped polyether-polyols with $M_n = 8000$ Da were prepared in this way.

It is well known [7] that crown ethers can form stable complexes with metal cations when the size of the crown ether cavity matches that of the cation (Scheme 1). This complexation leads to a considerable increase in the degree of ion-pair separation. In the anionic polymerization of propylene oxide and other oxiranes complexation of the cation causes a marked activating effect. As a result one observes positive impact on reaction rate, lower unsaturation level in the polymer [8] and higher yield of the final product [9].

Styrene oxide was polymerized recently with the use of different tin catalysts [10], rare earth coordination catalysts [11] or with acid-exchanged montmorillonite clay [12]. Poly(styrene oxide) can be used as drug carriers [13]. Polystyrene oxide–polyethylene oxide (PSO–PEO) block copolymers were used in the design of efficient nanocarriers for cancer chemotherapy [14, 15]. Based on PSO–PEO triblock copolymers were synthesized. It produced the drug-loaded micelles and their drug release profiles were analyzed for the anticancer drug, doxorubicin (DOXO) [15]. PSO was also used for production of polystyrene carbonate [16].

The aim of this work was reinvestigation of SO ROP course in the presence of potassium alkoxides as well as preparation and characterization of new PSO-polyols. Several initiators activated by 18C6 were chosen for the study, i.e., potassium methoxide, potassium *i*-propoxide, potassium *t*-butoxide, potassium 1-methylpropoxide, potassium 2-methylpropoxide, potassium 1-phenylethoxide, monopotassium salt of dipropylene glycol as well as tripotassium salt of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol. The polymers obtained by use of hydroxyalkoxides are especially interesting, because they possess several OH terminal groups after hydrolysis and can be used as potential macromonomers for synthesis



Scheme 1 Synthesis of potassium alkoxide in the presence of 18-crown-6 complexing agent

of new polyurethanes, used in the production of mattresses and also in the furniture industry, automotive industry, building industry and for special applications, for example, medicine. Preparation of the initiators as well as polymerizations were carried out in mild conditions, i.e., in tetrahydrofuran solution at room temperature.

Experiment

Materials

Styrene oxide (Aldrich) was dried over CaH_2 and then distilled at 467 K (194 °C). Anhydrous tetrahydrofuran (THF) (Acros Organics) was kept over CaH_2 and distilled at 339 K (66 °C). Potassium hydride (KH) (Aldrich) was purified according to the procedure described by Brown [17]. A 35 wt% dispersion of KH in mineral oil (Aldrich) was mixed with *n*-pentane in a dry argon atmosphere and then decanted. It was repeated three times followed by a threefold washing with dry THF. Finally, THF was evaporated in vacuum. The KH present was determined by a standard gas law calculation of the hydrogen liberated after treatment with 2-butanol ($1.0 \text{ H}_2 = 1.0 \text{ KH}$). The resulting solution was titrated to a phenolphthalein end point. Very little excess (<1%) of total base over hydride base (from gas evolution) indicated small hydrolysis of the original KH sample. Coronand 18C6 (1,4,7,10,13,16-hexaoxacyclooctadecane) (Merck), methanol, *i*-propanol, 1-phenylethanol, 1-methylpropanol, 2-methylpropanol, dipropylene glycol, 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol and potassium *t*-butoxide in THF solution (1.0 mol/dm^3) (all from Aldrich) were used as received for synthesis without further purification.

Preparation of initiators and styrene oxide polymerization

All syntheses were performed at 20 °C in a 50 cm^3 reactor equipped with a magnetic stirrer and a Teflon valve enabling substrate delivery and sampling under argon atmosphere. Monopotassium salts were obtained in the reaction of potassium hydride with an appropriate amount of alcohol or dipropylene glycol (DPG) dissolved in THF containing 18C6 at 20 °C. The initial concentrations of the monomer were 2.0 or 5.0 mol/dm^3 and the initial concentration of the initiator was 0.1 mol/dm^3 . For example, potassium hydride (0.08 g, 2.0 mmol) and THF (15.0 cm^3) were introduced into the reactor and then 18C6 (0.53 g, 2.0 mmol) and methanol (0.064 g, 2.0 mmol) were added by use of syringe. The mixture was stirred for 1.5 h until all hydrogen (44.7 cm^3) was evolved. It resulted in a suspension of pure anhydrous potassium methoxide activated ligand in the ether solution. That system was used as the initiator, when styrene oxide (4.6 cm^3 , 3.7 g, 40 mmol) was introduced into the reactor. The reaction mixture was then stirred for several days. After almost complete conversion of the monomer the reaction mixture was neutralized with HCl/ H_2O system (0.1 mol/dm^3 , 70 cm^3) and transferred to the separator containing chloroform (70 cm^3). After shaking, two layers were formed, i.e., an inferior polyether layer and a superior layer containing

water and the potassium salt. These layers were separated and the superior layer was removed. After three washes with fresh water, polyether was obtained by chloroform and water distillation in vacuum at 100 °C.

In another experiment, tripotassium salt of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol (TKHMCH) activated by 18C6 was prepared in a similar way. The initial concentration of the monomer was 2.0 or 4.0 mol/dm³ and the initial concentration of the initiator was 0.02 mol/dm³. Potassium hydride (0.048 g, 1.2 mmol), THF (5.0 cm³) and 18C6 (0.32 g, 1.2 mmol) were introduced into the reactor. Then TKHMCH (0.088 g, 0.4 mmol) was dissolved in boiling THF (10.0 cm³) and the solution obtained was dropped into the system at 20 °C. After mixing for 1.5 h, hydrogen (26.8 cm³) was evolved. Finally, styrene oxide (4.6 cm³, 3.7 g, 40 mmol) was added and the reaction mixture was stirred for several days until complete monomer conversion. The separation of polymer obtained was performed as described previously. At the stage of shaking with the HCl/H₂O system, some additional interlayer was formed that may contain polyether with fully converted OH groups or in equilibrium with the polyether with some rest OK groups. The presence of monomer during polymerization was monitored by chromatographic method. After ending of the polymerization, all reaction mixtures were homogeneous.

Measurements

100 MHz ¹³C nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ at 25 °C on a BrukerAvance 400 pulsed spectrometer equipped with 5 mm broadband probe and applying Waltz16 decoupling sequence. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. To obtain a good spectrum of the polymer 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 polymers were obtained by means of size exclusion chromatography (SEC) on a Shimadzu Prominence UFLC instrument at 40 °C on a Shodex 300 mm × 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. Dithranol was used as a matrix. Spectrophotometer measurements were performed on the FTIR ATR device (Shimadzu IR Prestige) equipped with diamond ATR crystal purified prior to measurement with isopropanol. Data were analyzed using LabSolutions program.

Results and discussion

In the present work polymerization of styrene oxide was carried out in the presence of ether 18-crown-6. This macrocyclic ligand is frequently used for activation of alkoxide anions due to strong complexation of metal cation. It results in the formation of crown-separated ion pairs and allows maintaining a high rate of polymerization of propylene oxide at low temperature [5].

^{13}C NMR was used as the main technique for analysis of the polymers obtained in order to determine the course of ROP. In some cases MALDI-TOF was also applied as a supporting method. Due to the relatively short polymer chains of the samples, ^{13}C NMR could be eventually applied to estimate the molar masses; however, in some cases the signals of the end groups were very small and close to the noise level or overlapped with the strong signals of the backbone carbons, and due to possible side reactions, simple integration of these signals may introduce significant error; therefore, the molar masses and dispersities of the polymers were estimated by SEC chromatography.

Determination of the mechanism of SO polymerization in the presence of simple potassium alkoxides activated by 18C6

Data characterizing the polymers obtained are presented in Table 1. They involve molar masses, dispersities and unsaturation of PSOs.

Figure 1 shows the characteristic signals of ^{13}C NMR spectra for the starting groups of the polymers obtained in the presence of three initiators, i.e., potassium methoxide (Fig. 1a-**I1**), potassium *i*-propoxide (Fig. 1b-**I2**) and potassium *t*-butoxide (Fig. 1c-**I3**).

Analysis of ^{13}C NMR spectrum indicated that initiation of SO polymerization with potassium methoxide (**I1**) (Fig. 1a) occurs by a different way than it was reported in the literature [2–4]. Methyl signal of the starting group $\underline{\text{C}}\text{H}_3\text{OCH}_2\text{-CH(Ph)O-}$ (59.21 ppm) is observed in the spectrum after quenching with HCl/H₂O resulting from SO ring opening in the β -position under influence of the initiator. A hypothetical second signal of starting group $\underline{\text{C}}\text{H}_3\text{OCH(Ph)CH}_2\text{O-}$ (at about 57.0 ppm) is absent in the spectrum which eliminates the possibility of monomer ring opening also in α -position. However, such a signal was detected in the spectrum of PSO quenched with CH₃I as the signal of the end group. The results obtained clearly indicated that in the initiation as well as propagation step the oxirane ring opened exclusively in the β -position.

A similar effect was observed in the polymerization initiated with potassium *t*-butoxide (**I3**) (Fig. 1c). However, in the presence of potassium *i*-propoxide (**I2**) the oxirane ring opens in the β - or α -position ($\sim 1/1$). In ^{13}C NMR spectrum of the polymer, two signals of CH₃ group are present (Fig. 1b). We proposed that these two signals were derived from two kinds of starting *i*-propoxy groups, i.e. $(\underline{\text{C}}\text{H}_3)_2\text{-CHOCH}_2\text{CH(Ph)O-}$ (22.21 ppm) and $(\underline{\text{C}}\text{H}_3)_2\text{CHOCH(Ph)CH}_2\text{O-}$ (22.05 ppm). Further splitting only of the latter one, may be due to the closer vicinity of its methyl groups to the asymmetric carbon -CHPh- . It was interesting that replacement of one CH₃₋ group in potassium *i*-propoxide by the greater CH₃CH₂₋ group partly conserves the observed phenomenon. In the presence of potassium 1-methylpropoxide (**I5**) oxirane ring also opens in the β - or α -position ($\sim 1/0.2$). Figure 2 shows the aliphatic part of the ^{13}C NMR spectrum of PSO obtained with the mentioned initiator. According to notation in Fig. 2, the predominating signals of the starting group formed during β -opening (carbons 1, 2 and 3) may be found at 9.73, 29.07, and 19.14 ppm, respectively, while those from α -opening (carbons 4, 5 and 6) at 9.88, 32.04, and 22.10, respectively. Splitting of

Table 1 Characterization of PSOs synthesized with the use of potassium alkoxides activated by 18C6; [initiator]₀ = 0.1 mol/dm³

Polymer	Initiator	[Monomer] ₀ mol/dm ³	Macromolecules with unsaturated starting groups mol-% ^a	Yield %	M _n SEC (Da)	M _w /M _n SEC	M _n (calcd.)	Time of reaction at 20 °C (h)
P1	CH ₃ O ⁻ (K ⁺) (I1) ^b	2.0	5.1	98.0	2200	1.09	2400	230
P2	CH ₃ O ⁻ (K ⁺) (I1)	5.0	9.4	85.2	4300	1.10	6000	410
P3	(CH ₃) ₂ CHO ⁻ (K ⁺) (I2)	2.0	6.1	95.3	2000	1.12	2400	220
P4	(CH ₃) ₂ CHO ⁻ (K ⁺) (I2)	5.0	9.7	86.1	4600	1.14	6000	425
P5	(CH ₃) ₃ CO ⁻ (K ⁺) (I3)	2.0	7.5	98.3	2700	1.13	2400	215
P6	(CH ₃) ₃ CO ⁻ (K ⁺) (I3)	5.0	9.8	87.5	4800	1.15	6000	420
P7	(CH ₃) ₂ CHCH ₂ O ⁻ (K ⁺) (I4)	2.0	8.0	95.4	2400	1.07	2400	240
P8	CH ₃ CH ₂ CH(CH ₃)O ⁻ (K ⁺) (I5)	2.0	11.2	96.3	2000	1.09	2400	235
P9	PhCH(CH ₃)O ⁻ (K ⁺) (I6)	2.0	19.1	92.2	1700	1.11	2400	245

^a Unsaturation of polymers was estimated by use of ¹³C NMR^b A circle denotes 18C6

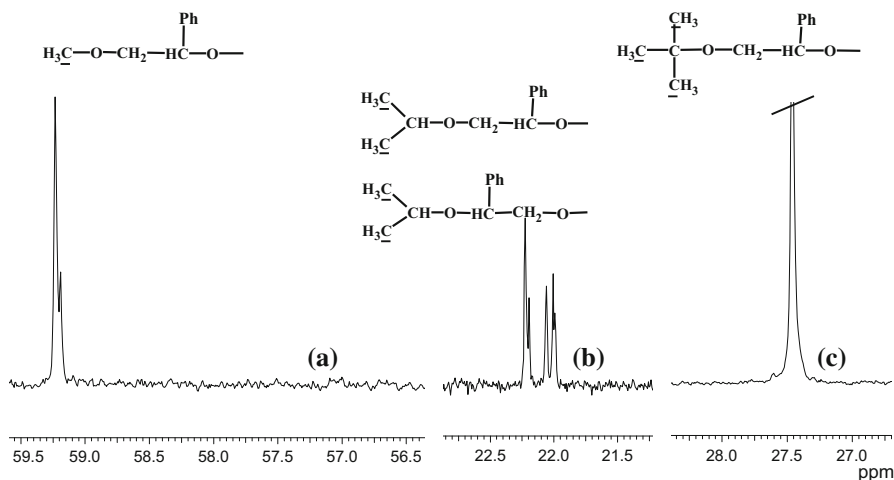


Fig. 1 Signals of methyl carbons present in starting groups of PSOs synthesized with (a) CH_3O^- (K^+) (**I1**), (b) $(\text{CH}_3)_2\text{CHO}^-$ (K^+) (**I2**), (c) $(\text{CH}_3)_3\text{CO}^-$ (K^+) (**I3**)

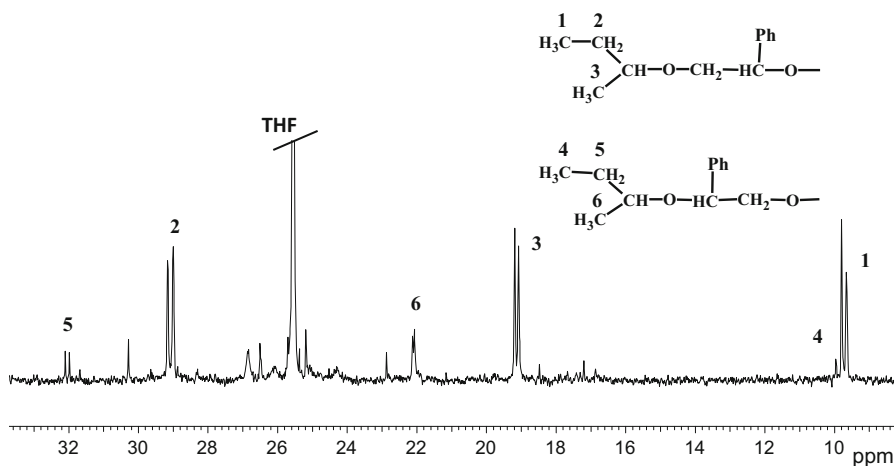


Fig. 2 Signals of methyl and methylene carbons present in starting groups of PSO (P8) synthesized with $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{O}^-$ (K^+) (**I5**)

all the mentioned signals into two lines may be due to the presence of asymmetric methine carbon in these groups as it was already observed in our earlier work on PPO [18]. The presence of additional minor signals in this region may indicate some side reactions; however, the source of these reactions is yet unknown.

However, replacement of one CH_3- group by $\text{Ph}-$ one in potassium 1-phenylethoxide (**I6**) or introduction of $-\text{CH}_2-$ group between *i*-Pr- and $-\text{O}^-$ (K^+) groups in potassium 2-methylpropoxide (**I4**) results in the ring opening during the

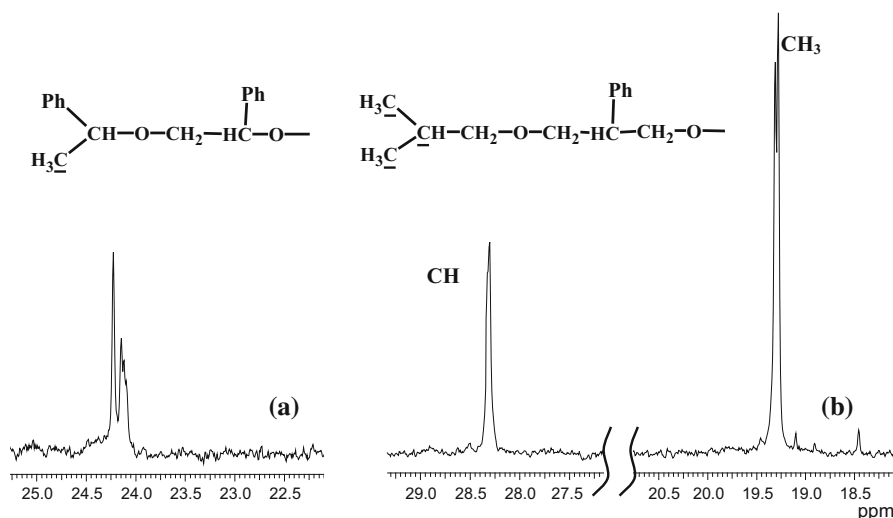


Fig. 3 Signals of methyl carbons present in starting groups of PSOs synthesized with $\text{PhCH}(\text{CH}_3)\text{O}^- (\text{K}^+)$ (**I6**)—spectrum (a—for P9) and $(\text{CH}_3)_2\text{CHCH}_2\text{O}^- (\text{K}^+)$ (**I4**)—spectrum (b—for P7)

initiation exclusively in the β -position (Fig. 3). Opening in the α -position should lead to creation of a second signal for methyl group, shifted of about 0.4 ppm but no such signal is observed (Fig. 3a).

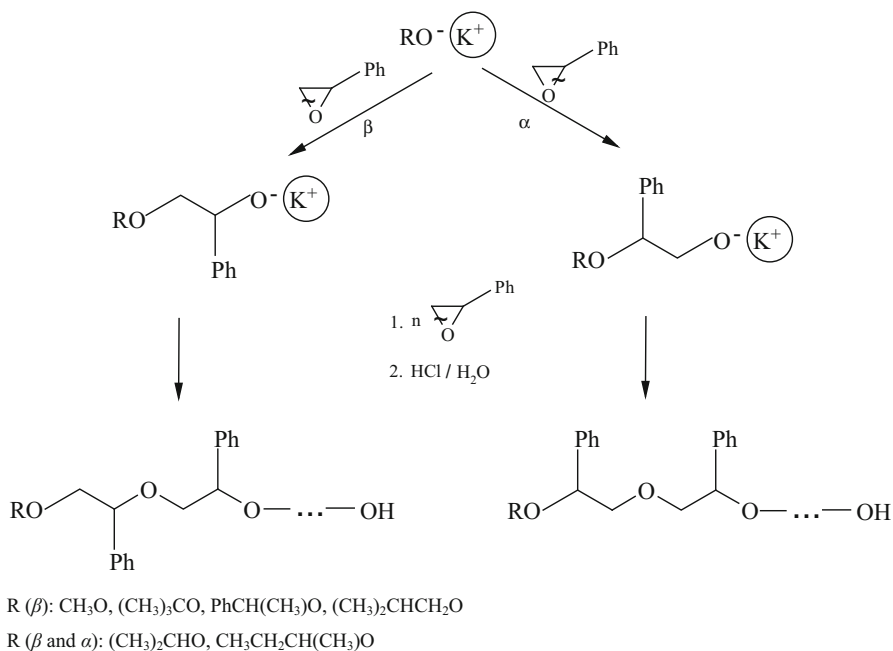
The results obtained indicate, that the structure of initiator used influences the direction of oxirane ring-opening in anionic polymerization of styrene oxide (Scheme 2).

In the unsaturated region of ^{13}C NMR spectra of the obtained polymers two weak signals were observed at 133.02 and 159.66 ppm (Fig. 4). It was proposed that these signals derived from carbons of unsaturated starting groups $\text{CH}_2=\text{C}(\text{Ph})-\text{O}-$ (quaternary carbon at 159.66 ppm). Their formation by chain transfer to the monomer was presented on Scheme 3.

This reaction proceeded by deprotonation of monomer methine group with growing chain end resulting from the presence of acidic H-atom in PhCH group. However, the lack of the signals in ^{13}C NMR spectrum at about 108 and 146 ppm of vinyl carbons in hypothetical starting group,

$\text{Ph}-\text{CH}=\text{CH}-\text{O}-$ indicated, that reported in the literature deprotonation of methylene group in SO molecule did not occur. Signal of carbonyl group was also absent in the spectrum. Unsaturation of polymers increases with initial concentration of the monomer (Table 1). Chain transfer to the monomer is responsible for this phenomenon (Scheme 2). However, unsaturation of polymers depends also on the kind of initiator used. The lowest unsaturation has PSO obtained with $\text{CH}_3\text{O}^- (\text{K}^+)$ ($\sim 5\%$), the highest one ($\sim 19\%$) exhibits polymer prepared with $\text{PhCH}(\text{CH}_3)\text{O}^- (\text{K}^+)$. It means, that the second source of unsaturation is deprotonation of the monomer by initiator.

Molar masses of synthesized polymers ($M_n = 1700\text{--}4800$ Da) are higher than those reported in the literature for polymers prepared in toluene solution at 80°C ($M_n = 980\text{--}1200$ Da) or in bulk at 100°C ($M_n = 2400\text{--}2900$ Da). Analysis of the



Scheme 2 ROP of SO initiated with potassium alkoxides activated by 18C6

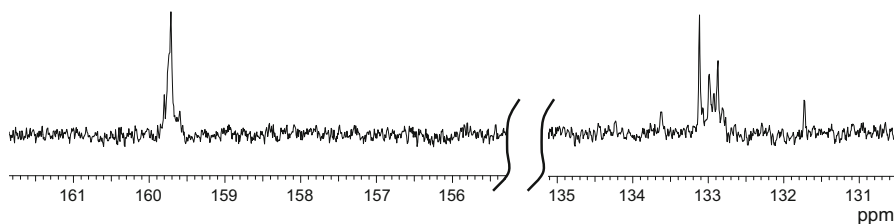


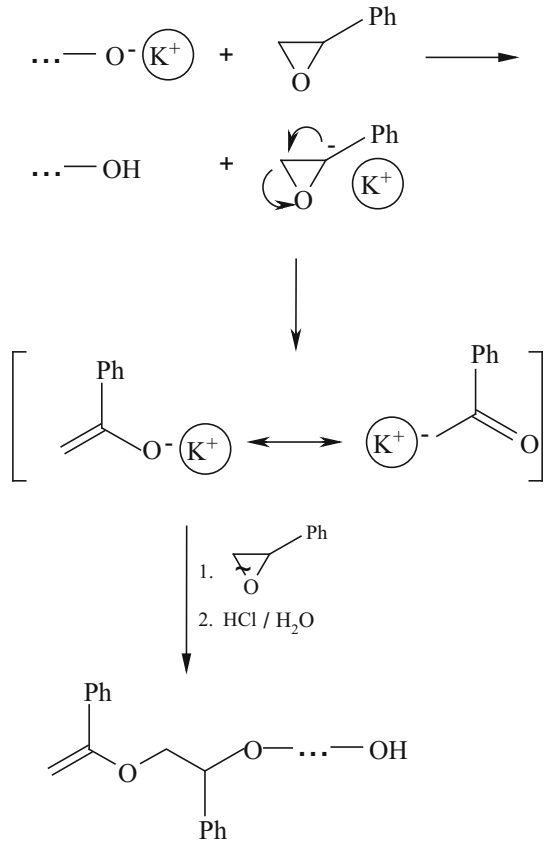
Fig. 4 Signals of unsaturated starting group present in PSOs (**13**) prepared with potassium alkoxides activated by 18C6

polymers by MALDI-TOF spectroscopy confirmed the formation of macromolecules with unsaturated starting groups. Figure 5 shows for example MALDI-TOF spectrum of PSO obtained with $(\text{CH}_3)_2\text{CHO}^-(\text{K}^+)$.

Dispersity of polymers is relatively low, i.e., $M_w/M_n = 1.07\text{--}1.15$, indicating high rate of cation exchange reaction. MALDI-TOF analysis of polymer 3 further confirmed its chemical structure (Fig. 5).

Three main series of signals were observed in the spectrum. The first series at m/z 1056.3–2133.9 represents macromolecules possessing isopropoxy starting group and OH end group. For example, signals at m/z 1178.1, 1538.7 and 1897.6 represent macromolecules containing 9, 12 and 15 mers of styrene oxide (M_n (calcd.) = 1180.6, 1541.0 and 1901.5 respectively). They form adducts with K^+

Scheme 3 Chain transfer to the monomer in SO polymerization initiated with potassium alkoxides activated by 18C6



ions. The second series at 1040.3–2117.9 represents macromolecules with the same structure, but forming adducts with Na^+ ions. However, the third series of peaks at m/z 1117.7–1839.0 represents macromolecules possessing unsaturated starting group and OH end group. They form adducts with K^+ ions. For example, signals at m/z 1239.4, 1479.8 and 1839.0 represent macromolecules containing 9, 11 and 14 mers of styrene oxide (M_n (calcd.) = 1240.6, 1480.9 and 1841.3 respectively).

Synthesis of PSO-polyols by polymerization of SO initiated with potassium hydroxyalkoxides activated by 18C6

Data concerning the PSOs with several hydroxyl end groups were presented in Table 2. They were synthesized in processes initiated with monopotassium salt of dipropylene glycol (K-DPG) (**I7**) or tripotassium salt of 2,2,6,6-tetrakis (hydroxymethyl) cyclohexanol (3K-TKHMCH) (**I8**) (Scheme 4).

Figure 6 shows ^{13}C NMR spectrum of macrodiol obtained at low initial concentration of monomer, i.e., $[\text{SO}]_0 = 2.0 \text{ mol/dm}^3$.

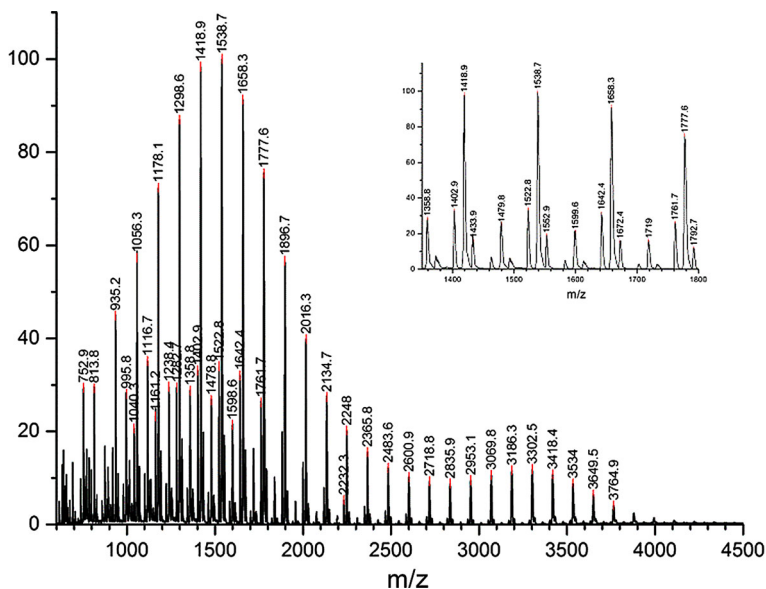
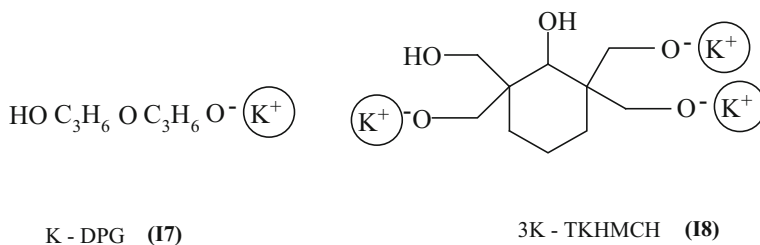


Fig. 5 MALDI-TOF spectrum of PSO-diol (P3) synthesized with the use of $(\text{CH}_3)_2\text{CHO}^- (\text{K}^+)$ (**12**) and quenched with $\text{HCl}/\text{H}_2\text{O}$

Table 2 Characterization of macrodiols and macropentols synthesized by anionic polymerization of SO initiated with potassium hydroxyalkoxides; $[\text{K-DPG}]_0 = 0.1 \text{ mol/dm}^3$; $[\text{3K-TKHMCH}]_0 = 0.02 \text{ mol/dm}^3$

Polymer	Initiator	$[\text{Monomer}]_0$ mol/dm^3	Yield %	M_n SEC [Da]	M_w/M_n SEC	M_n (Calcd.)	Time of reaction at 20°C [h]
P10	K-DPG (17)	2.0	98.8	2600	1.12	2400	450
P11	K-DPG (17)	5.0	68.1	4100	1.15	6000	520
P12	3K-TKHMCH (18)	2.0	88.1 10.3	} 2 fractions 3500 2700	1.42 1.17	12000 24000	600
P13	3K-TKHMCH (18)	4.0	22.0 42.7 20.9		} 3 fractions 5500 3000 1200		



Scheme 4 Potassium hydroxyalkoxides used for preparation of PSO-polyols-K-DPG (**17**) and 3K-TKHMCH (**18**)

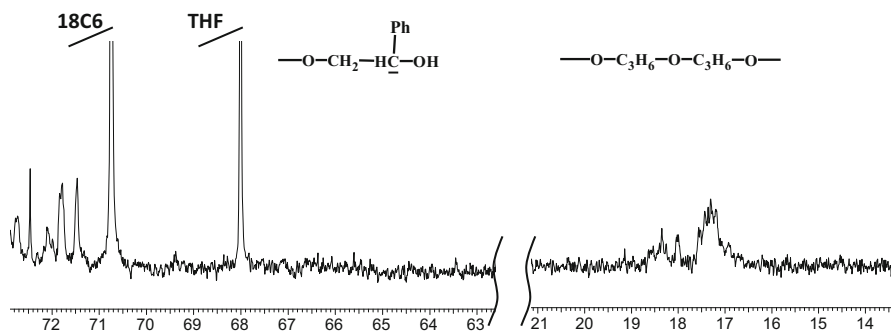


Fig. 6 ^{13}C NMR spectrum of PSO-diol (P10) derived in ROP in the presence of K-DPG (**17**) and quenched with HCl/H₂O

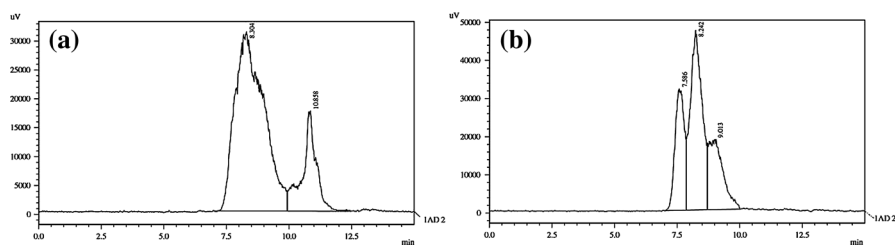


Fig. 7 SEC chromatogram for polymer 12 (p12) obtained with initiator **18** and polymer 13 (p13) obtained with initiator **18**

Signals at 17.1 ppm derived from CH_3 - groups of initiator. Signals of terminal groups $\text{CH}_2\text{CH}(\text{Ph})\text{OH}$ which should arrive at about 73.8 ppm cannot be precisely identified since they fall in the region of the strong main chain signal, nevertheless, a sharp signal at 73.65 ppm could be observed in this broad band. However, signals of starting groups derived from initiator, i.e., $-\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ which should arrive at about 66.6 ppm as well as signals of unsaturated starting groups were not observed in the spectrum.

Figure 7 presents SEC chromatogram recorded for polymer 12 (p12) obtained with initiator **18** and polymer 13 (p13) obtained with initiator **18**.

For polymer 12 (p12) two main fractions are present as the product of the synthesis, while for polymer 13 (p13) three fraction can be separated.

FTIR spectra were recorded for polymers P10–P13 using ATR technique (Fig. 8). For synthesised polymers the main chain is composed of alkane-like fragments ($-\text{CH}_2-$). Hence stretching of $-\text{C}-\text{H}$ reflects bands at 3000 – 2850 cm^{-1} is visible with bending/scissoring vibration of $\text{C}-\text{H}$ in the range 1470 – 1450 cm^{-1} and rocking ones of $\text{C}-\text{H}$ at 1370 – 1350 cm^{-1} and 750 – 720 cm^{-1} . Presence of aromatic phenyl ring is manifested with $\text{C}=\text{C}-\text{H}$ stretching bands located in the range above 3000 cm^{-1} (3100 – 3000 cm^{-1}). The absorption within the range of 1600 – 1585 cm^{-1} and 1500 – 1400 cm^{-1} is caused by stretching bands of $-\text{C}=\text{C}-$ in aromatic rings. Low intensity bands at 3492 cm^{-1} represent stretching vibration

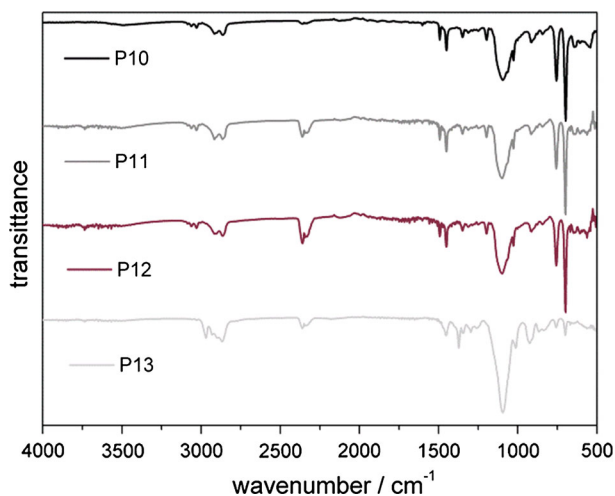


Fig. 8 FTIR ATR spectra for P10-P13: prepared with the use of K-DPG (**I10** and **I11**) and 3K-TKHMCH (**I12** and **I13**)

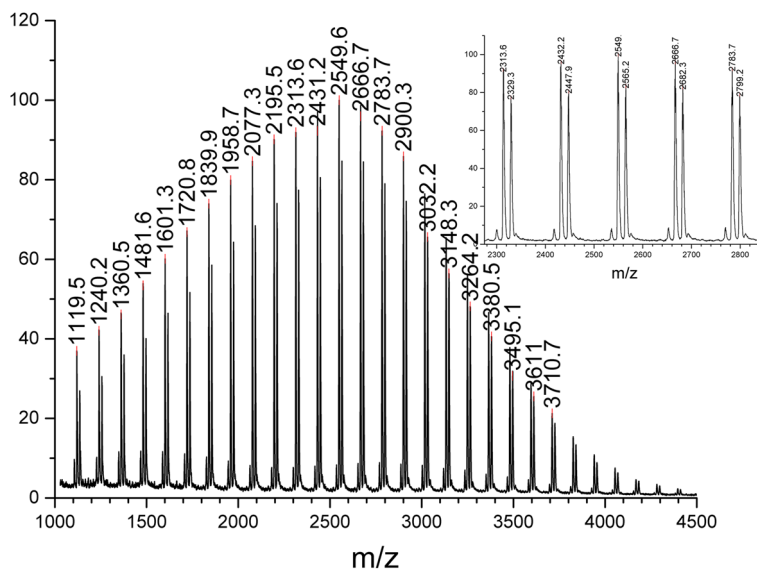
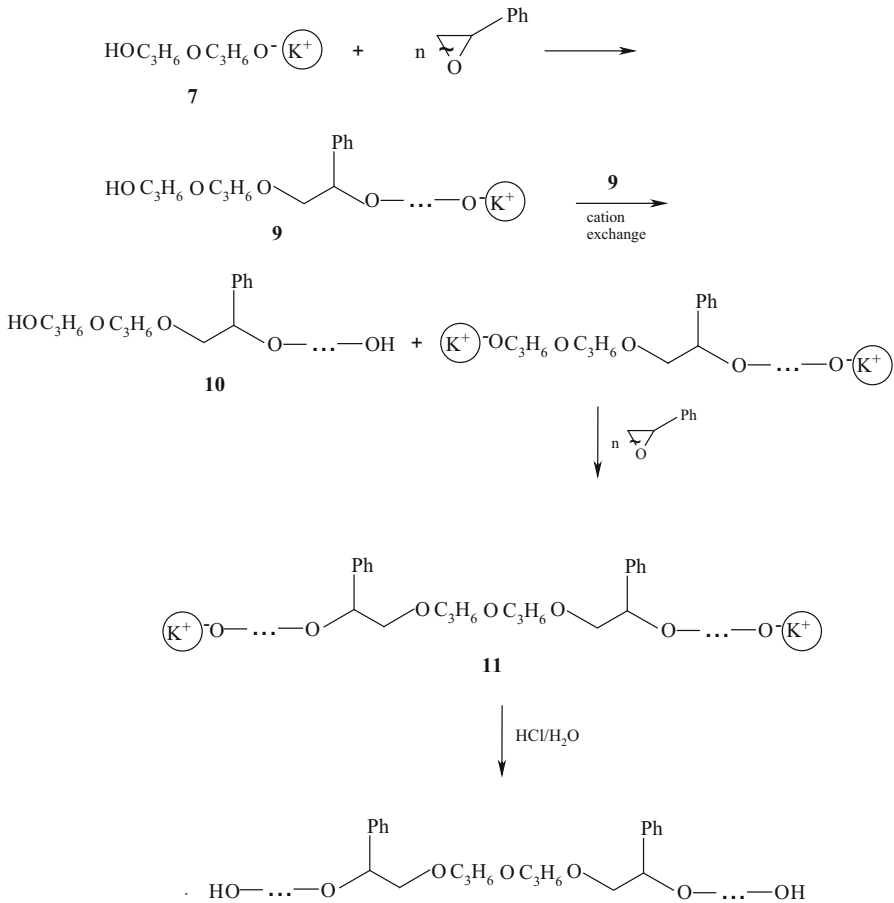


Fig. 9 MALDI-TOF spectrum of PSO-diol (P10) prepared with the use of K-DPG (**I7**) and quenched with HCl/H₂O

of associated O-H , while the peak at 1318 cm^{-1} is attributed to O-H bending vibration. Complementary C-O stretching band is visible in range $1260\text{--}1050\text{ cm}^{-1}$ with 1060 cm^{-1} stretching band of C-O for primary alcohol. It is overlaid with ether C-O-C band located at 1095 cm^{-1} characteristic for alkyl-substituted ether.

MALDI-TOF analysis of polymer P10 further confirmed its chemical structure (Fig. 9).



Scheme 5 ROP of styrene oxide initiated with K-DPG

Two series of signals were observed in the spectrum. The first series at m/z 1119.5–4055.3 represents macromolecules possessing central part $-\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}-$ derived from initiator and two OH terminal groups. For example, signals at m/z 1360.4, 1840.6 and 2432.2 represent macromolecules containing 10, 14 and 19 mers of styrene oxide (M_n (calcd.) = 1358.7, 1839.3 and 2440.1), respectively. They form as adducts with Na^+ ions. The second series at m/z 1135.5–4071.3 represents macromolecules with the same structure, but forming adducts with K^+ ions. For example, signals at m/z 1618.1, 1974.1 and 2447.9 belong to macromolecules with 12, 15 and 19 mers of styrene oxide (M_n (calcd.) = 1614.5, 1975.1 and 2456.1).

Based on the results obtained we proposed the course of ROP for SO (Scheme 5).

Rapid cation exchange reaction between macromolecules **10** and **11** is responsible for activation of the former resulting consequently in the lack of starting $\text{HOCH}(\text{CH}_3)\text{CH}_2-$ group. Deprotonation of hydroxyl groups present in polymer chains with alkoxide groups is very important reaction. It makes possible

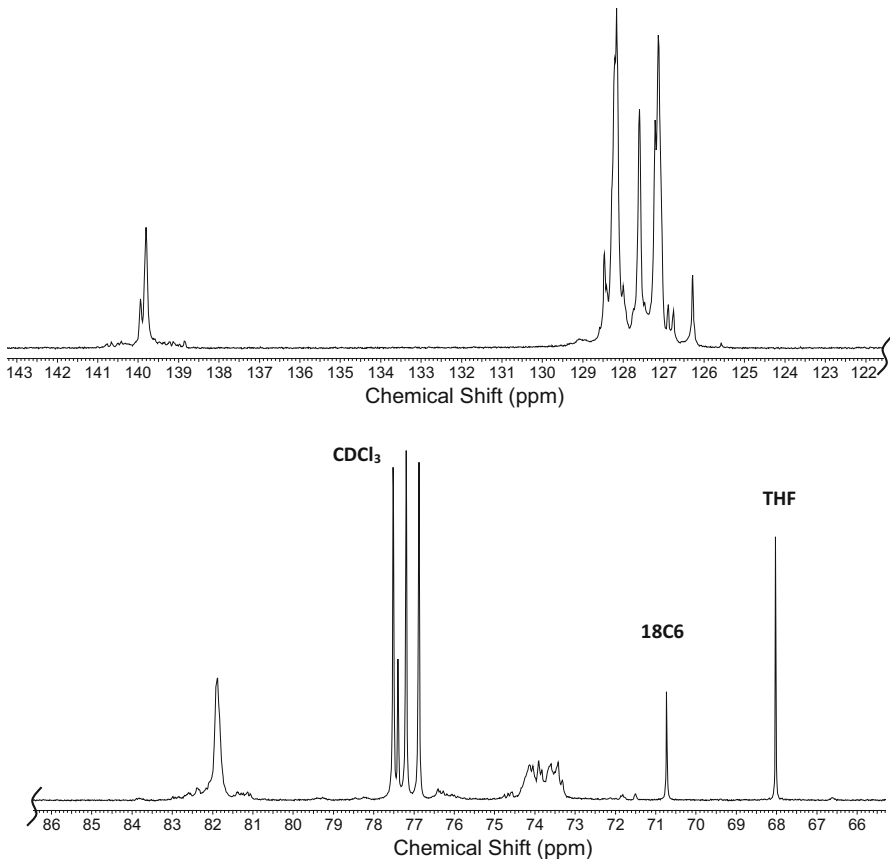


Fig. 10 ^{13}C NMR spectrum of PSO-pentol (P13) derived in ROP by use of 3K-THMCH (**18**) and quenched with $\text{HCl}/\text{H}_2\text{O}$

growth of chains in two directions and does not influence the concentration of active centers and polymer chains, i.e., does not influence M_n of polymers. Moreover, this reaction strongly limits chain transfer reaction to the monomer and thus avoids decreasing of M_n .

In the last series of experiments tripotassium salt of TKHMCH (**18**) was applied for SO polymerization. Figure 10 presents ^{13}C NMR spectrum of the polymer obtained at $[\text{SO}]_0 = 4.0 \text{ mol}/\text{dm}^3$.

In this spectrum the small signals at about 76.3 and 74.6 ppm can be ascribed respectively to the first two CH_2 carbons in the $-\underline{\text{C}}\text{H}_2-\text{O}-\underline{\text{C}}\text{H}_2-\text{CH}(\text{Ph})-$ beginning part of the polymer chains connected to the initiator ring and indicating formation of the polymer, however, the carbon signals of the initiator ring itself are too weak to be observed. Nevertheless, MALDI-TOF analysis of the polymer confirmed its chemical structure (Fig. 11).

Two series of signals were shown in the spectrum. It was proposed that the first series of peaks at m/z , for example 897.8, 1137.5 and 1975.8 represents

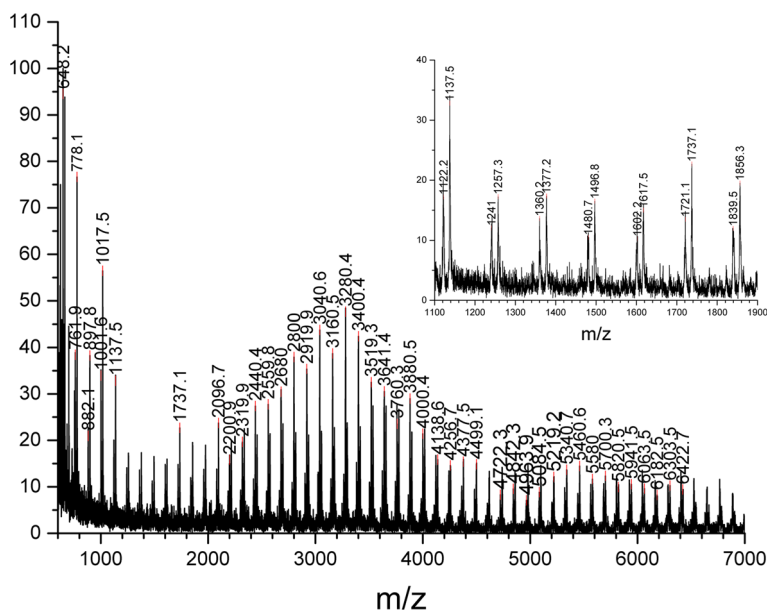
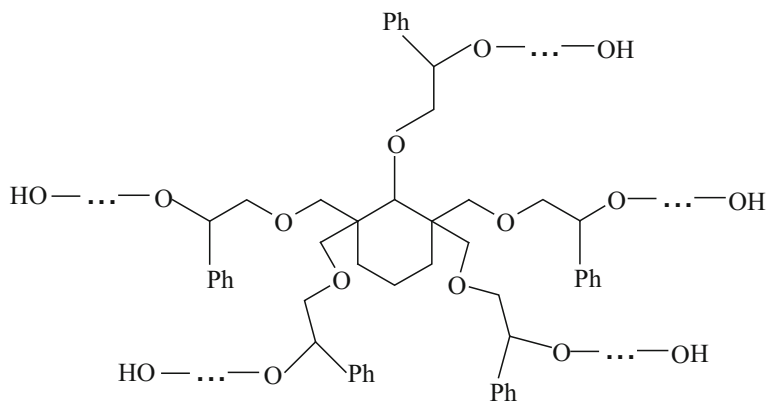


Fig. 11 MALDI-TOF spectrum of PSO-pentol (P13) synthesized with the use of 3K-THMCH (**18**) and quenched with water



Scheme 6 Star-shaped macromolecules with five PSO-arms formed in SO ROP initiated with 3K-TKHMCH (**18**) and quenched with HCl/H₂O

macromolecules having central part derived from initiator as well as four PSO arms with OH end groups and one arm with OK group. These macromolecules contain 5, 7 and 14 mers of SO, respectively, and form adducts with K⁺ ion (M_n (calcd.) = 898.2, 1138.5 and 1979.6, respectively). The second series of the signals at m/z 1002.1, 1122.2 and 1960.4 represent macromolecules with the same structure which contain 6, 7 and 14 mers (M_n (calcd.) = 1001.3, 1122.4 and 1963.4, respectively) and form adducts with Na⁺ ion.

We proposed that the polymerization course is similar to that initiated with (**17**), but in this case star-shaped macromolecules are formed (Scheme 6).

It is worth noting, that polymers obtained with salt (**18**) consist of two or three fractions detected by the SEC method. This phenomenon can be explained by a strong tendency during polymerization to the formation of various macromolecular aggregates containing OK and OH groups with different reactivities [19].

Conclusions

Potassium alkoxides and hydroxyalkoxides activated by 18C6 are effective initiators of styrene oxide polymerization in THF solution at ambient temperature. The structure of polymers depends strongly on the kind of the initiators. The main characteristic features of the studied processes are:

- Initiation of SO polymerization with potassium methoxide occurs exclusively by oxirane ring opening in the β -position and not in the β and α positions.
- Similar course of initiation was observed in the presence of potassium *t*-butoxide, 2-methylpropoxide and 1-phenylethoxide.
- Unexpectedly, potassium *i*-propoxide or 1-methylpropoxide opens the oxirane ring in the β or α position.
- The polymers obtained indicate unsaturation resulting exclusively from deprotonation of monomer methine groups with active center of growing chain and initiator.
- Molar masses of polymers ($M_n = 1700\text{--}4800$ Da) are much higher than reported in literature.
- Using monopotassium salt of dipropylene glycol and tripotassium salt of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol it was possible to synthesize PSO-polyols without unsaturation, which could be useful for preparation of new polyurethanes.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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