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Article

Application of Monopotassium Dipropylene Glycoxide for Homopolymerization and Copolymerization of Monosubstituted Oxiranes: Characterization of Synthesized Macrodiols by MALDI-TOF Mass Spectrometry

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Abstract: Monopotassium dipropylene glycoxide, activated by a 18-crown-6 cation complexing agent (K-DPG/L, where DPG (dipropylene glycol) is a mixture of isomers) was used as an effective initiator of the homopolymerization and copolymerization of several monosubstituted oxiranes, i.e., propylene oxide (PO), 1,2-butylene oxide (BO), and some glycidyl ethers such as allyl, isopropyl, phenyl, and benzyl ones (AGE, IPGE, PGE, and BGE, respectively). The copolymers are novel and can be prospectively used for the fabrication of new thermoplastic or crosslinked polyurethanes. All processes were carried out in homogeneous mild conditions, i.e., tetrahydrofuran solution at room temperature and normal pressure. They resulted in new unimodal macrodiols with $M_n = M_{calc}$ in the range of 1500–8300, low dispersity $M_w/M_n = 1.08$ – 1.18 and a chemical structure well defined by several techniques, i.e., MALDI-TOF, size exclusion chromatography (SEC), ¹³C NMR, and FTIR. Monopotassium salts of homopolyether-diols, i.e., PPO-diol, PBO-diol, and PAGE-diol, appeared to be useful macroinitiators for the preparation of new triblock copolyether-diols by polymerization of glycidyl ethers. In BO/BGE random copolymerization initiated with K-DPG/L, macromolecules of copolyether-diol were exclusively formed. Macromolecules of copolyether-diol accompanied by homopolyether PPO-diol were identified in the PO/PGE system. However, AGE and PGE reacted by giving random copolyether-diol as well as homopolymer-diols, i.e., PAGE-diol and PPGE-diol. Macromolecules of prepared copolyether-diols contain various numbers of mers deriving from comonomers; the kind of comonomer determines the composition of the product. Several prepared homopolyether-diols and copolyether-diols could be useful for the synthesis of new thermoplastic polyurethanes.

Keywords: oxiranes; homopolymerization; copolymerization; macrodiols; MALDI-TOF

1. Introduction

Polyether-polyols are the most important macromonomers for the synthesis of polyurethane elastomers and crosslinked foams [1–8]. They are usually prepared via neat anionic ring-opening polymerization of ethylene oxide (EO), propylene oxide (PO), or 1,2-butylene oxide (BO) using KOH (catalyst) and 1,2-propylene glycol or glycerol (starters) at a high temperature (>100 °C) and pressure. The molar masses (M_n) of polyether-diols and polyether-triols fabricated industrially from PO are usually 2000–4000 and 3000–6500, respectively [1]. The application of several novel initiators for PO anionic polymerization, i.e., dipotassium salts of resorcinol, 4,4'-bisphenol, or 4,4'-sulfonyldiphenol,

gave polyether-diols with relatively low $M_n = 1000\text{--}3000$ [9]. Recently [10], we used for initiation dipotassium salts of various aliphatic glycols activated by coronand 18-crown-6 (18C6). This allowed us to prepare bimodal PPOs containing a fraction with two terminal OK groups ($M_n = 10,000$, ~30% yield) and fraction with unsaturated allyloxy and OK terminal groups ($M_n = 30,000$, ~70% yield). Both kinds of terminal groups can be easily converted to OH ones [2]. Higher unsaturation (~83%) was observed in PPOs obtained in the presence of a suspension of anhydrous KOH in tetrahydrofuran (THF) [11]. Moreover, cyclic oligo(potassium glycidoxide)s with three or six OK groups of activated 18C6 were applied as macroinitiators for the polymerization of PO, BO, and styrene oxide (SO) [12]. Star-shaped polyether-polyols with $M_n = 1200\text{--}8000$ were prepared in this way. Similar products were recently obtained by the polymerization of PO [13] and SO [14] initiated with potassium salts of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol. These polymers can be used as substrates for the synthesis of new crosslinked polyurethanes [13].

The most popular classes of polyether-diols are PPO-diols, block copolymers PO-EO with terminal PEO blocks, block copolymers PO-EO with internal PEO blocks, and random PO-EO copolymers [1]. They are used especially for polyurethane elastomers, coatings, adhesives, and sealants [15,16]. The most extensively studied triblock copolyether-diol is PEO/PPO/PEO, a polymeric nonionic surfactant, which is commercially available as Pluronic (BASF) or Symperonic (ICI) [15–17]. In this polymer, PPO builds the hydrophobic block, whereas PEO has two hydrophilic blocks. Then, a number of ABA and BAB triblock copolymers of ethoxyethyl glycidyl ether (EEGE) and PO were prepared by sequential anionic polymerization initiated with cesium salt of dipropylene glycol [17]. It is known that these copolymers can form nanosized aggregates and exhibit different temperature behavior depending on the copolymer architecture.

In the synthesis of polyether-diols, the most frequently oxirane used is propylene oxide. The literature data concerning application of other monosubstituted oxiranes are rather scarce. Stolarzewicz et al. [18] studied the polymerization of chlorophenyl glycidyl ethers in the presence of powdered KOH and proposed that the process was initiated both in solution and on the surface of the initiator. A similar effect was also observed in the polymerization of PO [19], BO, SO, and various glycidyl ethers mediated with a suspension of anhydrous KOH in THF [20]. The molar mass, dispersity, and modality of synthesized polyether-diols depend strongly on the initial concentration of reagents, their solubility in the reaction mixture, and the presence of water or cation complexing agents, i.e., coronand 18C6 and cryptand C222. Recently, we applied another type of initiator (hydroxyalkoxide), i.e., monopotassium dipropylene glycoxide activated by 18C6 for homogenous polymerization of PO [10] and SO [14], as well as copolymerization of the latter with PO and glycidyl ethers [21]. This initiator contains two active sites in the molecule, resulting in polyether-diols and a very low number of macromolecules with unsaturated end groups, reduced by the presence of OH end groups in polymer chains. Thus, this initiator seemed to be much more useful than KOH in the synthesis of polyether-diols from monosubstituted oxiranes. It is active even without the addition of crown ether, but this addition increased their activity due to the formation of crown separated ion pairs. It results in increase of polymerization rate and yield of product.

In the present work, we applied monopotassium dipropylene glycoxide activated by 18C6 for the preparation of several new homopolyether-diols and copolyether-diols, i.e., triblock or random ones. PO, BO, isopropyl glycidyl ether (IPGE), allyl glycidyl ether (AGE), phenyl glycidyl ether (PGE), and benzyl glycidyl ether (BGE) were used as monomers. These copolymers are novel and bring innovation to the work. All processes were performed in mild conditions, i.e., in THF solution at room temperature. Characterization of the polymers was made by SEC, MALDI-TOF MS, and supporting techniques, such as ^{13}C NMR and FTIR. The main analytical tool was MALDI-TOF MS, which enables insight into the composition of the polymers and thorough characterization of the obtained polymers. Synthesized materials could be potentially useful for the preparation of new elastomeric or crosslinked polyurethanes in reactions with diisocyanates or poly(diisocyanates), respectively.

2. Experimental

2.1. Materials

Monomers, i.e., propylene oxide, 1,2-butylene oxide, isopropyl glycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, and benzyl glycidyl ether (all from Sigma-Aldrich, Poznan, Poland, ACS reagent), were dried over CaH_2 and distilled at 306 K (33 °C), 336 K (63 °C), 414 K (131 °C), 427 K (154 °C), 518 K (245 °C), and 344 K (71 °C)/11 Torr, respectively. Anhydrous tetrahydrofuran (THF) (Acros Organics, Poznan, Poland, ACS reagent) was kept over CaH_2 and distilled at 339 K (66 °C) prior to use. A 35 wt % dispersion of KH in mineral oil (Sigma-Aldrich, Poznan, Poland, ACS reagent) was mixed with *n*-pentane in a dry argon atmosphere and then decanted. This was repeated three times, followed by a three-fold washing with dry THF. Finally, THF was evaporated in a 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 the small hydrolysis of the original KH sample. Dipropylene glycol (mixture of isomers) (Sigma-Aldrich, Poznan, Poland, ACS reagent) and 18-crown-6 (18C6) (Merck, Warszawa, Poland, ACS reagent) were used without purification.

2.2. The Synthesis

All syntheses were carried out at room temperature in a 50 cm³ reactor equipped with a magnetic stirrer and a Teflon valve, enabling substrate delivery and sampling under an argon atmosphere.

2.2.1. Homopolyether-Diols

A monopotassium salt of dipropylene glycol (K-DPG) was obtained through the reaction of potassium hydride with an appropriate amount of glycol dissolved in THF at 20 °C. The initial concentrations of the monomer were 2.0 or 5.0 mol/dm³ and the initial concentration of the initiator was 0.1 mol/dm³. For example, potassium hydride (0.08 g, 2.0 mmol) and THF (13 cm³) containing 18C6 (0.53 g, 2.0 mmol) were introduced into a 50 cm³ reactor equipped with a magnetic stirrer and a Teflon valve, enabling substrate delivery and sampling under an argon atmosphere. Then, dipropylene glycol (2.0 mmol) was added to the THF solution (0.5 mol/dm³, 4.0 cm³) by a syringe. The reaction mixture was stirred for 30 min until all hydrogen (44.7 cm³) was dissolved. This resulted in a solution of pure anhydrous monopotassium salt of dipropylene glycol activated ligand in THF. That system was used as the initiator, when propylene oxide (2.8 cm³, 2.3 g, 40.0 mmol) was introduced into the reactor. The reaction mixture was then stirred for several days. The course of polymerization was followed by assessing the changes in the content of oxirane groups in samples taken at various times from the reaction mixture. The content of oxirane groups was determined by the dioxane method [22]. A 0.2–0.7 g sample was taken from the reaction mixture and dissolved in 10 cm³ of a 0.2 mol/dm³ solution of HCl in 1,4-dioxane, the whole being then allowed to stand for 1 h at room temperature. The solution was then titrated with 0.1 mol/dm³ KOH using phenolphthalein as an indicator, with a blank determination being run simultaneously. Final conversion of the monomers (~99%) was calculated by NMR technique taking into account signals of oxirane groups in the spectrum. After complete conversion of the monomer, the reaction mixture was neutralized with a HCl/H₂O system (0.1 mol/dm³, 70 cm³) and transferred to a separator containing chloroform (70 cm³). After shaking for 5 min, two layers formed, a bottom polyether layer and a top layer containing water and the potassium salt. These layers were separated and the top layer was removed. After three washes with distilled water, polyether was obtained by evaporating chloroform and water.

2.2.2. Triblock Copolyether-Diols

Potassium hydride (0.08 g, 2.0 mmol) and tetrahydrofuran (12.5 cm³) containing 18C6 (0.53 g, 2.0 mmol) were introduced into the reactor and then a 0.5 mol/dm³ solution of dipropylene glycol

in tetrahydrofuran (4.0 cm^3) was added. The reaction mixture was stirred for 20 min until all the hydrogen (44.7 cm^3) was evolved. This resulted in a solution of monopotassium salt of dipropylene glycol activated with a 18C6 complexing agent. That system was then used as the initiator when 1,2-butylene oxide (3.5 cm^3 , 0.42 g, 40 mmol) was introduced into the reactor. In this system, the initial concentration of the monomer was equal to 2.0 mol/dm^3 and the initial concentration of the initiator was 0.1 mol/dm^3 . The reaction mixture was then stirred for several days. After complete conversion of the monomer, an equimolar amount of IPGE (4.7 cm^3) was introduced into the reactor and stirred until total conversion of IPGE was achieved. Then the reaction mixture was neutralized with a HCl/H₂O system (0.1 mol/dm^3 , 50 cm^3) and transferred to a separator containing chloroform (70 cm^3). After shaking for 5 min, two layers were obtained, a bottom copolyether layer and a top layer containing water and the potassium salt. These layers were separated and the top layer was removed. After three washes with distilled water, copolyether was obtained by evaporating chloroform and water in a vacuum. In subsequent experiments, various copolyethers were prepared in a similar way. The concentration of monomers during the polymerization was monitored by the NMR method. The final conversion was ~99%, while the yields of the products were 97–99%.

2.2.3. Random Copolyether-Diols

Potassium hydride (0.08 g, 2.0 mmol) and tetrahydrofuran (6.4 cm^3) containing 18C6 (0.53 g, 2.0 mmol) were introduced into the reactor and then a 0.5 mol/dm^3 solution of dipropylene glycol in tetrahydrofuran (4.0 cm^3) was added. The reaction mixture was then stirred for 20 min until all the hydrogen (44.7 cm^3) was evolved. This resulted in a solution of monopotassium salt of dipropylene glycol activated with a 18C6 complexing agent. That system was then used as the initiator, when a mixture of 1,2-butylene oxide (3.5 cm^3 , 0.42 g, 40 mmol) and equimolar amount of benzyl glycidyl ether (6.1 cm^3) was introduced into the reactor and stirred until the complete conversion of monomers. Then, the reaction mixture was neutralized with a HCl/H₂O system (0.1 mol/dm^3 , 50 cm^3) and transferred to a separator containing chloroform (70 cm^3). After shaking for 5 min, two layers were obtained, a bottom polymer layer and a top layer containing water and the potassium salt. These layers were separated and the top layer was removed. After three washes with distilled water, copolyether was obtained by evaporating chloroform and water in a vacuum. In subsequent experiments, other copolymers were prepared in a similar way. The final conversion was ~99% and the yields of the products were 97–99%.

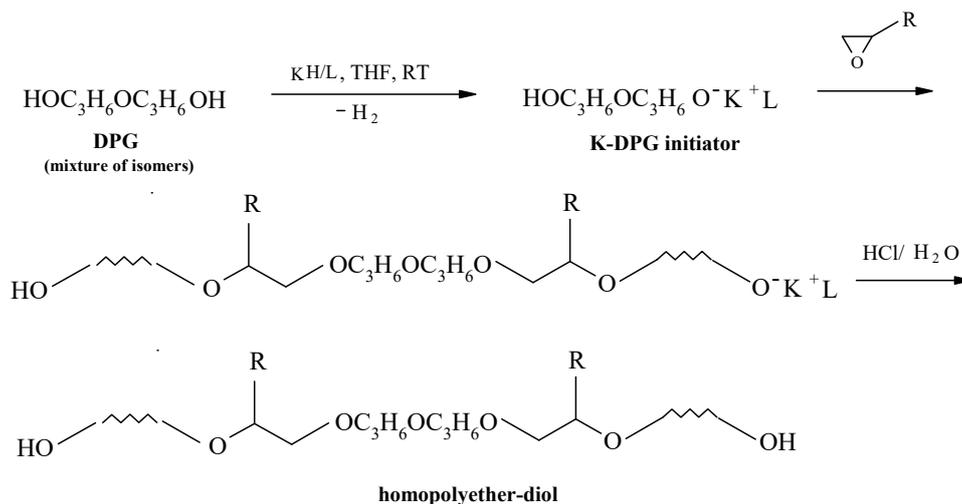
2.3. Measurements

First, 100 MHz ¹³C nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ at 25 °C on a BrukerAvance 400 pulsed spectrometer equipped with a 5 mm broadband probe and a 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 × 8 mm OHpac column, using tetrahydrofuran as a solvent. Poly(propylene glycol)s 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. Infrared (IR) spectra of samples were recorded on a Shimadzu IR Prestige spectrometer with an attenuated total reflectance (ATR) accessory. The diamond ATR crystal was purified prior to each measurement with isopropanol. Data were analyzed using the LabSolutions program. Each sample was scanned at a resolution of 2 cm^{-1} .

3. Results and Discussion

3.1. Homopolyether-Diols

Several macrodiols were synthesized from monosubstituted oxiranes in a homogeneous system at mild conditions according to the reaction shown in Scheme 1. The role of the 18C6 (L) ligand was the complexation of counterion in order to increase the reactivity of the initiator and the number of alkoxides in the growing polymer chain by the formation of crown ether separated ion pairs. This resulted in an increase in the initiator solubility, reaction rate, and yield of the product.



Scheme 1. Preparation of initiator and homopolyether-diols by anionic ring-opening polymerization of monosubstituted oxiranes, where: R: CH₃, CH₃CH₂, CH₂=CHCH₂OCH₂, (CH₃)₂CHOCH₂, PhOCH₂ or PhCH₂OCH₂, L: 18C6.

Conversion curves of the monomers are shown in Figure 1. The monomers were polymerized at various rates depending on the polar and steric effects of the substituent [23]. The reaction times were relatively long, which can result from intra-and/or intermolecular proton exchange between the OH and OK groups [21].

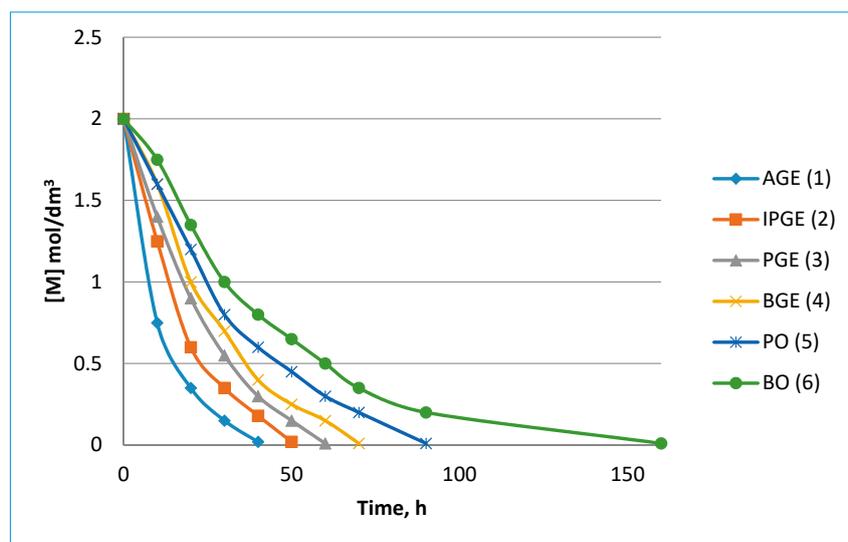


Figure 1. Monomer concentration vs. time of polymerization initiated with K-DPG activated by 18C6 in THF solution; $[M]_0 = 2.0 \text{ mol/dm}^3$; $[I]_0 = [18C6]_0 = 0.1 \text{ mol/dm}^3$; AGE (1), IPGE (2), PGE (3), BGE (4), PO (5), and BO (6).

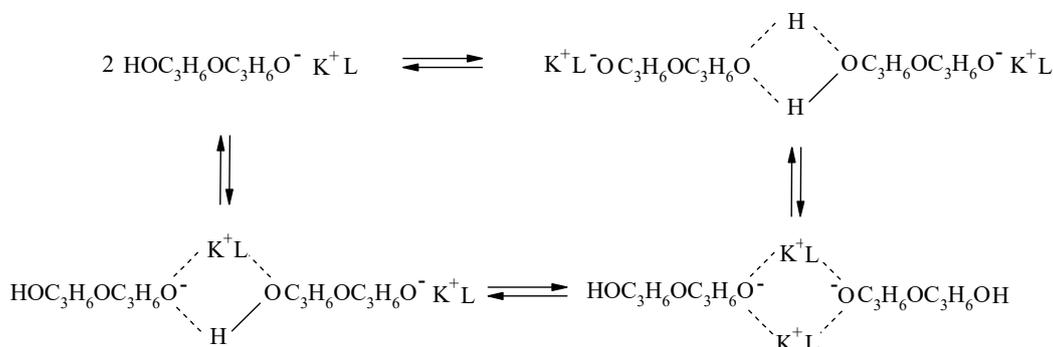
Table 1 shows data concerning the average molar masses (M_n) and dispersities (M_w/M_n) of the mentioned polymers, as well as the initiator efficiency ($f = M_{\text{calc}}/M_n$) for complete conversion of the monomer. All polymers are unimodal and their dispersities are rather low ($M_w/M_n = 1.08\text{--}1.16$).

Table 1. Characterization of polyether-diols prepared with K-DPG activated by 18C6 as an initiator in THF at room temperature; $[I]_0 = [18C6]_0 = 0.1 \text{ mol/dm}^3$.

No.	Monomer	$[M]_0 \text{ mol/dm}^3$	Yield %	Reaction Time, h	$M_{\text{calc}}^a/$	$M_n \text{ (SEC)}$	$M_w/M_n \text{ (SEC)}$	Initiator Efficiency, $f^b/$
1	PO	2.0	99	95	1161	1500	1.09	0.77
2	PO	5.0	98	230	2903	3200	1.12	0.91
3	PO	10.0	99	400	5805	6000	1.13	0.96
4	BO	2.0	98	170	1442	1900	1.10	-
5	BO	5.0	99	300	3605	4100	1.11	-
6	BO	9.0	97	510	6489	6700	1.14	-
7	AGE	2.0	99	45	2283	2700	1.14	-
8	AGE	5.0	98	110	5708	5800	1.13	-
9	IPGE	2.0	99	50	2322	2500	1.08	-
10	IPGE	5.0	97	120	5805	5900	1.09	-
11	PGE	2.0	99	60	3000	3500	1.13	-
12	PGE	5.0	96	140	7500	7600	1.14	-
13	BGE	2.0	99	80	3283	3600	1.15	-
14	BGE	5.0	97	190	8208	8300	1.16	-

$$^a/ M_{\text{calc}} = ([M]_0/[I]_0)M_{\text{mon}}. \quad ^b/ f = M_{\text{calc}}/M_n \text{ (SEC)}.$$

Molar masses (M_n) of PPO-diols synthesized with K-DPG/L are higher than the calculated ones (M_{calc}), indicating initiator efficiency $f < 1$. This effect can be explained by the strong tendency of the soluble initiator to the formation of various ionic aggregates existing in equilibrium (Scheme 2). Their reactivity varies, depending on the chemical structure and the polarity of the reaction mixture, which depends on the initial monomer concentration and possible monomer participation in the formation of the aggregates. These may influence on different initiator's efficiency.



Scheme 2. Equilibrium between two molecules of K-DPG/L and their ionic aggregates.

It was observed by the ^{13}C NMR technique that the unsaturation of PPO-diols obtained with K-DPG is represented exclusively by allyloxy groups, $\text{CH}_2=\text{CHCH}_2\text{O}-$ (116.71 ppm and 134.88 ppm, respectively), resulting from monomer deprotonation by $\text{O}^-\text{K}^+\text{L}$ groups of initiator and polymer chains (Figure 2). It is relatively low (1–4%) and increases with the initial monomer concentration. The presence of OH end groups in macromolecules during the polymerization avoids the isomerization of allyloxy groups to *cis*-propenyloxy ones.

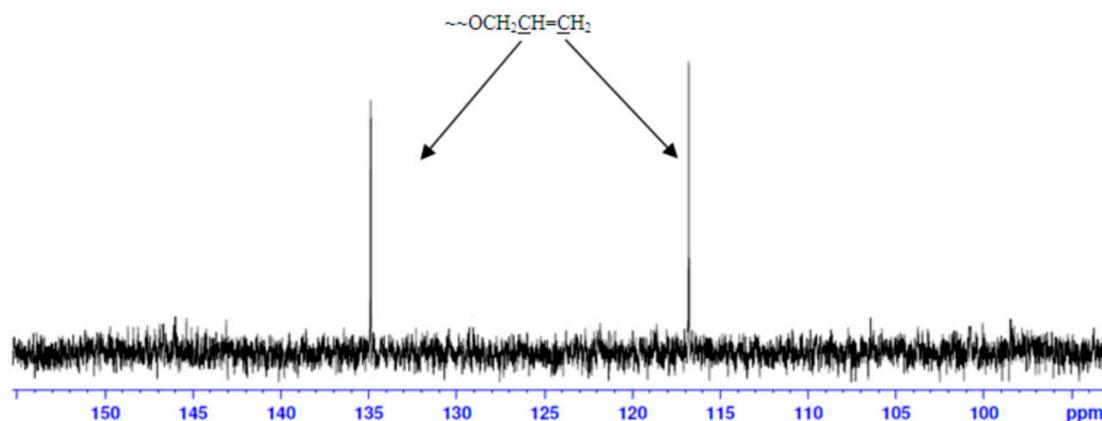
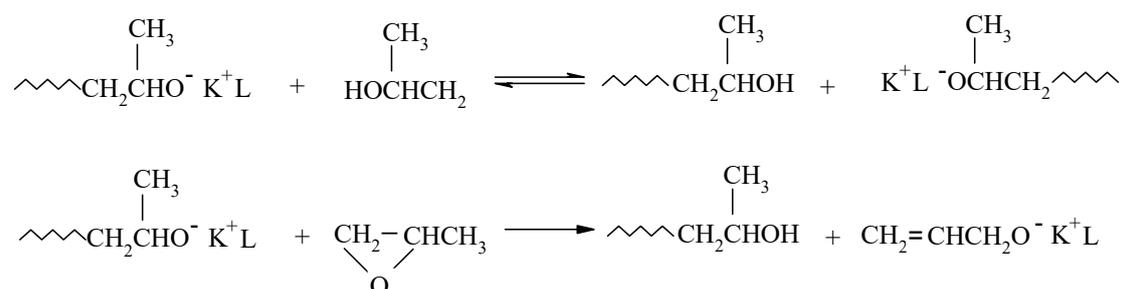


Figure 2. ^{13}C NMR spectrum of PPO-diol (1) showing signals of unsaturated allyloxy starting groups.

In comparison, the unsaturation of polyethers was markedly higher when powdered anhydrous KOH was used as an initiator ($\sim 83\%$) at $[\text{M}]_0$ and $[\text{I}]_0$ equal to 2.0 and 0.1 mol/dm 3 [11]. In the last case, mainly macromolecules containing isomeric *cis*-propenyloxy starting groups were formed. Moreover, the average molar mass of the polymer is much higher ($M_n = 6000$). The low unsaturation of the currently studied system results from the presence of OH groups in macromolecules. Evidently, the deprotonation of the latter by alkoxide end groups is faster than the deprotonation of the CH $_3$ group in the monomer molecule, which markedly reduces the number of unsaturated groups (Scheme 3).



Scheme 3. Cation exchange between potassium alkoxide and hydroxyl group and deprotonation of the CH $_3$ group in the monomer.

All PPO-diols (1–3) contain the same starting and ending $-\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ groups after quenching with HCl/H $_2\text{O}$. For example, the ^{13}C NMR spectrum of PPO-diol (1) revealed two signals of methine carbon bonded to the OH end group at 65.55 (65.54 and 65.56 ppm) and at about 67.1 ppm (67.09 and 67.15) ppm (Figure 3).

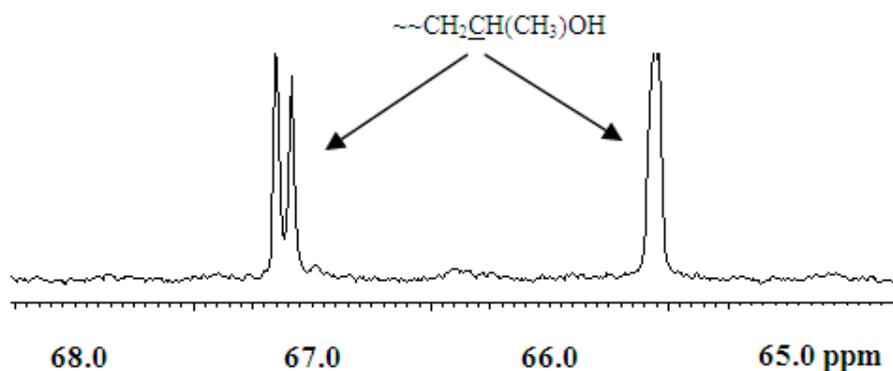


Figure 3. ^{13}C NMR spectrum showing the region of terminal groups in PPO-diol (1) prepared with K-DPG/L.

The splitting of the signal of the last units in the chain ends has already been discussed in our previous paper [11].

MALDI-TOF analysis of the polymer confirmed its structure (Figure 4). Two series of signals were observed in the spectrum. The first one at m/z 620.9 to 2593.5 represents macromolecules possessing the central part ($-\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}-$) derived from the initiator and two terminal OH groups. For example, signals at m/z 736.9, 1317.7, and 2130.1 represent macromolecules containing 10, 20, and 30 mers of propylene oxide ($M_{\text{calc}} = 738.0, 1318.8, \text{ and } 2132.9$, respectively). They exist as adducts with sodium ions. The second series at m/z 637.0 to 2609.6 represents macromolecules with the same structure forming adducts with potassium ions. For example, signals at m/z 1043.3, 1681.8, and 2436.2 belong to macromolecules with 15, 26, and 39 mers of propylene oxide ($M_{\text{calc}} = 1044.5, 1683.3, \text{ and } 2438.4$, respectively). However, signals of macromolecules with allyloxy starting groups were not detected in the spectrum. It is worth noting that, in PBO-diols (4–6) and other polyether-diols, unsaturation was not observed using ^{13}C NMR and MALDI-TOF techniques due to the effect of the substituent on the acidity of CH protons in the monomer molecule. In the ^{13}C NMR spectrum of PBO-diol (4), a signal of the CH_3 group of the initiator was observed at 17.10 ppm. The signals of the $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{OH}$ end group were at 73.46 and 73.70 ppm. However, signals at 65.55 and 67.10 pm derived from the initiator were not observed. This indicated that propagation occurred in two directions.

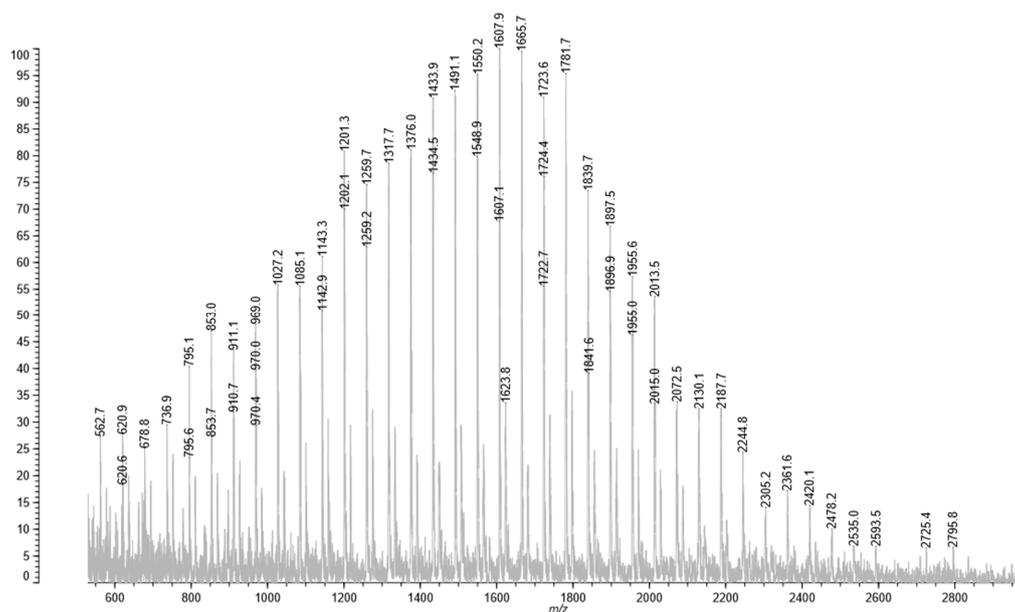


Figure 4. MALDI-TOF spectrum of PPO-diol (1) obtained with K-DPG/L.

In order to determine the chemical structure of PBO-diols, the MALDI-TOF technique was applied. The spectrum of the appropriate polymer is shown in Figure 5.

The spectrum in Figure 5 reveals two series of signals at m/z 600 to 4000. The first series at m/z 661.9 to 3762.7 represents macromolecules containing a central part derived from the initiator, several BO mers, and two end OH groups. For example, signals at m/z 1239.5, 2465.2, and 2897.3 represent macromolecules containing 15, 32, and 38 mers of BO ($M_{\text{calc}} = 1238.8, 2464.7, \text{ and } 2897.4$, respectively). They formed adducts with sodium ions. The second series at m/z 605.9 to 3778.8 represents macromolecules with the same structure, which form adducts with potassium ions. For example, signals at m/z 750.8, 2049.1, and 2697.5 belong to macromolecules with 8, 26, and 35 mers of BO ($M_{\text{calc}} = 750.2, 2048.1, \text{ and } 2697.1$, respectively).

For polyether-diols, FTIR ATR spectra were recorded to confirm their chemical structure based on selected mer units. The spectrum of PBO-diol (4) is shown in Figure 6.

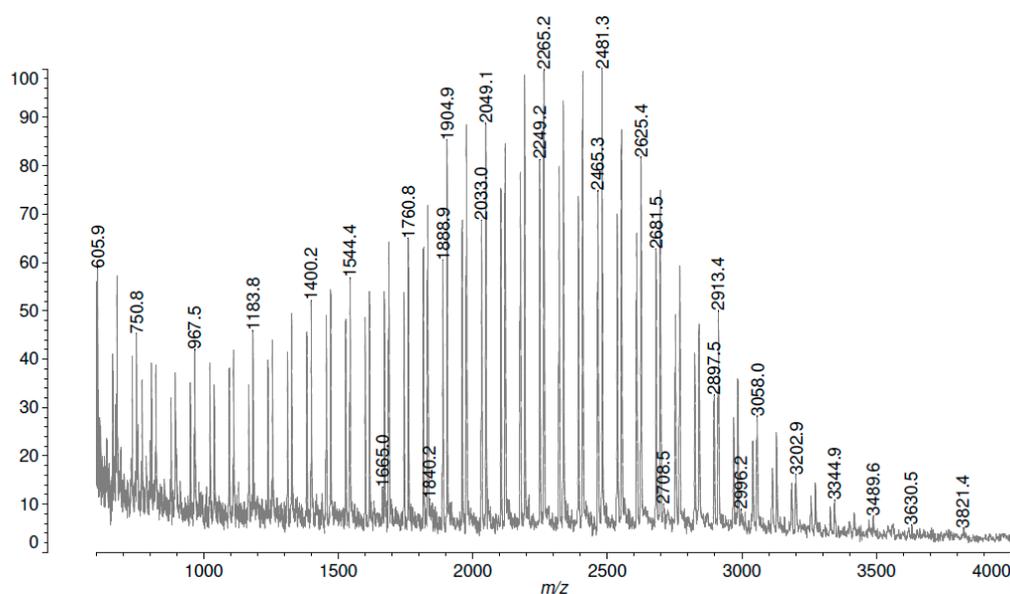


Figure 5. MALDI-TOF spectrum of PBO-diol (4) obtained with K-DPG/L.

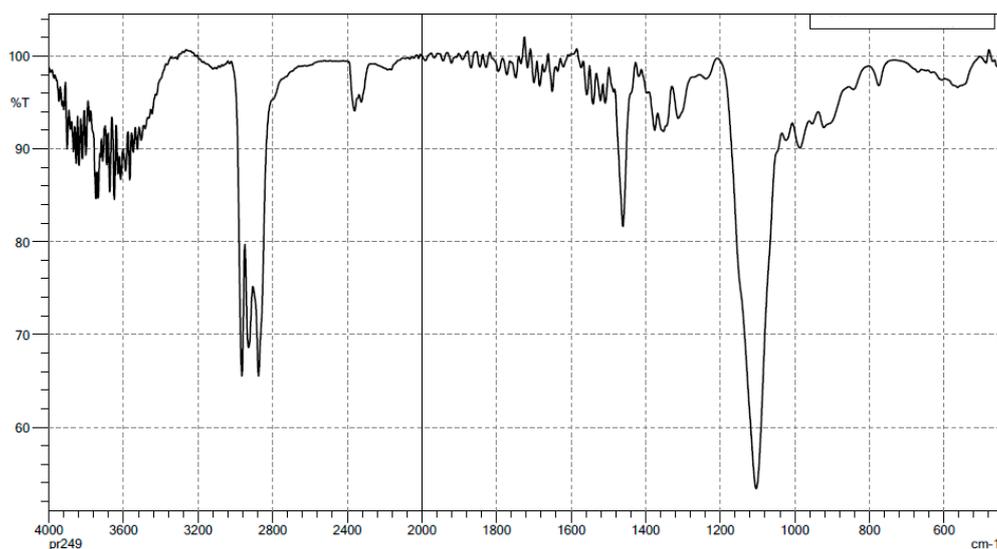


Figure 6. FTIR spectrum of PBO-diol (4).

Bands at $3000\text{--}2850\text{ cm}^{-1}$ reflect alkane-like fragments ($-\text{CH}_2-$) of the main chains together with the bending/scissoring vibration of C–H in the range $1460\text{--}1440\text{ cm}^{-1}$ and rocking ones of C–H at $1370\text{--}1350\text{ cm}^{-1}$. For synthesized polyether bands, 3490 cm^{-1} represents the stretching vibration of associated $-\text{O}-\text{H}$, while the absorption peak at 1320 cm^{-1} is attributed to O–H bending vibration. Hydroxyl characteristic bands might also be identified at 1060 cm^{-1} for primary hydroxyl stretching [24]. For all polyethers, a strong C–O stretching band located in the $1200\text{--}1050\text{ cm}^{-1}$ wave number range is visible, but it is overlaid with an ether C–O–C band located at 1095 cm^{-1} , characteristic of alkyl-substituted ether [25].

MALDI-TOF mass spectrometry was also used for the determination of the chemical structure of poly(glycidyl ether)s. The spectrum of PAGE-diol is presented in Figure 7.

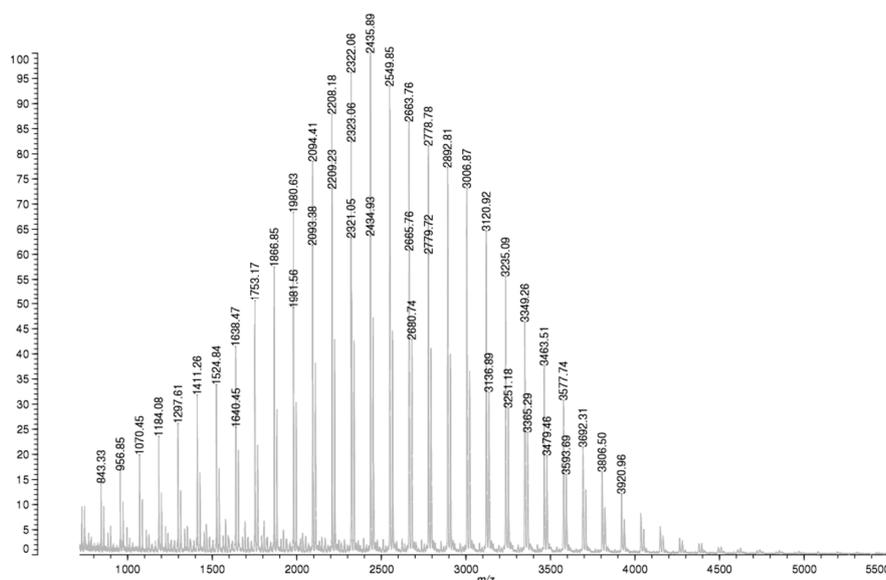


Figure 7. MALDI-TOF spectrum of PAGE-diol (7) prepared with K-DPG/L.

Two series of signals were observed in the spectrum in Figure 7. The first one at m/z 727.9 to 4263.5 represents macromolecules possessing a central part derived from the initiator and two terminal OH groups. For example, signals at m/z 1070.4, 2667.3, and 3921.7 represent macromolecules containing 8, 22, and 33 mers of allyl glycidyl ether ($M_{\text{calc}} = 1070.3$, 2668.3, and 3923.8, respectively). They form adducts with sodium ions. The second series at m/z 744.0 to 4279.6 represents macromolecules with the same structure, which form adducts with potassium ions. For example, signals at m/z 1428.8, 3026.7, and 3595.5 belong to macromolecules with 11, 25, and 30 mers of the monomer ($M_{\text{calc}} = 1428.8$, 3026.8, and 3597.5, respectively).

Figure 8 presents the ^{13}C NMR spectrum of PAGE-diol (7). The signal of the CH_3 group of the initiator was observed at 17.10 ppm. The signals at 68.62 and 69.01 ppm can be attributed to the methine carbon of $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2)\text{OH}$ end group. It can also be stated that the alternative structure of the end group, i.e., $-\text{OCH}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2)\text{CH}_2\text{OH}$, is highly improbable since in this case the signals of CH and CH_2 carbons in the vicinity of the OH group should arrive at about 81.3 and 62.9 ppm, respectively, and there are no signals in these regions. This indicates regular chain propagation, and hence the opening of oxirane ring only in the β position.

It is also worth noting that the isomerization of allyloxy groups does not occur under the influence of $-\text{O}^-\text{K}^+\text{L}$ active centers. The signals of *cis*-propenyloxy groups $\text{CH}_3\text{CH}=\text{CHO}$ previously observed at 9.2, 101.1 and 145.9 ppm in the polymerization of AGE initiated with anhydrous KOH (12%) [20] are very weak (0.1%). This is caused by the influence of the OH group derived from the initiator.

Figure 9 shows the MALDI-TOF spectrum of PPGE-diol. Two series of signals were observed in the spectrum (Figure 9). The first series at m/z 924.0 to 5873.0 represents macromolecules possessing a central part derived from the initiator and two terminal OH groups. For example, signals at m/z 1225.3, 3176.1, and 4674.9 represent macromolecules containing 7, 20, and 30 mers of phenyl glycidyl ether ($M_{\text{calc}} = 1224.5$, 3176.7, and 4678.4, respectively). They form adducts with potassium ions. The second series at m/z 909.7 to 5856.9 represents macromolecules with the same structure, which form adducts with sodium ions. For example, signals at m/z 1959.6, 2710.1, and 4359.0 belong to macromolecules with 12, 17, and 28 mers of phenyl glycidyl ether ($M_{\text{calc}} = 1959.2$, 2710.0, and 4361.9, respectively).

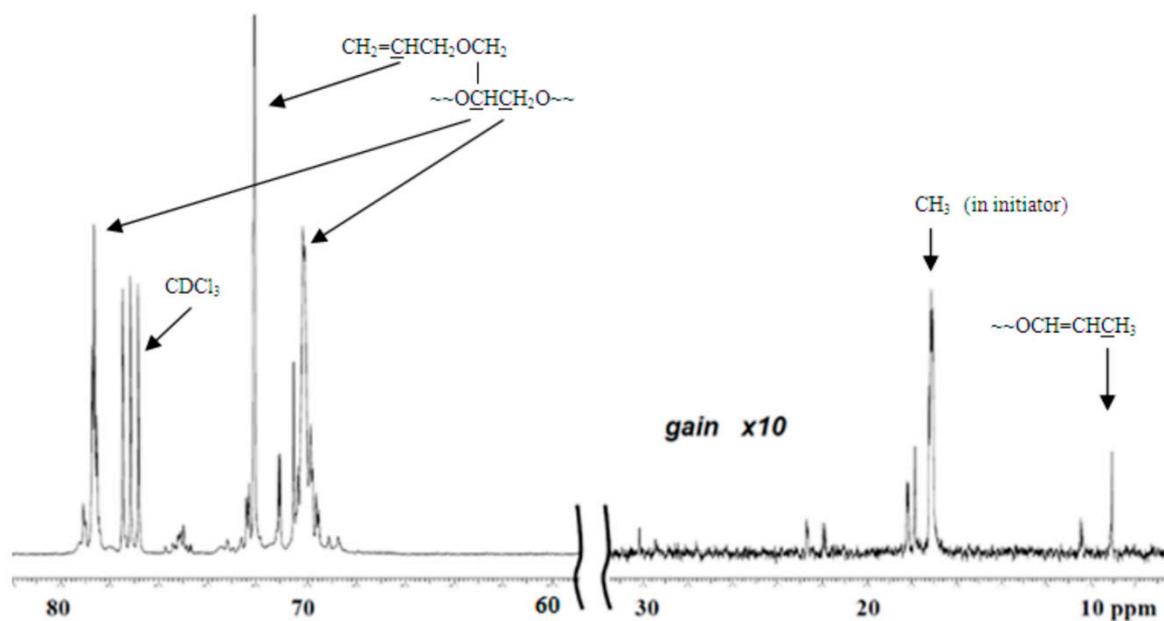


Figure 8. ^{13}C NMR spectrum of PAGE-diol (7) obtained with K-DPG.

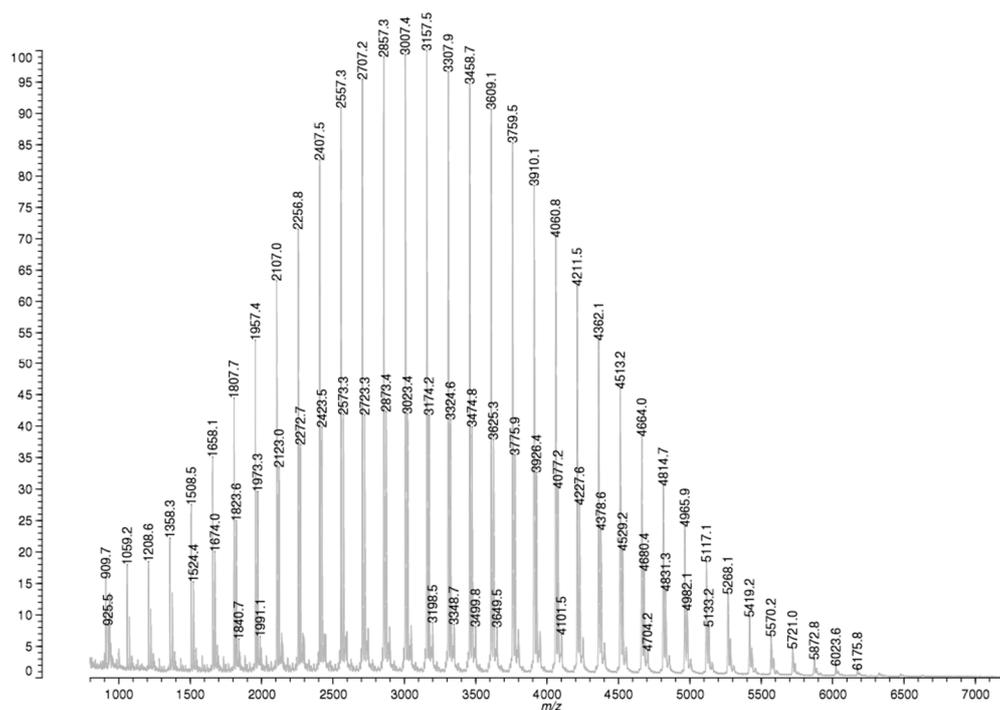
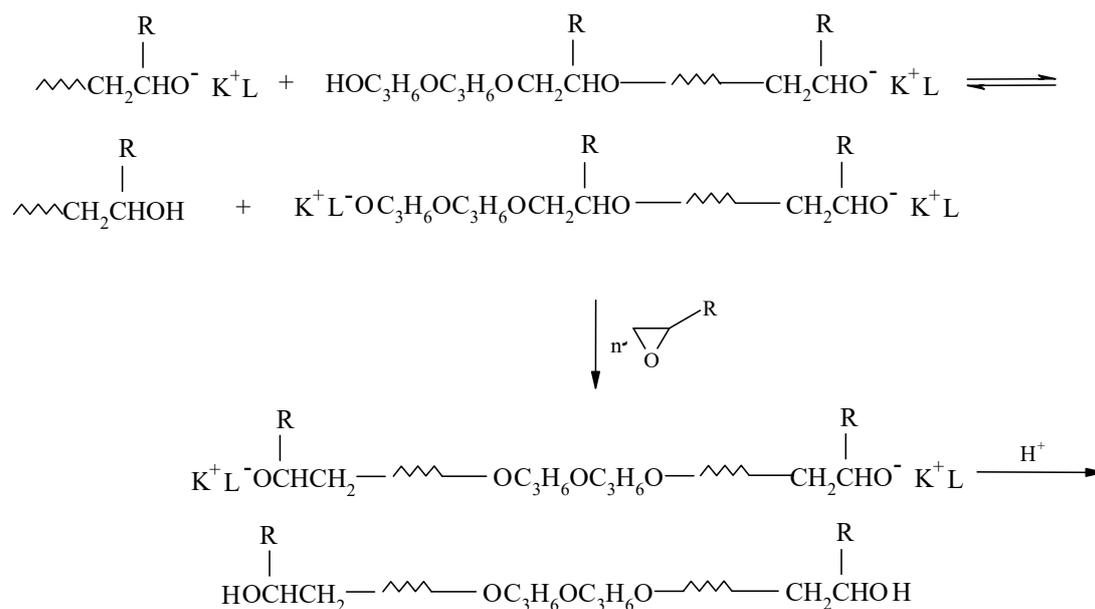


Figure 9. MALDI-TOF spectrum of PPGE-diol (11) synthesized with K-DPG/L.

Similar results were obtained for other polyether-diols synthesized in this work. This means that, during the polymerization, fast counterion exchange occurs between two macromolecules, which causes the propagation in two directions (Scheme 4).



Scheme 4. Formation of macromolecules with two active centers in growing chains.

When comparing the average molecular weight determined by MALDI-TOF and SEC, it can be seen that the results obtained by both methods are comparable but still show some discrepancies. For the samples with lower dispersities ($M_w/M_n < 1.10$), the SEC-derived values are slightly lower (e.g., for sample 1: $M_n = 1500$ (SEC), $M_n = 1600$ (MALDI-TOF)), while for samples with higher dispersities ($M_w/M_n > 1.10$), the SEC-derived values are slightly higher (e.g., for sample 7: $M_n = 2700$ (SEC), $M_n = 2450$ (MALDI-TOF)). This discrepancy is connected with the fact that the dispersity of the samples is a well-known factor that influences the MALDI-TOF spectra [26,27] and standards used for SEC calibration.

Summarizing, the application of potassium hydroxyalkoxide for the polymerization of monosubstituted oxiranes allows us to prepare several new linear polyether-polyols in mild conditions. Especially interesting for the synthesis of new polyurethane elastomers are macrodiols (Table 1, no 4–14) due to their unimodality and relatively high molar masses. The preparation of rigid crosslinked polyurethanes can also be possible in the reaction of macrodiols with poly(diisocyanates). They also appear to be useful as macroinitiators for the synthesis of new triblock copolyether-diols.

3.2. Triblock Copolyether-Diols

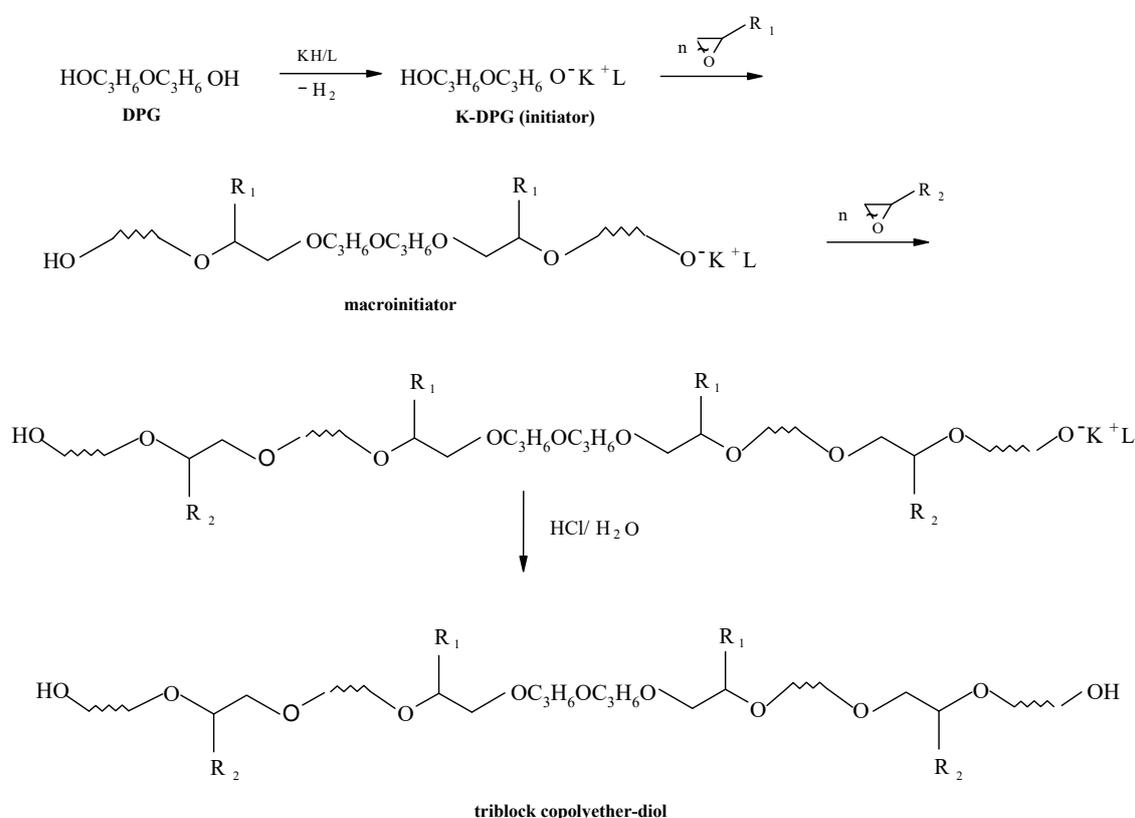
Several triblock copolyether-diols were synthesized using three macroinitiators based on PO(1), BO(4), and AGE(7). In each experiment, a macroinitiator was prepared by the ring-opening polymerization of the chosen monosubstituted oxirane (A) at $[A]_0 = 2.0 \text{ mol/dm}^3$, initiated with monopotassium dipropylene glycoide at $[I]_0 = 0.1 \text{ mol/dm}^3$ in the presence of macrocyclic ligand 18-crown-6 (K-DPG/L). After complete conversion of the monomer, the second oxirane (B) was added to the reaction mixture and underwent quantitative copolymerization. Six triblock copolyether-diols were obtained after neutralization with HCl/H₂O. The products were analyzed by several techniques. The SEC method indicated that all copolymers are unimodal. Their full characterization by this technique was shown in Table 2.

Table 2. Characterization data of triblock copolyether-diols by size exclusion chromatography (SEC) chromatography.

No.	Copolymer	Yield %	Reaction Time, h	Retention Time, min		$M_{\text{calc}}^a/$	M_n SEC	M_w/M_n SEC
				Macroinitiator	Copolymer			
15	PAGE/PPO/PAGE	99.4	150	7.60	6.90	3578	3400	1.16
16	PPGE/PPO/PPGE	99.2	160	7.60	6.81	4299	4000	1.09
17	PAGE/PBO/PAGE	99.5	225	7.21	6.59	3859	3600	1.18
18	PIPGE/PBO/PIPGE	99.0	220	7.21	6.61	3899	3700	1.17
19	PIPGE/PAGE/PIPGE	99.3	110	6.18	5.90	4740	4500	1.13
20	PBGE/PAGE/PBGE	99.1	145	6.18	5.62	5700	5200	1.10

$$^a/ M_{\text{calc}} = ([A]_0/[I]_0)M_A + ([B]_0/[I]_0)M_B + M_{\text{DPG}}$$

The copolymerization course involving the synthesis of initiator and macroinitiator is shown in Scheme 5.



Scheme 5. Preparation of triblock copolyether-diols by ring-opening polymerization of monosubstituted oxiranes, where: R_1 : CH_3 and R_2 : $\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$ or CH_2OPh (for copolymer 15 or 16), R_1 : CH_2CH_3 and R_2 : $\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$ or $\text{CH}_2\text{OCH}(\text{CH}_3)_2$ (for copolymer 17 or 18), R_1 : $\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$ and R_2 : $\text{CH}_2\text{OCH}(\text{CH}_3)_2$ or $\text{CH}_2\text{OCH}_2\text{Ph}$ (for copolymer 19 or 20).

In order to confirm the structure of macromolecules formed in the copolymerization, ^{13}C NMR spectroscopy was applied. Figure 10 shows, for example, the spectrum of PAGE/PPO/PAGE copolymer (1). It reveals strong signals of carbons present in polymer chains, i.e., CH_2 and CH (at 70–80 ppm), as well as substituents, i.e., CH_3 (at 17.3 ppm) and $\text{OCH}_2\text{CH}=\text{CH}_2$ (at 116.6 and 134.9 ppm). The signal of terminal carbon of the $\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2)\text{OH}$ group was identified at 68.62 and 69.01 ppm. However, signals of terminal carbon of $\text{CH}(\text{CH}_3)\text{OH}$ group (at 65.55 and 67.10 ppm) were not found in the spectrum.

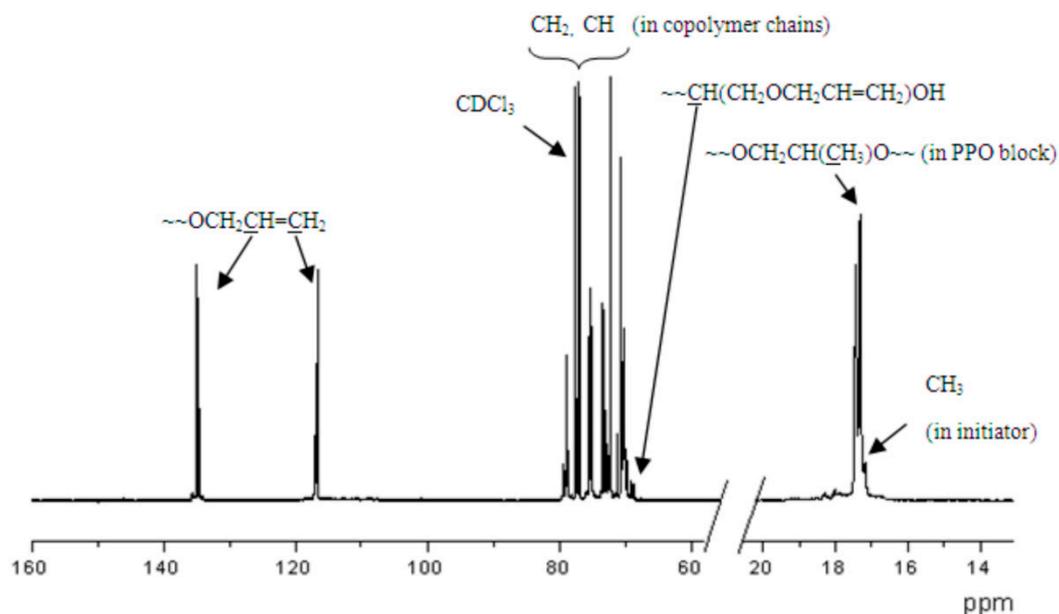


Figure 10. ^{13}C NMR spectrum of PAGE/PPO/PAGE triblock copolyether-diol (15).

The lack of ^{13}C NMR spectrum carbon signals of the end group derived from the macroinitiator indicated that, during the copolymerization, rapid cation exchange takes place. This allows polymer chains to grow in two directions. A similar phenomenon was observed in the copolymerization of other oxiranes.

It is also worth noting that, for systems containing AGE as a comonomer, ^{13}C NMR analysis of copolymers (Figure 11) indicated weak signals of *cis*-propenyloxy groups, i.e., $\text{OCH}=\text{CHCH}_3$ (at 101.1 and 145.9 ppm). This resulted from the isomerization of allyl groups under the influence of active centers of growing polymer chains (Table 3). This effect was observed, before now, in the homopolymerization of AGE mediated with anhydrous KOH-activated cation complexing agents [19].

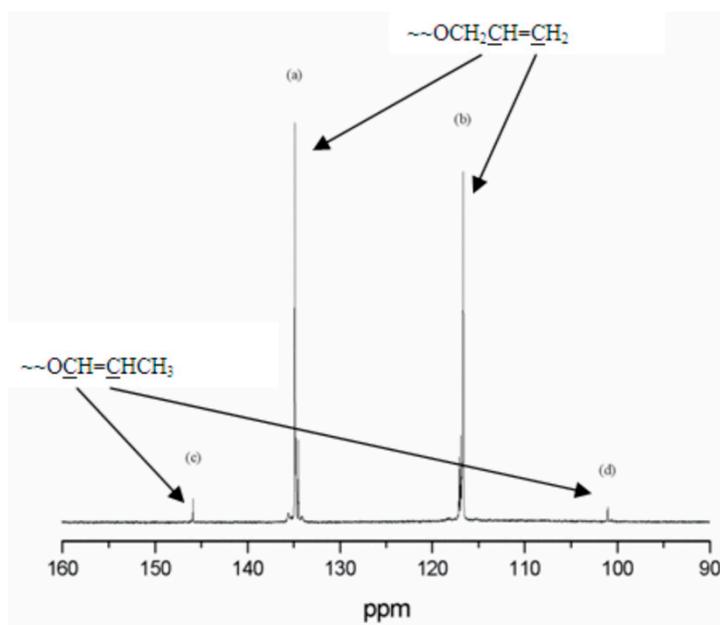
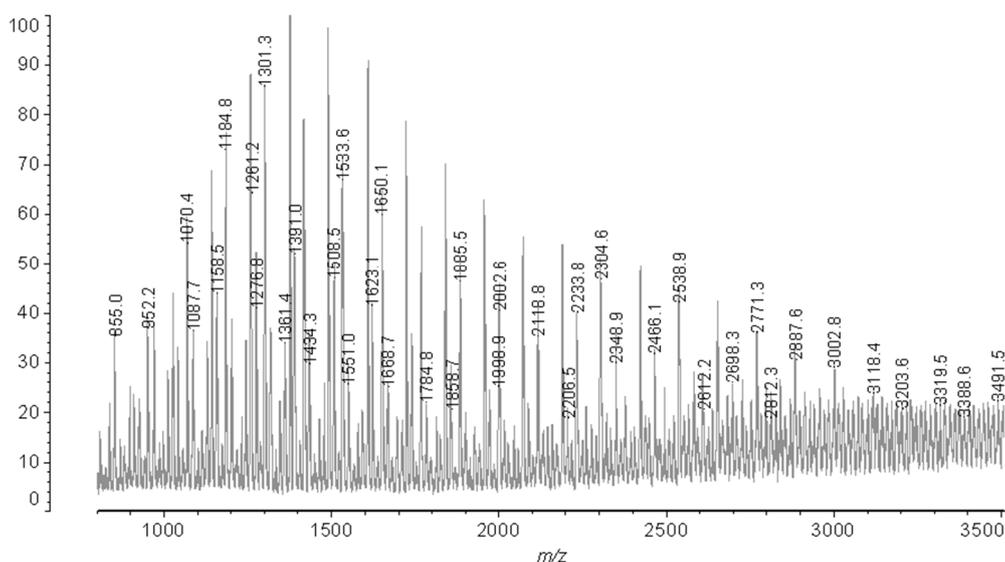


Figure 11. Signals of allyloxy (a,b) and *cis*-propenyloxy (c,d) groups observed in the unsaturated region of the ^{13}C NMR spectrum of PAGE/PBO/PAGE copolyether-diol (17).

Table 3. Content of *cis*-propenyloxy groups derived from isomerization of allyloxy groups in copolyether-diols.

No.	Copolymer	OCH ₂ CH=CH ₂ (mol %)	OCH=CHCH ₃ (mol %)
15	PAGE/PPO/PAGE	99.6	0.2
17	PAGE/PBO/PAGE	94.9	5.1
19	PIPGE/PAGE/PIPGE	97.5	2.5
20	PBGE/PAGE/PBGE	97.2	2.8

Employing MALDI-TOF mass spectrometry for the analysis of copolymers allows us to obtain additional data about the structure of macromolecules formed during the process. Figure 12 presents, for example, the MALDI-TOF spectrum of PIPGE/PBO/PIPGE-diol (18).

**Figure 12.** MALDI-TOF spectrum of PIPGE/PBO/PIPGE-diol (18).

Several signals revealed in the spectrum represent macromolecules containing a block of PBO and two blocks of PIPGE, which possess a central fragment $-\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}-$ derived from the initiator and two end OH groups. They form adducts with sodium ions. Characterization data of this copolymer involving the main macromolecules at m/z 1301.3 to 4802.9 are shown in Table 4. Signals of the highest intensities ($>40\%$) represent macromolecules containing 3–29 mers of BO and 7–28 mers of IPGE. Macromolecules (1–12) possessing 3, 4, 7, 14, 17, and 20 mers of BO contain $\geq 50\%$ of IPGE mers. On the other hand, macromolecules with 21, 22, and 26–29 mers of BO contain $\leq 50\%$ of IPGE mers. The average ratio of BO/IPGE is 40/60.

Another example is PIPGE/PAGE/PIPGE-diol (19), for which the MALDI-TOF spectrum is shown in Figure 13.

Several signals in the spectrum represent macromolecules that form adducts with sodium ions. Characterization data of this copolymer, involving the main macromolecules at m/z 2932.1 to 5220.4, are presented in Table 5. Signals of the highest intensity ($>40\%$) represent macromolecules with 6–27 mers of AGE and 14–23 mers of IPGE. Macromolecules (1–7) possessing 6, 9, 12, or 15–17 mers of AGE contain $>50\%$ of IPGE mers, whereas macromolecules with 18, 20, 21, 23, 24, or 27 mers of AGE contain $<50\%$ of IPGE mers. The average ratio of AGE/IPGE is 50/50 in this case.

Table 4. Composition of PIPGE/PBO/PIPGE triblock copolyether-diol (18) determined by MALDI-TOF mass spectrometry.

No.	Formula ^a	Intensity of Signal (>40%)	m/z (MALDI-TOF)	m/z (calc)	BO/IPGE (mol %/mol %)
1	IPGE ₄ BO ₃ IPGE ₄	82.3	1301.3	1302.8	27/73
2	IPGE ₅ BO ₃ IPGE ₅	47.7	1535.6	1535.1	23/77
3	IPGE ₆ BO ₃ IPGE ₅	76.3	1650.1	1651.3	21/79
4	IPGE ₈ BO ₃ IPGE ₈	81.7	2233.8	2232.1	16/84
5	IPGE ₈ BO ₄ IPGE ₈	40.2	2304.6	2304.1	20/80
6	IPGE ₁₄ BO ₄ IPGE ₁₃	56.4	3580.0	3581.8	13/87
7	IPGE ₄ BO ₇ IPGE ₃	100	1360.4	1358.9	50/50
8	IPGE ₁₄ BO ₇ IPGE ₁₄	50.8	3798.7	3798.3	20/80
9	IPGE ₁₃ BO ₁₄ IPGE ₁₂	64.3	4069.0	4069.7	36/64
10	IPGE ₁₁ BO ₁₇ IPGE ₁₀	42.9	3823.8	3822.4	45/55
11	IPGE ₁₂ BO ₁₇ IPGE ₁₁	43.5	4055.3	4054.7	42/58
12	IPGE ₁₁ BO ₂₀ IPGE ₁₀	40.1	4037.8	4038.7	49/51
13	IPGE ₈ BO ₂₁ IPGE ₈	41.8	3530.0	3530.0	57/43
14	IPGE ₁₀ BO ₂₁ IPGE ₉	57.0	3879.8	3878.5	53/47
15	IPGE ₁₁ BO ₂₂ IPGE ₁₁	44.1	4299.7	4299.1	50/50
16	IPGE ₁₁ BO ₂₆ IPGE ₁₀	51.1	4470.5	4471.4	55/45
17	IPGE ₈ BO ₂₇ IPGE ₇	47.4	3846.0	3846.5	64/36
18	IPGE ₁₀ BO ₂₈ IPGE ₁₀	45.4	4500.1	4499.5	58/42
19	IPGE ₉ BO ₂₉ IPGE ₈	40.3	4223.5	4223.1	63/37
20	IPGE ₁₁ BO ₂₉ IPGE ₁₁	51.7	4802.9	4803.9	57/43

^a The formula does not involve the fragment $-OC_3H_6OC_3H_6O-$, derived from the initiator as well as two end H atoms.

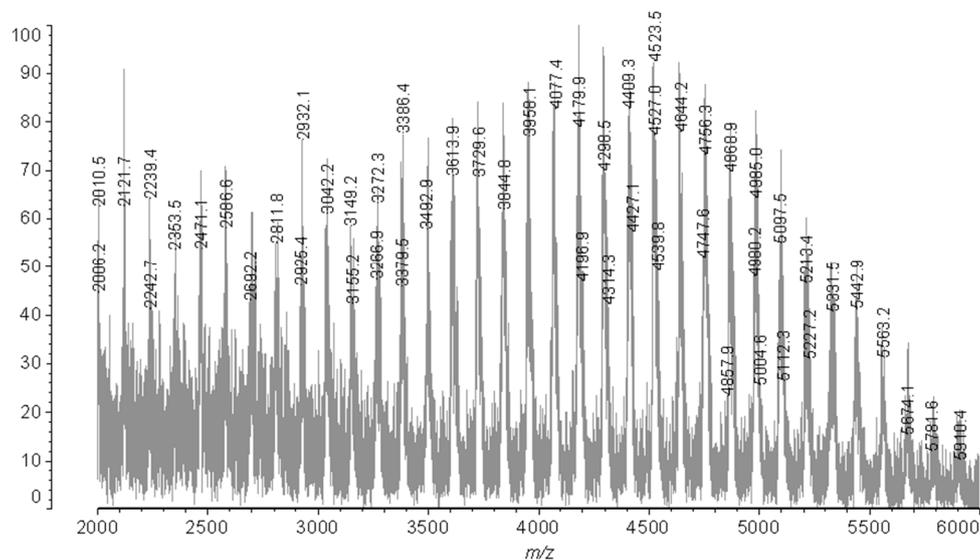


Figure 13. MALDI-TOF spectrum of PIPGE/PAGE/PIPGE-diol (19).

Table 5. Composition of PIPGE/PAGE/PIPGE triblock copolyether-diol (19) determined by MALDI-TOF mass spectrometry.

No.	Formula ^a	Intensity of the Main Signal (>40%)	m/z (exp)	m/z (calc)	AGE/IPGE (mol %/mol %)
1	IPGE ₉ AGE ₆ IPGE ₉	49.3	2932.1	2932.9	25/75
2	IPGE ₁₂ AGE ₅ IPGE ₁₁	74.4	3856.5	3856.1	28/72
3	IPGE ₉ AGE ₁₂ IPGE ₉	43.9	3618.3	3617.7	40/60
4	IPGE ₁₀ AGE ₁₂ IPGE ₉	42.1	3734.0	3733.9	39/61
5	IPGE ₁₀ AGE ₁₅ IPGE ₉	100	4077.4	4076.3	44/56
6	IPGE ₉ AGE ₁₆ IPGE ₈	42.0	3958.1	3958.1	49/51
7	IPGE ₁₀ AGE ₁₇ IPGE ₉	68.1	4304.4	4304.6	47/53
8	IPGE ₈ AGE ₁₈ IPGE ₇	59.6	3954.4	3953.9	55/45
9	IPGE ₇ AGE ₂₀ IPGE ₇	93.5	4065.5	4065.9	60/40
10	IPGE ₉ AGE ₂₁ IPGE ₉	76.7	4644.2	4644.7	54/46
11	IPGE ₈ AGE ₂₃ IPGE ₇	69.6	4523.5	4524.4	60/40
12	IPGE ₁₁ AGE ₂₃ IPGE ₁₀	45.7	5220.4	5221.4	52/48
13	IPGE ₉ AGE ₂₄ IPGE ₈	71.7	4869.0	4870.9	60/40
14	IPGE ₇ AGE ₂₇ IPGE ₆	88.1	4747.6	4748.7	68/32
15	IPGE ₈ AGE ₂₇ IPGE ₈	40.1	5097.5	5097.7	63/37

^a The formula does not involve the fragment $-\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}-$, derived from the initiator as well as two end H atoms.

3.3. Random Copolyether-Diols

Additional, three new random copolyether-diols were synthesized in this study by using monopotassium salt of dipropylene glycol as an initiator, which was activated by macrocyclic ligand 18-crown-6 (K-DPG/L). In all systems, the initial concentration of each monomer was 2.0 and the initial concentration of each initiator was 0.1 mol/dm³. Two monosubstituted oxiranes as comonomers were mixed and added to the initiator solution in tetrahydrofuran. After several hours at room temperature, this results in copolyether-diols after protonation (Scheme 6).



where: (a) A:BO and B:BGE
 (b) A:PO and B:PGE
 (c) A:AGE and B: PGE
 L: 18C6

Scheme 6. Preparation of initiator and random copolyether-diols by ring-opening copolymerization of monosubstituted oxiranes.

The products obtained were analyzed by several methods. The SEC method indicated that all copolymers are unimodal. Their characterization is shown in Table 6.

Table 6. Characterization of copolyether-diols by SEC technique.

No.	Copolymer	Yield (%)	Reaction Time, h	M _{calc} ^a	M _n (SEC)	M _w /M _n (SEC)
21	BO/BGE	99.7	250	4850.4	4500	1.11
22	PO/PGE	98.9	165	4299.2	4100	1.15
23	AGE/PGE	99.2	120	5420.4	5100	1.18

^a M_{calc} = ([A]₀/[I]₀)M_A + ([B]₀/[I]₀)M_B + M_{DPG}.

In general, the ^{13}C NMR spectra of copolymers reveal strong signals of carbons present in polymer chains (CH_2 and CH) and substituents, as well as weak signals in carbons' terminal groups (Table 7).

Table 7. ^{13}C NMR chemical shifts (in ppm) of terminal carbons present in copolyether-diols.

No.	Copolymer	$\delta_{\text{CH(R)OH}}$ (Chain)
21	BO/BGE	73.46 and 73.70 69.36
22	PO/PGE	65.55 and 67.10 69.42
23	AGE/PGE	68.62 and 69.1 69.42

Weak signals of CH_3 carbons derived from initiator were observed in the ^{13}C NMR spectrum at 17.3 ppm of copolymers (21) and (23). The lack of signals from the terminal carbon of the $\text{CH}(\text{CH}_3)\text{OH}$ group from the initiator at 65.0 and 67.1 ppm indicated that propagation occurs in two directions. This is possible due to cation exchange reaction. In the spectrum of copolymer (22), carbon signals of the allyl group (at 117.0 and 136.0 ppm) were not found, which indicated that the chain transfer reaction to PO did not occur. However, in the spectrum of copolymer (23), weak signals of *cis*-propenyloxy groups were shown (at 101.0 and 146.0 ppm), resulting from isomerization of the allyloxy groups in the substituent.

Analysis of copolymers by MALDI-TOF mass spectrometry provided additional data concerning their structure. The spectrum of the BO/BGE copolymer is shown in Figure 14.

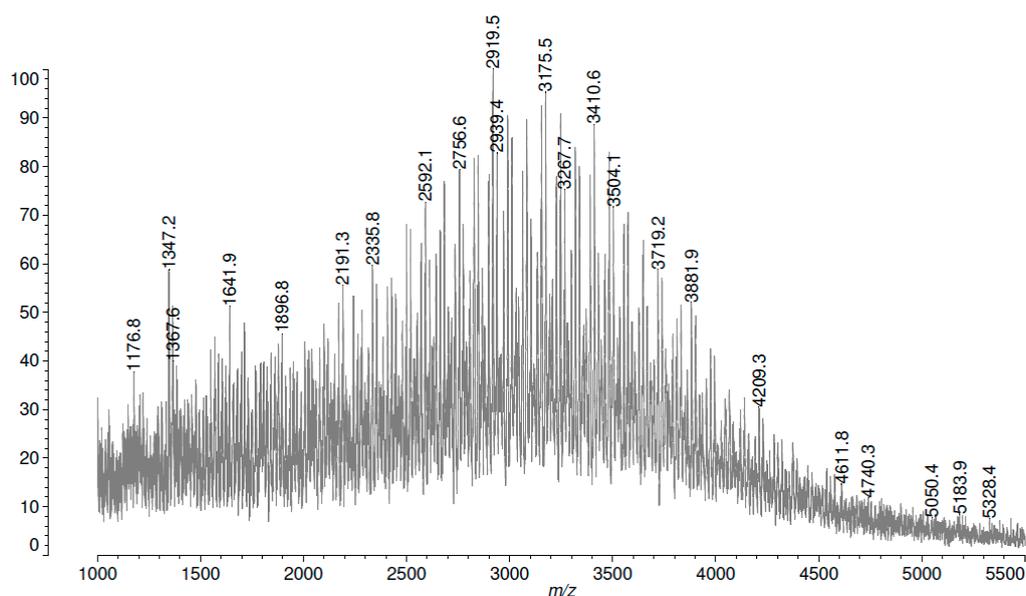


Figure 14. MALDI-TOF spectrum of BO/BGE copolyether-diol (21).

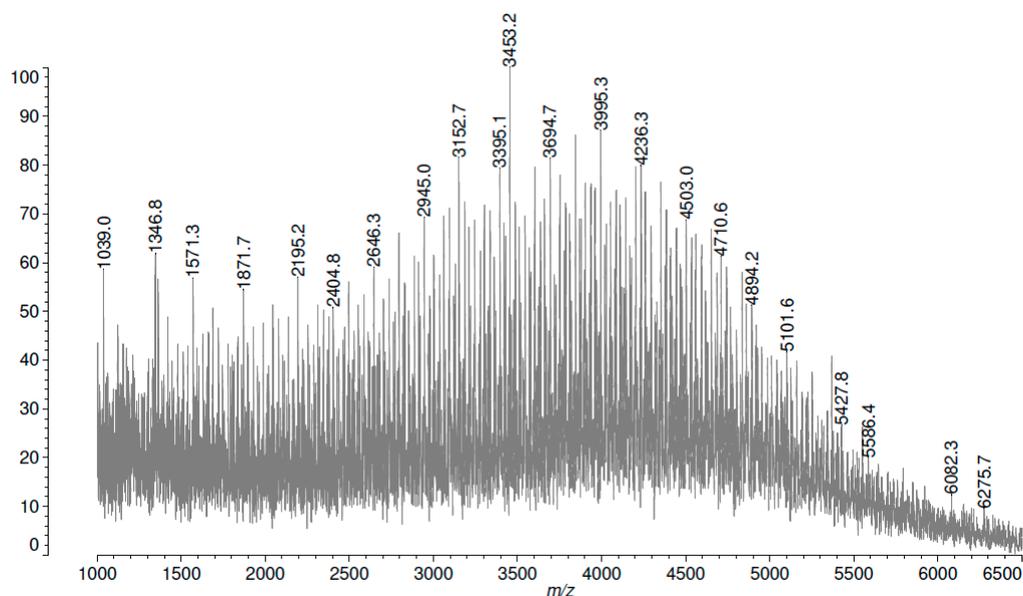
Several signals were observed in the spectrum at m/z 1500 to 4000. They represent macromolecules containing central fragment $-\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}-$ derived from the initiator, two end H atoms, and various numbers of mers of both monomers. The composition of copolyether-diols that form adducts with sodium ions was determined and is presented in Table 8. Macromolecules containing 9–14 mers of BO and 9–16 mers of BGE were identified with an average BO/BGE ratio of 1/1. Signals of homopolymers, i.e., PBO-diols and PBGE-diols, were not found in the spectrum.

Table 8. Composition of BO/BGE random copolyether-diol (21) determined by MALDI-TOF mass spectrometry.

No.	Formula ^a	Number of BGE Mers (<i>n</i>) and Intensities of the Main Signals (>40%) ^b	Signals of Highest Intensity (>40%)		
			m/z (exp)	m/z (calc)	BO/BGE (mol %/mol %)
1	BO ₉ BGE _n	9 (49.1), 13, 15, 16	2191.3	2193.3	50/50
		5, 10, 11 (47.6)	2683.7	2685.2	48/52
2	BO ₁₀ BGE _n	14 (83.3)	3176.5	3177.1	42/58
		15 (70.2)	3338.6	3340.7	40/60
		8, 12 (100)	2919.5	2920.9	48/5
3	BO ₁₁ BGE _n	14 (86.5)	3248.8	3249.3	44/56
		15 (52.0)	3412.6	3413.5	43/57
		16 (45.2)	3574.9	3577.0	40/60
4	BO ₁₂ BGE _n	12 (78.0)	2991.0	2993.0	50/50
		14, 15 (66.0)	3484.1	3485.6	44/56
5	BO ₁₃ BGE _n	12 (67.7)	3064.5	3065.1	52/48
		13 (62.6)	3228.3	3229.3	50/50
6	BO ₁₄ BGE _n	11 (40.1)	2974.5	2973.0	56/44

^a The formula does not involve the fragment $-\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}-$, derived from the initiator as well as two end H atoms. ^b The intensities of other signals are 10–40%.

Figure 15 presents the MALDI-TOF spectrum of the PO/PGE copolymer.

**Figure 15.** MALDI-TOF spectrum of PO/PGE copolyether-diol (22).

The spectrum of this copolymer reveals several peaks in the range of m/z 1000 to 5500. The composition of copolyether-diols that form adducts with sodium ions was determined (Table 9). Macromolecules containing 2–8 mers of PO and 16–28 mers of PGE were identified. In all macromolecules, the PO/PGE ratio is about 1/4. This means that PO indicates the tendency to homopolymerization. Indeed, several signals of PPO-diols were identified in the spectrum (Table 10). Homopolymers of PO contain a relatively high number of mers, i.e., in the range 45–81.

Table 9. Composition of PO/PGE random copolyether–diol (22) determined by MALDI-TOF mass spectrometry.

No.	Formula	Number of PGE Mers (<i>n</i>) and Intensities of the Main Signals (>40%)	Signals of Highest Intensity (>40%)		
			m/z (exp)	m/z (calc)	PO/PGE (mol %/mol %)
1	PO ₂ PGE _n	22 (55.3), 23, 24 26, 27	3578.3	3577.1	8/92
		16, 19 (78.4)	3185.2	3184.6	14/86
2	PO ₃ PGE _n	24(48.9)	3936.1	3935.5	11/89
		25(42.2)	4086.2	4085.7	11/89
		26, 27(43.9)	4386.5	4386.0	10/90
		19, 20 (92.7)	3393.1	3392.0	17/83
3	PO ₄ PGE _n	23 (60.1)	3844.4	3843.4	15/85
		24 (60.9)	3995.3	3993.6	14/86
		25 (69.1)	4144.3	4143.7	14/86
		27 (58.5), 28	4445.4	4444.1	13/86
		18 (55.4), 19	3152.7	3150.7	21/79
		20 (100), 21	3453.2	3451.0	20/80
4	PO ₅ PGE _n	23 (87.2)	3902.3	3901.5	18/82
		24 (80.9), 25	4052.1	4051.7	17/83
		26 (87.8)	4352.7	4352.0	16/84
		27 (78.5)	4503.0	4502.2	16/84
		28 (56.2)	4652.5	4662.3	15/84
5	PO ₆ PGE _n	16, 20, 21, 22 24, 25 (70.4)	4260.5	4259.7	19/81
		26, 27 (66.7)	4559.9	4560.4	18/82
		28 (60.6)	4710.6	4710.2	16/84
6	PO ₇ PGE _n	19, 21, 22, 24, 28			
7	PO ₈ PGE _n	24, 25			

Table 10. PPO-diols accompanied by PO/PGE copolymerization initiated with K-DPG/L.

No.	Formula	Intensities of the Main Signals (>10%)	m/z (exp)	m/z (calc)
1	PO ₄₅	34.8	2772.4	2770.9
2	PO ₄₇	42.0	2886.9	2887.0
3	PO ₄₉	48.1	3003.1	3003.2
4	PO ₅₀	69.4	3061.9	3061.3
5	PO ₅₁	19.2	3119.8	3119.4
6	PO ₇₆	27.2	4570.7	4571.4
7	PO ₇₉	58.2	4744.6	4745.6
8	PO ₈₁	30.7	4860.4	4861.8

Figure 16 shows the MALDI-TOF spectrum of the AGE/PGE copolymer.

Several signals were present in the spectrum in the range of m/z 1000 to 6000 (Table 11). They represent macromolecules of copolyether-diols containing 7 or 12–14 mers of AGE and 4–24 mers of PGE were identified. For example, macromolecules containing 14 mers of AGE contain 5–23 mers of PGE. Analysis of the spectrum also indicated signals that represent homopolymers, i.e., PAGE-diols and PPGE-diols (Tables 12 and 13).

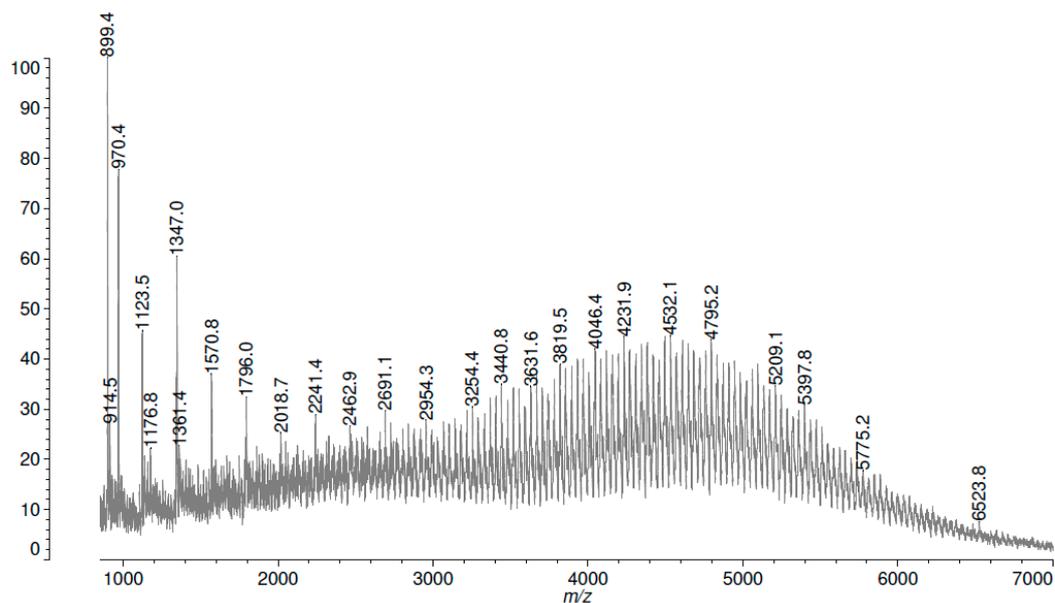


Figure 16. MALDI-TOF spectrum of AGE/PGE copolyether-diol (23).

Table 11. Composition of AGE/PGE random copolyether-diol determined by MALDI-TOF mass spectrometry.

No.	Formula	Number of PGE Mers (<i>n</i>) and Intensities of the Main Signals (>40%)	Signals of Highest Intensity (>40%)		
			m/z (exp)	m/z (calc)	AGE/PGE (mol %/mol %)
1	AGE ₇ PGE _n	7, 13, 14, 15, 16, 17, 18 (80.3)	3668.9	3669.3	28/72
		19, 20(72.7), 21, 23	3969.2	3969.6	26/74
		24(78.3)	4571.0	4570.2	22/78
		4, 7, 9, 14, 15 (64.5)	3780.1	3779.4	44/56
2	AGE ₁₂ PGE _n	16, 17, 18 (54.8)	4230.9	4229.9	40/60
		19 (100)	4381.5	4381.5	39/61
		20 (96.6)	4532.1	4530.3	38/62
		21, 22, 23(58.8)	4981.7	4980.8	37/63
3	AGE ₁₃ PGE _n	24 (60.6)	5130.1	5130.9	36/64
		4, 6, 7, 9, 18, 20	4795.2	4794.6	38/62
		21(41.2), 22, 23, 24			
		5, 6, 7, 11, 15, 16			
4	AGE ₁₄ PGE _n	18 (77.2)	4459.1	4458.2	44/56
		20 (68.6), 21	4759.5	4758.5	41/59
		22 (50.0)	5059.6	5058.9	39/61
		23 (50.6)	5209.1	5209.0	38/62

Table 12. PAGE-diols accompanied by AGE/PGE copolymerization initiated with K-DPG/L.

No.	Formula	Intensities of the Main Signals (>10%)	m/z (MALDI-TOF)	m/z (calc)
1	AGE ₃₄	10.1	4039.7	4038.9
2	AGE ₃₅	16.7	4153.8	4153.1
3	AGE ₃₆	10.5	4268.5	4267.2
4	AGE ₃₇	99.9	4382.5	4381.4
5	AGE ₃₈	89.9	4496.2	4495.5
6	AGE ₃₉	67.8	4610.2	4609.6
7	AGE ₄₀	13.1	4722.5	4723.8

Table 13. PPGE-diols accompanied AGE/PGE copolymerization initiated with K-DPG/L.

No.	Formula	Intensities of the Main Signals (>10%)	m/z (MALDI-TOF)	m/z (calc)
1	PGE ₂₇	12.2	4212.2	4211.8
2	PGE ₂₈	15.2	4362.0	4361.9
3	PGE ₂₉	16.1	4511.3	4512.1
4	PGE ₃₂	10.2	4961.1	4962.6
5	PGE ₃₃	10.7	5111.5	5112.8
6	PGE ₃₄	14.6	5261.0	5262.9

All the results derived from the MALDI-TOF MS analysis confirmed the presence of a copolymeric structure in the studied random copolyether-diols, with a lack of homopolymeric diol macromolecules for BO/BGE, and some of them for the PO/PGE and AGE/PGE systems.

4. Conclusions

The application of monopotassium dipropylene glycoxide activated 18C6 for anionic ring-opening polymerization of monosubstituted oxiranes allowed us to prepare several kinds of new macrodiols. These are homopolyether-diols and copolyether-diols, i.e., triblock and random ones, which were characterized by SEC, ¹³C NMR, MALDI-TOF, and FTIR techniques. The main conclusions are as follows:

- It is possible to initiate polymerizations of the discussed oxiranes in mild homogeneous conditions, i.e., in THF solution at room temperature and normal pressure.
- The growth of polymer chains occurs in two directions due to cation exchange reaction.
- Synthesized macrodiols are unimodal and have $M_n \approx M_{calc}$ (1500–8300) and low dispersity ($M_w/M_n = 1.08–1.18$).
- Monopotassium salts of homopolyether-diols, i.e., PPO-diol, PBO-diol, and PAGE-diol, appeared to be useful macroinitiators for the preparation of new triblock copolyether-diols from glycidyl ethers.
- In BO/BGE, random copolymerization initiated with K-DPG/18C6 macromolecules of copolyether-diol formed exclusively.
- Macromolecules of copolyether-diol and also homopolyether PPO-diol were identified in the PO/PGE system.
- AGE and PGE comonomers reacted to create random copolyether-diol as well as homopolymers, i.e., PAGE-diol and PPGE-diol.
- Several prepared homopolymer-diols and copolyether-diols could be useful for the fabrication of new thermoplastic or crosslinked polyurethanes.

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