



Ring-opening polymerization of monosubstituted oxiranes in the presence of potassium hydride: determination of initiation course and structure of macromolecules by MALDI-TOF mass spectrometry

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Received: 17 April 2019 / Accepted: 10 October 2019 / Published online: 20 November 2019
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Abstract

Several monosubstituted oxiranes were polymerized with suspension of potassium hydride (KH) in tetrahydrofuran (THF) at room temperature. This heterogeneous process resulted in polyethers with various starting groups depending on the kind of monomer. The macromolecules formed in ring-opening polymerization of monosubstituted oxiranes were analyzed by Matrix Assisted Laser Desorption/Ionization - Time of Flight Mass Spectrometry (MALDI-TOF MS). It was stated, that initiation of propylene oxide (PO) polymerization with KH proceeded via three ways, i.e. cleavage of oxirane ring in the β -position, monomer deprotonation and deoxygenation. Potassium isopropoxide, potassium allyloxide and potassium hydroxide were the real initiators. The main reactions, which occur in the initiation step, depend on the type of monomer used. In the case of allyl glycidyl ether (AGE) and phenyl glycidyl ether (PGE) deprotonation of the monomer did not occur. During initiation of glycidyl ethers oxirane ring was opened and also linear ether bond between glycidyl group and oxygen atom was cleaved under influence of KH. Interestingly, formation of new kinds of macromolecules was observed in the systems containing glycidyl ethers, which do not possess mers of the monomers used. Mechanisms of the studied processes were presented and discussed. Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) was used as supporting technique for analysis of the obtained polymers. Number average molar masses of the polymers (M_n) determined by Size Exclusion Chromatography (SEC) were about two times higher than calculated ones. It indicated that half of used KH did not take part in the initiation step.

Keywords Potassium hydride · Anionic ring-opening polymerization · Oxiranes · MALDI-TOF spectrometry · Polyethers

Introduction

Polyethers are important class of synthetic polymers, which are applied in many areas of industry and medicine. They are synthesized by ring-opening polymerization of oxiranes [1–3]. The most useful is anionic polymerization of ethylene oxide (EO) and propylene oxide (PO) due to wide utility of the polymers obtained [1, 4]. Some of expected application are their use as

impact modifiers, surfactants, dispersants, fuel additives, wetting agents, lubricants, rheological modifiers, biomedical application, adhesives [5–7], de-emulsifiers [8] and components in the fabrication of block copolymers and polyurethane elastomers or foams [3, 4, 9]. Initiators most frequently used for polymerization of monosubstituted oxiranes, e.g. PO are potassium hydroxide [10–12] and potassium salts of alcohols, glycols or glycerol [13–15]. In some cases cation complexing agents, e.g. coronand 18-crown-6 were applied for activation of chain growth centers [14, 16, 17]. Other salts for example potassium potasside $\text{K}^+(15\text{-crown}5)_2\text{K}^-$ [18, 19] or potassium hydride K^+H^- /activated with various crown ethers [20–23] were also used for initiation of the polymerization of many oxiranes. Among saline hydrides KH appeared to present the optimum balance of potential reactivity and potential considerations [24]. The solvents, which are most suitable for reactions of KH are ethers, especially tetrahydrofuran (THF). All

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reactions, in which KH is extremely reactive as a base proceed at the crystal surface apparently. Prolonged stirring of KH with THF, followed by decantation, reveals no detectable dissolved hydride [24]. However, many of the potassium salts produced by use of KH are moderately to highly soluble in THF. In the previous work [22] it was shown that the initiation and propagation reactions take place on the surface of the potassium hydride. The initiation occurs as long as the monomer is present in the reaction mixture. The cavity size of 18-crown-6 is most suitable to form 1:1 complex with potassium cation, which can exist both in solution and on hydride surface. Other ligands as 15-crown-5 or 12-crown-4 form in the solution sandwich composed of 2:1 complex. However, the existence of such complexes on the surface of solid phase is not possible [20]. In this case 1:1 complex could be exclusively formed. In consequence, the effects related to heterogeneity of polymerization influence the reaction rate and number average molecular masses of PPOs. Then, Stolarzewicz et al. [25] proposed the course of PO polymerization mediated with KH. The authors observed, that in this system potassium isopropoxide and unexpectedly, potassium hydroxide were formed, which became the real initiators of the polymerization. The course of the polymerization of other oxiranes was not studied. Therefore, in this work we decided to determine in details the mechanism of propylene oxide polymerization initiated with KH and, comparatively, also other oxiranes, i.e. allyl glycidyl ether (AGE) and phenyl glycidyl ether (PGE). Especially interesting are glycidyl ethers, because of the fact that these monomers possess two kinds of ether bonds, i.e. cyclic and linear ones. The latter could be also cleaved under influence of hydride anion resulting in new kinds of macromolecules. All processes were carried out in THF solution at room temperature under argon atmosphere. SEC, ^{13}C NMR and MALDI-TOF techniques were used for analysis of the obtained polymers.

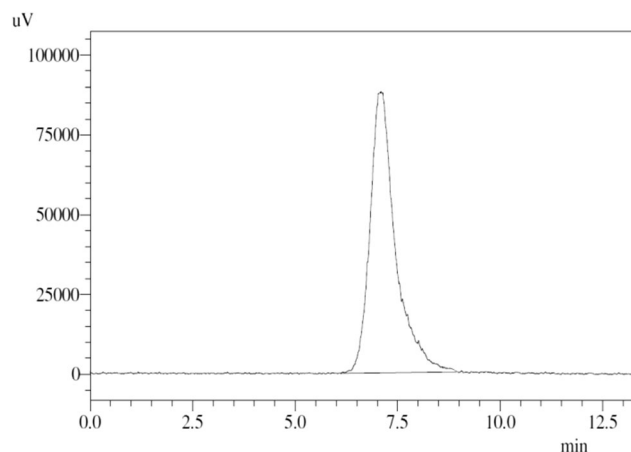


Fig. 1 SEC chromatogram of methylated PPO prepared in the presence of KH

Experimental

Materials

Monomers, i.e. propylene oxide, allyl glycidyl ether and phenyl glycidyl ether (all from Aldrich, Poland) were dried over CaH_2 and distilled at 306 K (33 °C), 427 K (154 °C) and 518 K (245 °C), respectively. Anhydrous tetrahydrofuran (THF) (Acros Organics, Poland) was kept over CaH_2 and distilled at 339 K (66 °C) and redistilled over Na/K alloy prior to use. Potassium hydride (KH) (Aldrich, Poland) was purified according to the procedure described by Brown [17]. The KH present was determined by a standard gas law calculation of the hydrogen liberated ($1.0 \text{ H}_2 = 1.0 \text{ KH}$). Very low excess (<1%) of total base over hydride base (from gas evolution after stirring with 2-butanol) indicated little hydrolysis of the original KH sample.

Table 1 Characterization of polyethers synthesized with use of potassium hydride in THF; $[\text{monomer}]_0 = 2.0 \cdot 10^3 \text{ mmol/mL}$ and $[\text{initiator}]_0 = 100 \text{ mmol/L}$.

Polymer	Monomer	Yield (%)	M_n SEC (Da)	M_w/M_n (SEC)	M_n (calcd.) ^{a/}	Initiation efficiency (f) ^{b/}	Time of reaction (h)
PPO		99.0	2300	1.15	1161.6	0.50	700
PAGE		99.3	4400	1.19	2282.8	0.52	330
PPGE		98.7	5700	1.23	3002.4	0.53	420

^{a/} $M_n(\text{calcd.}) = ([\text{mon}]_0 / [\text{KH}]_0) \cdot M_{\text{mon}}$

^{b/} $f = M(\text{calcd}) / M_n(\text{SEC})$

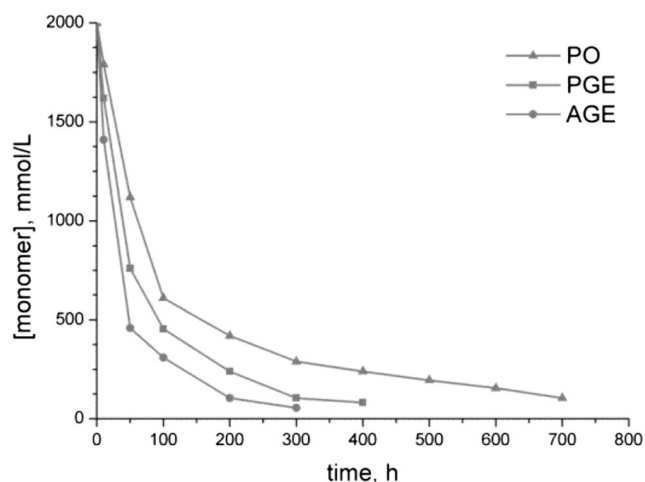
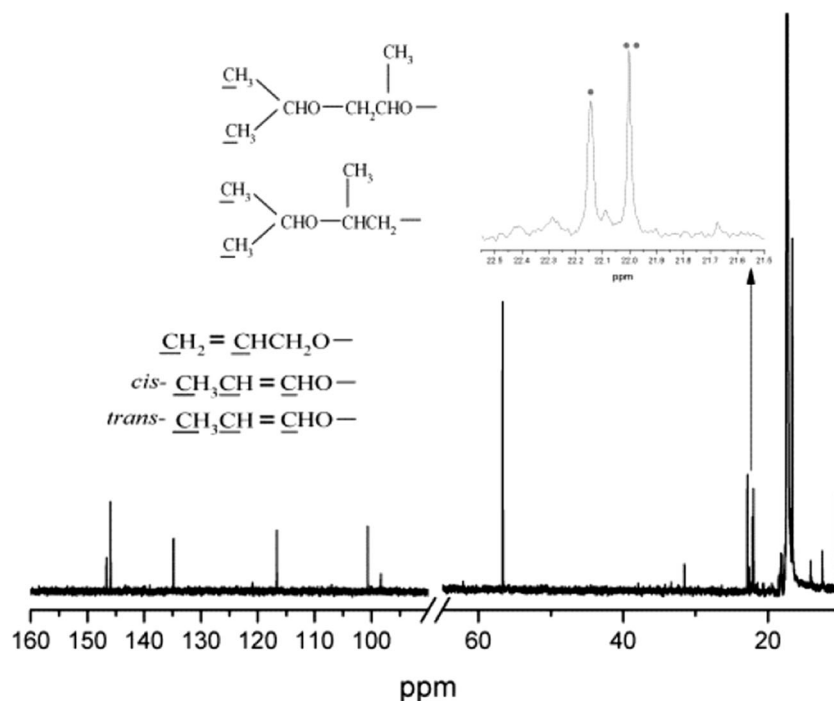


Fig. 2 Monomer concentration vs time for the polymerization of PO (1), PGE (2) and AGE (3) initiated with KH in THF, $[\text{monomer}]_0 = 2.0 \cdot 10^3$ mmol/mL, $[\text{initiator}]_0 = 100$ mmol/L

Synthesis

All syntheses were carried out at room temperature in a 50 mL reactor equipped with a magnetic stirrer and a Teflon valve enabling substrates delivery and sampling under argon atmosphere. For example, potassium hydride (0.08 g, 2.0 mmol) and tetrahydrofuran (17.0 mL) were introduced into the reactor and then propylene oxide (2.8 mL, 2.3 g, 40 mmol) was added. The reaction mixture was stirred during several days until all monomer was converted. During the polymerization gaseous product was evolved. After ending of the process some unreacted KH was present in the reactor. Then, CH_3I

Fig. 3 ^{13}C NMR spectrum of methylated PPO involving carbon signals of starting and end groups

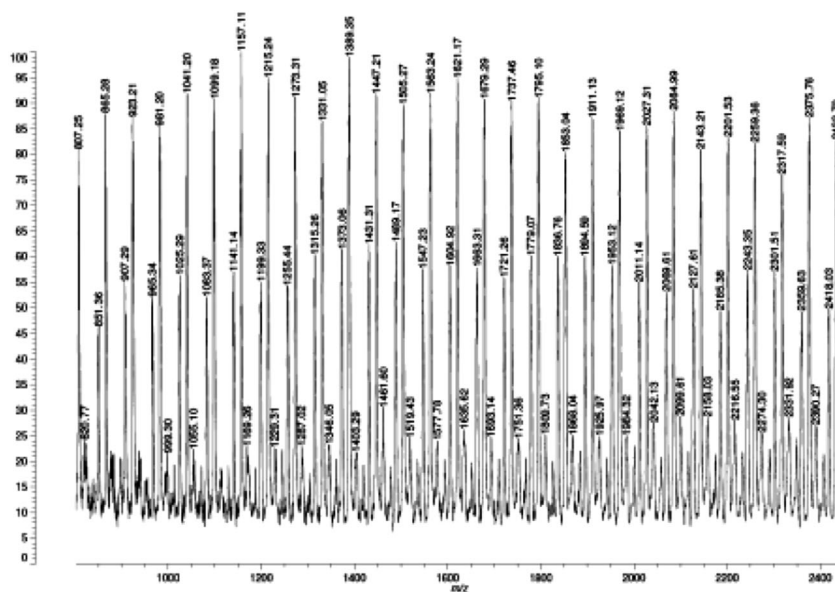


as quenching agent was added to the system and stirred during 10 min. After separation of solution from precipitated KI polymer was obtained by evaporation of solvent in vacuum. The concentration of monomer during polymerization was monitored by the 1,4-dioxane method [26]. Chromatographic method indicated the presence of hydrogen in gaseous phase and propylene in liquid phase. The final conversion was ~99% and the yield of PPO obtained was ~98%. In the next experiments other polyethers, namely PAGE and PPGE were synthesized in the same conditions at initial concentration of monomer $[\text{M}]_0 = 2.0 \cdot 10^3$ mmol/mL and initiator $[\text{I}]_0 = 100$ mmol/L.

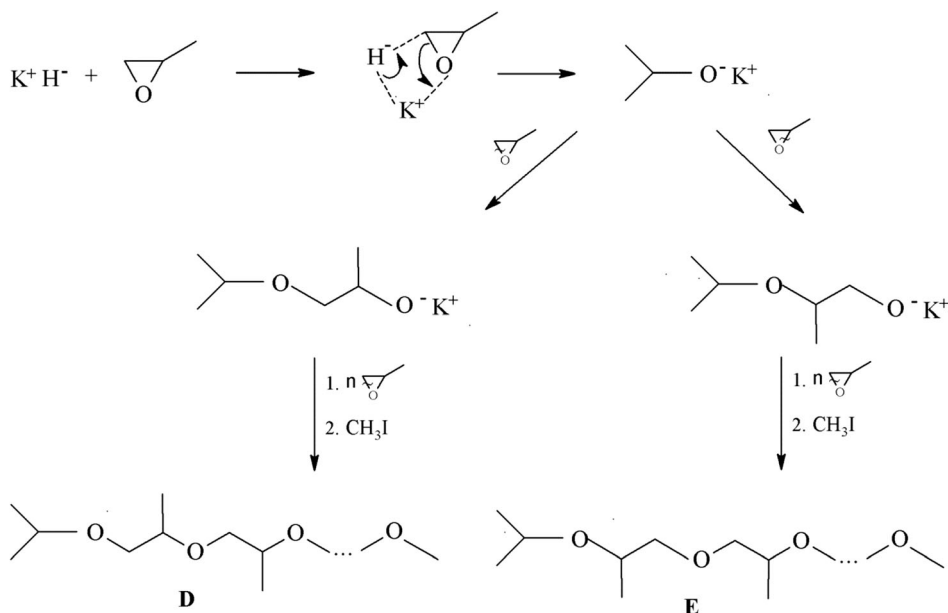
Measurements

100 MHz ^{13}C NMR spectra were recorded in CDCl_3 at 25 °C on a BrukerAvance 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 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. Number average 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 \times 8 mm OHpac column using tetrahydrofuran as a solvent. Polystyrenes were used as calibration standards. Matrix-assisted laser desorption/ionization-time of

Fig. 4 Part of MALDI-TOF spectrum of methylated PPO

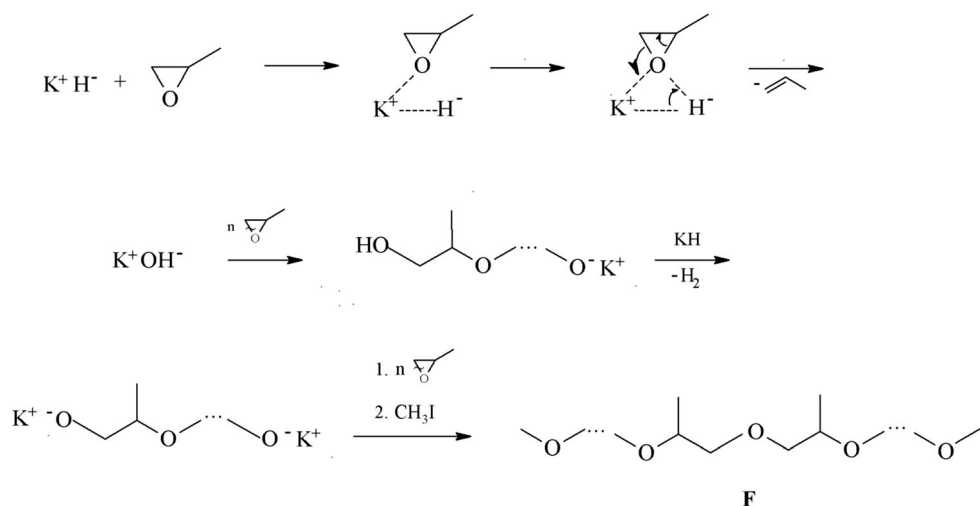


Scheme 2 Polymerization of PO initiated with KH, which behaves as nucleophilic reagent [23]



Molar masses of the polymers obtained were about two times higher, than calculated ones due to the fact, that half part of initial amount of KH used as initiator remains unreacted. One of the reason of this phenomenon could be formation of nonactive higher aggregates by KH molecules in the reaction mixture containing several chemical species, i.e. solvent, monomer and polymers. The latter could strongly influence the polarity of the system. Similar phenomena was observed previously for polymerization of the same monomers initiated with KH activated by 18-crown-6 in the tetrahydrofuran. Polar and steric effects of substituent in monomer molecule influencing on rate of polymerization was responsible for this effect [21]. Dispersities of the polymers were relatively high, probably due to slow initiation of the polymerization. All polymers were unimodal. Figure 1 shows for example SED chromatogram of PPO.

Scheme 3 Polymerization of PO initiated with KH by deoxygenation of the monomer [23]

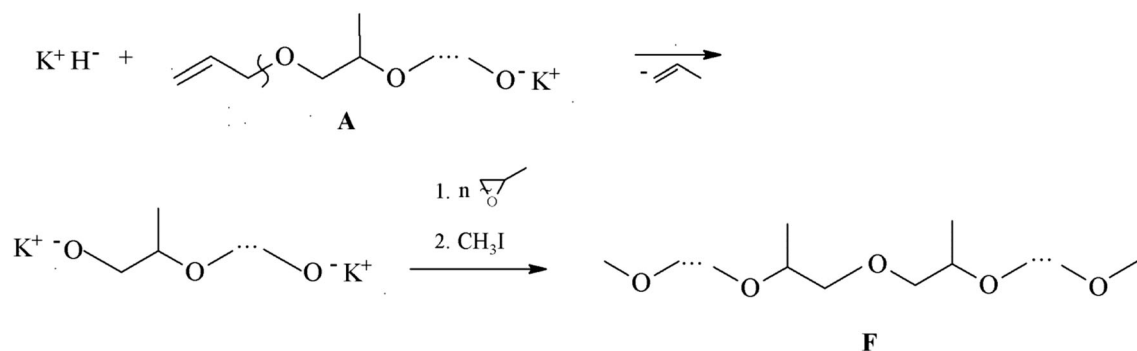


The monomer consumption during the polymerization of oxiranes is shown in Fig. 2.

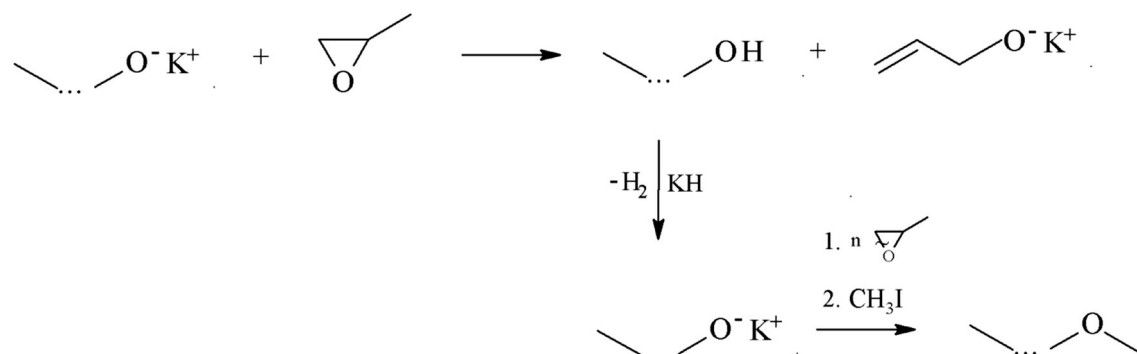
At conversion of the monomer above ~70% polymerization proceed markedly slower. It caused increasing of reaction time, especially in the case of PO. Results of polymers analysis by MALDI-TOF and ^{13}C NMR techniques, which allows to propose mechanism of initiation step of the polymerization are presented below.

Polymerization of propylene oxide

It was observed, that during heterogeneous polymerization of PO initiated with KH hydrogen and propylene were evolved in gaseous and liquid phase, respectively. ^{13}C NMR analysis of the polymer after methylation indicated in the spectrum (Fig. 3) carbon signals of three kinds of unsaturated starting groups,



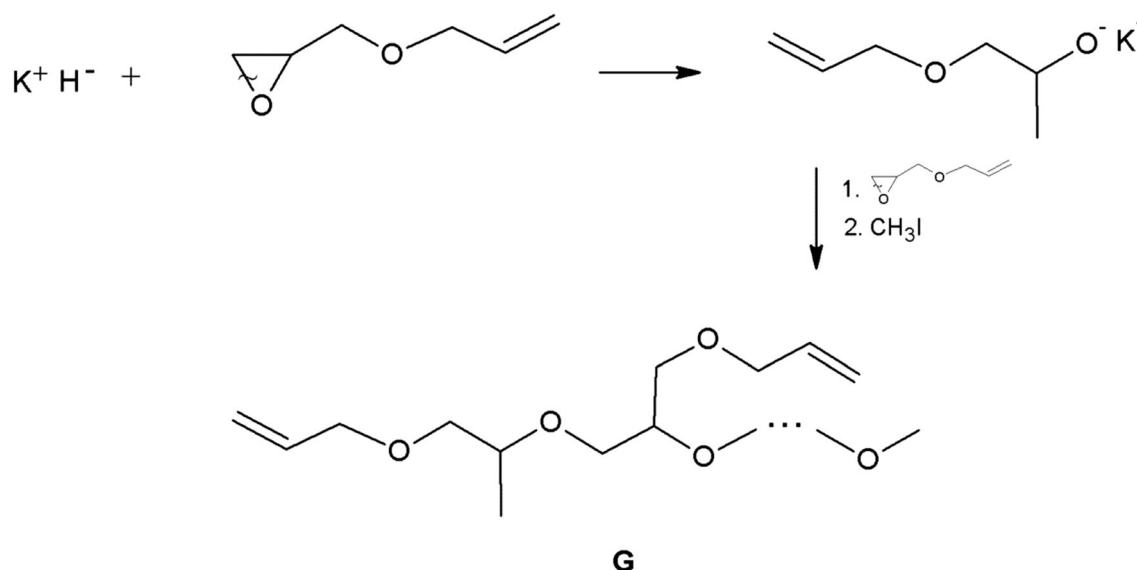
Scheme 4 Hypothetical reaction of KH with allyloxy starting group



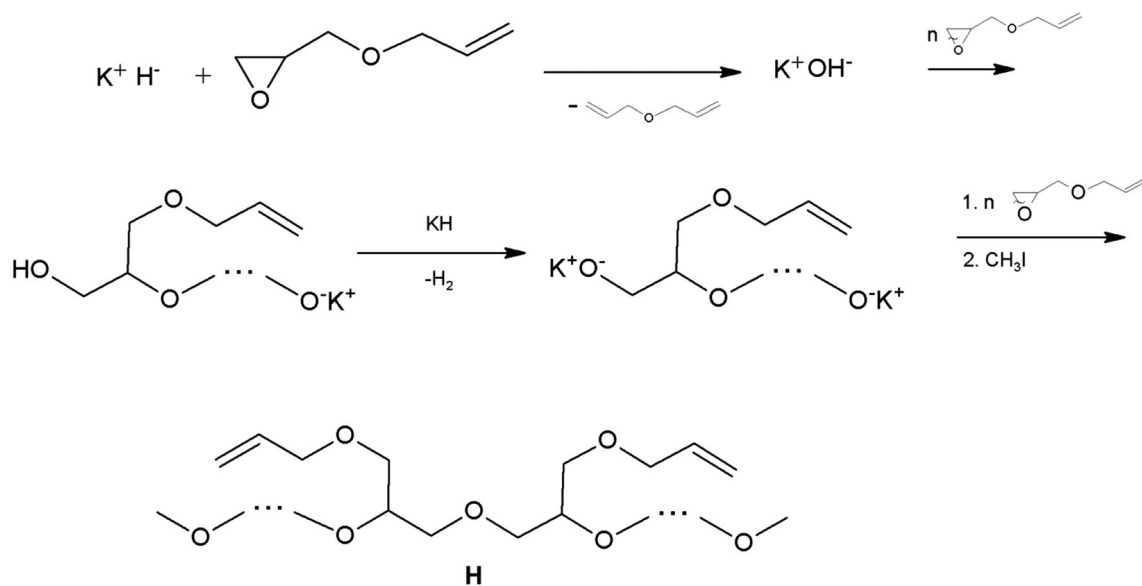
Scheme 5 Chain transfer with monomer and deprotonation of hydroxyl end groups by KH [23]

i.e. allyloxy $\text{CH}_2=\text{CHCHO}$ - (at 116.4 and 134.6 ppm), *cis*-propenyloxy (at 10.5, 100.4 and 145.7 ppm) and *trans*-propenyloxy (at 10.5, 98.2 and 146.5 ppm), as well as two kinds of isopropoxy starting groups, i.e. $(\text{CH}_3)_2\text{CHO}$ - (at 21.97 and 22.11 ppm). Carbon signal of $-\text{OCH}_3$ end group (at 56.5 ppm) was also present in the spectrum. However, signals expected for

carbon of $-\text{CH}(\text{CH}_3)\text{OH}$ end group (at 65.6 ppm) were not observed due to deprotonation of OH group with KH. It was known [3, 12], that *cis*- and *trans*-propenyloxy groups resulted from isomerization of allyloxy groups. However, two signals of isopropoxy groups could come from two different chain beginnings formed during initiation [14].



Scheme 6 Polymerization of AGE initiated with KH, which behaves as nucleophilic reagent



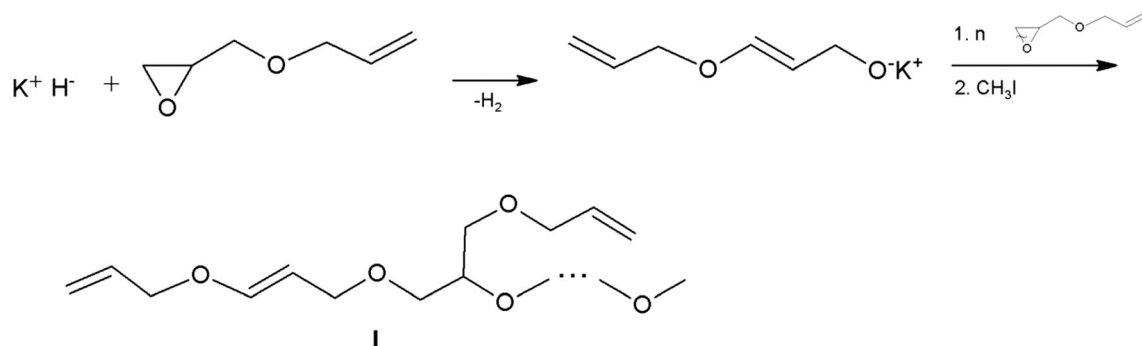
Scheme 7 Polymerization of AGE initiated with KH by deoxygenation of monomer

However, MALDI-TOF spectrum of the polymer revealed several series of signals, which belong to three kinds of macromolecules (Fig. 4).

The main series of signals at m/z 807.3 to 2433.7 represents macromolecules containing isopropoxy starting groups and methoxy end groups. They formed adducts with potassium ions. For example, signals at m/z 981.2, 1679.3 and 2259.4 belongs to macromolecules possessing 16, 28 and 38 mers of PO, respectively ($M_{\text{calc}} = 984.4, 1681.3$ and 2262.1 , respectively, where $M_{\text{calc}} = M_{\text{H}} + nM_{\text{PO}} + M_{\text{CH}_3} + M_{\text{K}}$). The same observed series of signals probably represents also macromolecules with allyloxy starting groups. For example, signals at m/z 1157.1, 1505.3 and 1969.1 represent macromolecules containing 18, 24 and 32 mers of PO ($M_{\text{calc}} = 1156.6, 1505.1$ and 1969.7 , respectively). The series of signals at m/z 851.4 to 2418.0, for example 1141.1, 1604.9 and 2301.5 belong to previously mentioned macromolecules, which formed adducts with sodium ions. The series of weak signals at m/z 999.3 to 2390.3 represents macromolecules containing additional oxygen atom and two methoxy end groups. They formed adducts with sodium ions. For example, signals at m/z

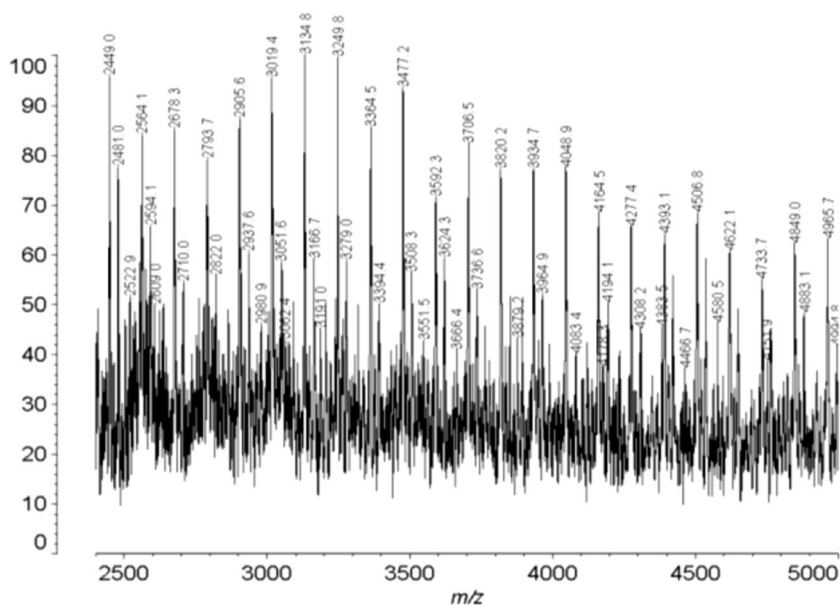
1055.1, 1461.6 and 2158.0 belongs to macromolecules possessing 17, 24 and 36 mers of PO, respectively ($M_{\text{calc}} = 1056.4, 1462.9$ and 2159.9 , respectively). The series accompanied the previous series represent macromolecules, which formed adducts with potassium ions, e.g. signals at m/z 1071.2, 1477.7 and 2174.1. Upon the obtained results we propose the course of polymerization. In the first step of the process three reactions occurs, leading to the formation of real initiators of the polymerization. Scheme 1 shows deprotonation of monomer with KH resulting in potassium allyloxide, which initiates polymerization. During propagation isomerization of allyloxy groups to *cis*- and *trans*-propenyloxy takes place mediated with KH and monomer, which undergoes deprotonation. Three kinds of macromolecules, i.e. **A**, **B** and **C** were formed in this process.

In the second reaction KH opens oxirane ring of PO in the β -position resulting in potassium isopropoxide (Scheme 2). Unexpectedly, this alkoxide reacts with PO by ring-opening in the β - and also in the α -position. It results in the formation of two kinds of macromolecules, i.e. **D** and **E** containing isopropoxy starting groups [15].



Scheme 8 Polymerization of AGE initiated with KH, which reacts as a base

Fig. 5 Part of MALDI-TOF spectrum of methylated PAGE



The third reaction of KH with monomer leads to macromolecules **F** possessing two methoxy terminal groups. This unusual deoxygenation reaction was suggested by Stolarzewicz et al. [24] and rationalized in the present work (Scheme 3). During the polymerization deprotonation of hydroxyl starting group by KH takes place, which generates the second alkoxide chain growth centre, resulting in macromolecules **F**. Propylene did not take part in the process.

Additional reaction was also taken into account as a source of macromolecules **F**. It is presented on Scheme 4.

In order to confirm possibility of such reaction model polymerization of PO initiated with potassium allyloxide was carried out. In this system macromolecules with allyloxy, *cis*- and *trans*-propenyloxy starting groups were formed. After complete monomer conversion KH was added to the

reaction mixture and mixed during several hours. The system was then treated with CH₃I. MALDI-TOF analysis of the polymer obtained did not indicate the formation of macromolecules **F**. Thus, reaction presented on Scheme 4 can be excluded.

In this characteristic for anionic polymerization of PO the occurrence of chain transfer reaction with monomer, which accompanied propagation (Scheme 5). Deprotonation of hydroxyl end groups by KH caused regeneration of active chain growth centers.

Polymerization of glycidyl ethers

Three reactions of KH with AGE which mediated polymerization were postulated and presented on Schemes 6, 7 and 8.

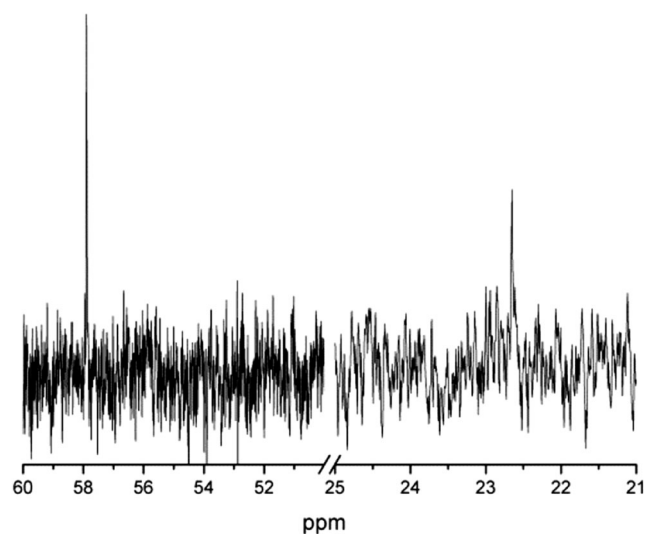


Fig. 6 ¹³C NMR spectrum of PAGE involving signals of CH₃ end group present in macromolecules **G** and **H**

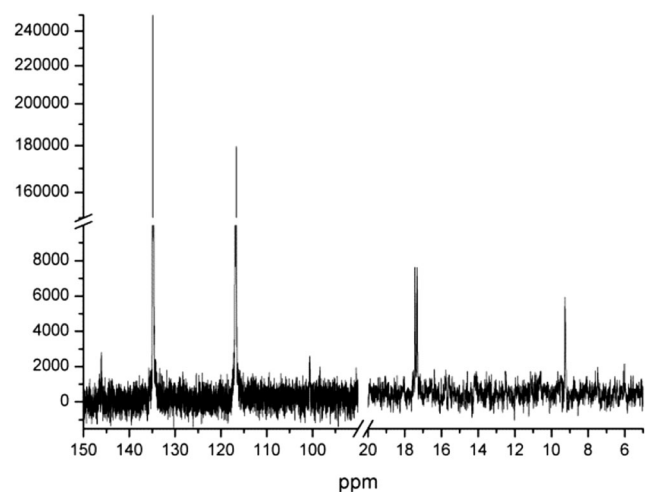
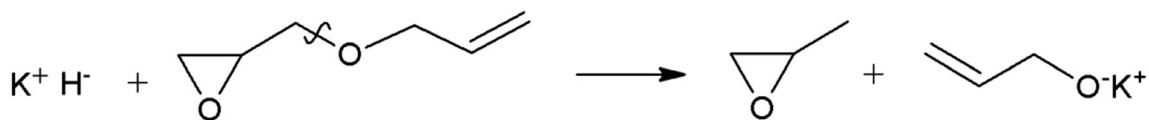


Fig. 7 Signals of allyloxy groups accompanied with *cis*-propenyloxy ones in the ¹³C NMR spectrum of PAGE



Scheme 9 Unexpected linear ether bond cleavage in AGE molecule under influence of KH

Several series of signals were observed in the spectrum of polymer at m/z in range 2600 to 4200 (Fig. 5). It was stated that the main series represents macromolecules **G**, which form adducts with potassium ions. For example, signals at m/z 2793.7, 3706.5 and 4277.4 belong to macromolecules possessing 24, 32 and 37 mers of AGE, respectively ($M_{\text{calc}} = 2794.4, 3707.5$ and 4278.1 respectively). Next series of signals represents macromolecules **H**, which form adducts with potassium ions. Exemplary signals at m/z 2710.0, 3394.4 and 4194.1 belong to macromolecules with 23, 29 and 36 mers of AGE, respectively ($M_{\text{calc}} = 2710.3, 3395.1$ and 4194.1). Two signals of CH_3 group present in macromolecules **G** and **H** were observed in ^{13}C NMR spectrum of the polymer, i.e. at 22.6 ppm [$\text{CH}_2 = \text{CHCH}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{O}-$] and 57.9 ppm ($-\text{OCH}_3$) which confirm formation of mentioned macromolecules (Fig. 6).

Signals at 9.2, 100.4 and 145.7 ppm indicated that small part of the allyloxy groups in substituents (signals at 16.4 and 134.6 ppm) undergo isomerization to *cis*-propenyloxy ones (Fig. 7). It is worth noting that signals of unsaturated carbons present in postulated macromolecules **I** ($-\text{OCH}=\text{CHCH}_2\text{O}-$) on Scheme 8 were not observed. It indicates that deprotonation of AGE by KH does not occur.

However, additional signals of CH_3 groups was also shown in the spectrum, i.e. signal at 17.4 ppm, which is characteristic for mers of propylene oxide. In order to explain their presence we assumed that in the studied system additional reaction takes place during initiation step (Scheme 9).

In the next step propylene oxide as comonomer is added to the growing chain of active macromolecule **G** (Scheme 10) and macromolecules **J** were formed. In other process potassium allyloxy reacts as initiator.

In the MALDI-TOF spectrum (Fig. 5) one series of weak signals can represent macromolecules **J**, which form adducts

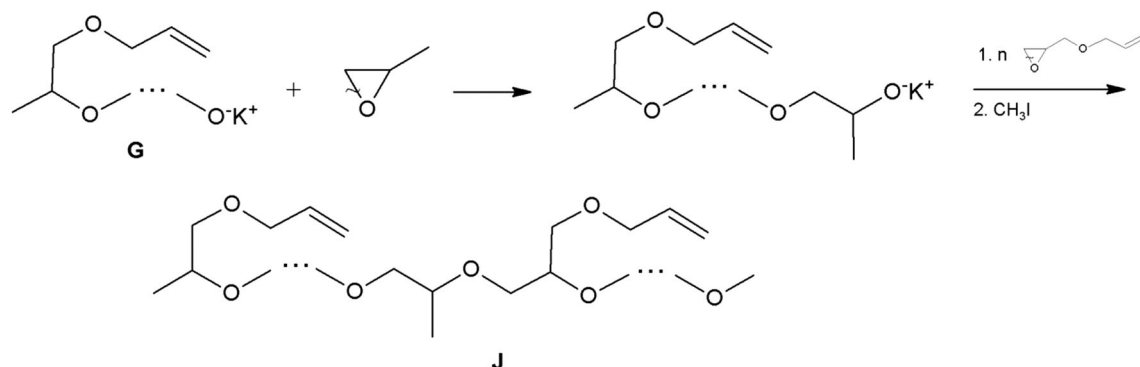
with potassium ions. For example, signals at m/z 3191.0, 3306.1 and 3879.2 belong to macromolecules possessing 27 mers of AGE and 1 mer of PO, respectively ($M_{\text{calc}} = 3194.9, 3309.0$ and 3879.7).

MALDI-TOF spectrum of PPGE indicated signals of macromolecules **K** resulting from oxirane ring opening with KH, however signals of macromolecules containing two methoxy terminal groups were not observed (Fig. 8). It indicated that in this system during initiation potassium hydroxide was not formed.

Several series of signals were observed in the spectrum. The main series at m/z 1200 to 6200 reveals signals of macromolecules **K**, which form adducts with potassium ions. For example, signals at m/z 1255.4, 3057.1 and 4560.9 belong to macromolecules containing 8, 20 and 30 mers of PGE, respectively ($M_{\text{calc}} = 1256.7, 3059.1$ and 4561.1 respectively). The second series reveals weak signals of macromolecules, which belong to macromolecules **L**, containing one mer of PO. For example, macromolecules represented by signals at m/z 3264.4, 5220.1 and 6124.1 contain 21, 34 and 40 mers of PGE, respectively ($M_{\text{calc}} = 3267.4, 5220.0$ and 6121.2 respectively). The third series reveals weak signals of macromolecules **M** containing starting $\text{PhO}-$ group. For example, macromolecules represented by signals at m/z 1199.0, 1347.9 and 3001.3 contain 7, 8 and 19 mers of PGE, respectively ($M_{\text{calc}} = 1199.5, 1349.7$ and 3001.9 respectively). Macromolecules **K** and **M** form adducts with potassium ions.

It was proposed that new kind of macromolecules i.e. **L** and **M** were also formed in the polymerization of PGE mediated with KH, which cleaved linear ether bond in monomer (side reaction on Scheme 11).

^{13}C NMR analysis of PPGE confirmed the presence of CH_3 group in macromolecules, i.e. at 17.4, 22.2 and 58.2 as it was observed previously for PAGE. The lack of carbon signal in



Scheme 10 Copolymerization of AGE with PO as a side reaction

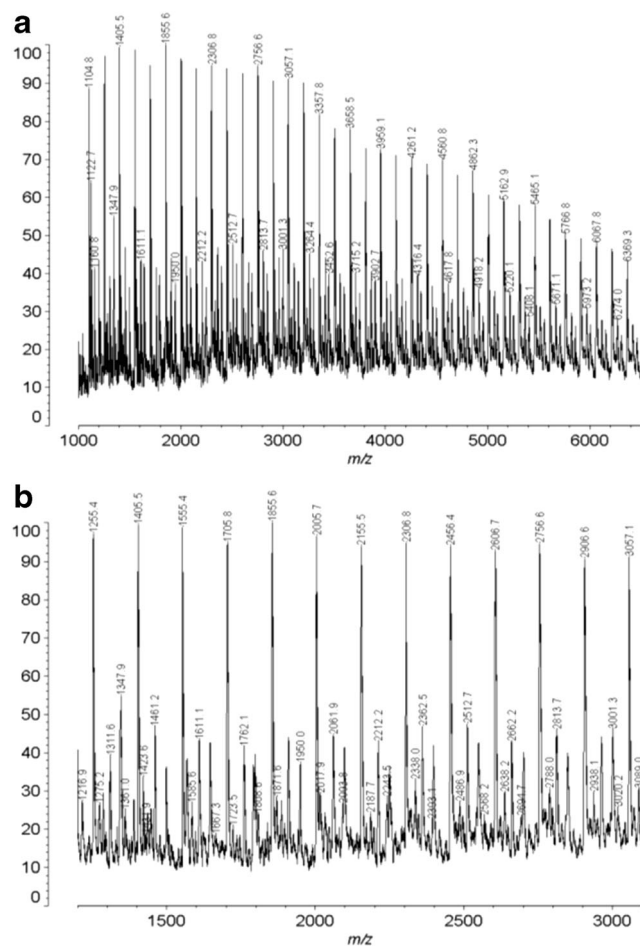


Fig. 8 Parts of MALDI-TOF spectrum of methylated PPGE in ranges: (a) 1000–6300, (b) 1200–3100

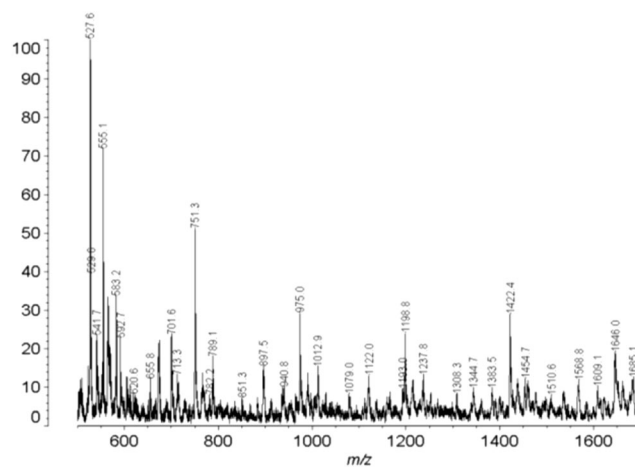
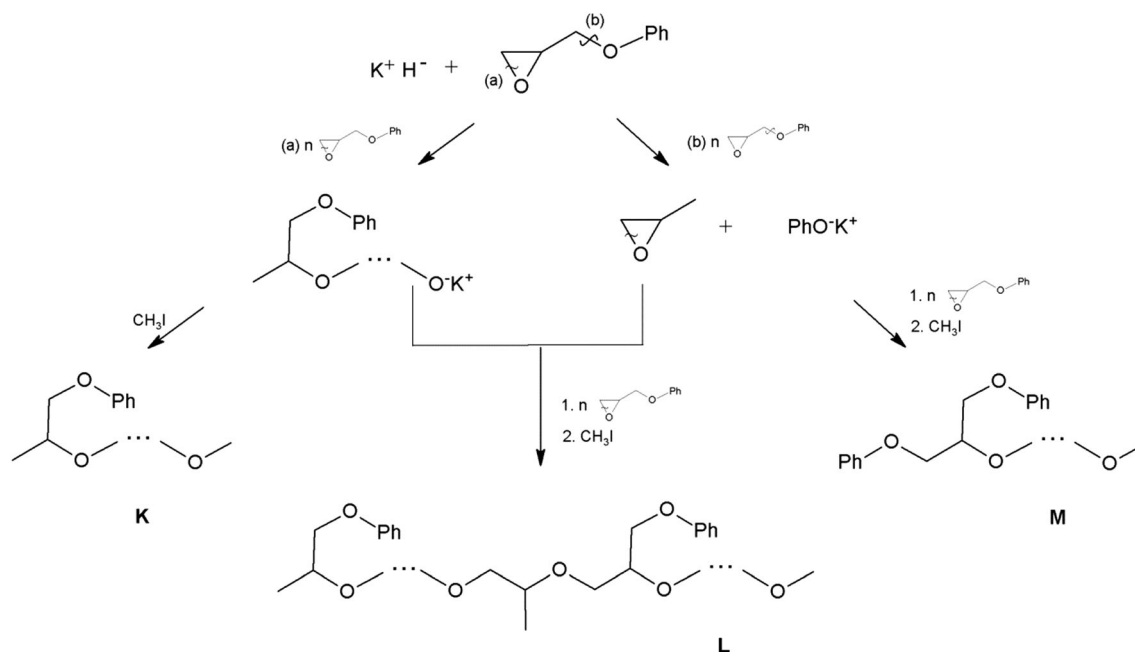


Fig. 9 MALDI-TOF spectrum of methylated PAGE in the range of m/z 600 to 1700

the unsaturated region of the spectrum indicated that deprotonation of the monomer by KH did not occur.

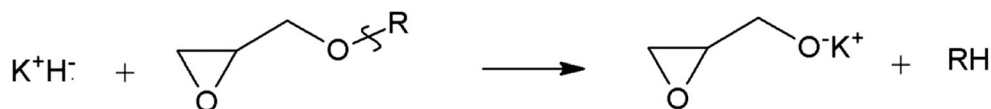
Characteristic feature of MALDI-TOF spectra of poly(glycidyl ether)s prepared in the present work was the presence of additional signals at m/z 600 to 2500. Exemplary spectrum of PAGE is shown in Fig. 9.

Several series of signal are observed in the spectrum. These unexpected signals derived from macromolecules, which do not contain AGE or PGE mers. On the other hand, it is worth noting that common part of these monomers are glycidoxo group. It could be suggested, that these new macromolecules may be a consequence of side reaction between KH and glycidyl ether occurring with second linear ether bond cleavage (Scheme 12).



Scheme 11 Polymerization of PGE initiated with KH which behaves as nucleophilic reagent

Scheme 12 Hypothetical reaction leading to the formation of potassium glycidoxide



It was assumed that main series at m/z 751.3, 975.0, 1198.8, 1422.5 and 1646.0 reveals signals of cyclic macromolecules formed by polymerization of glycidol initiated with potassium glycidoxide. They contain one mer of glycidoxide, methyl group and 9, 12, 15, 18 and 21 mers of glycidol ($M_{\text{calc}} = 755.0, 977.0, 1199.0, 1421.0$ and 1643.0 respectively) and form adducts with H^+ ions. The second series at m/z 897.5, 1122.0, 1344.7 and 1568.8 reveals signals of macromolecules with one mer of glycidoxide, methyl group and 11, 14, 17 and 20 mers of glycidol ($M_{\text{calc}} = 903.0, 1125.0, 1347.0$ and 1569.0 respectively) and form adducts with H^+ ions. The third series of signals at m/z 789.1, 864.0, 940.8, 1013.0, 1088.0, 1165.5, 1237.8, 1308.3, 1383.5, 1454.7, 1536.7, 1609.1 and 1685.1 belong to cyclic macromolecules containing one mer of glycidoxide, methyl group and 9 to 21 mers of glycidol ($M_{\text{calc}} = 793.0, 867.0, 941.0, 1015.0, 1089.0, 1163.0, 1237.0, 1311.0, 1385.0, 1459.0, 1533.0, 1607.0$ and 1681.0 respectively) and form adducts with potassium ions. Similar series of signals were observed in MALDI-TOF spectra of PPGE. However, the course of this process has been not explained because the source of glycidol is unknown. It might be formed by hydrolysis of potassium glycidoxide. It is also worth noting, that postulated macromolecules were not detected by MALDI-TOF technique in the polymerization of AGE and PGE initiated with potassium hydroxide or potassium *t*-butoxide or other anionic species in the same conditions. We would like to continue the developing of our research in the future, taking into account also other oxiranes, mainly various glycidyl ethers in order to explain the influence of the kind of substituent on the initiation course in the polymerization mediated with KH, also in the presence of crown ethers. That discussion is not complete and needs to be expanded with additional experiments.

Conclusions

Potassium hydride is active initiator of anionic polymerization of monosubstituted oxiranes, such as propylene oxide, allyl glycidyl ether and phenyl glycidyl ether. In this work it was observed that mechanism of initiation depends on the kind of monomer. The main reactions, which occurs in the initiation step are:

- All monomers undergo ring-opening in the β -position
- Deprotonation of monomer occurs exclusively with propylene oxide

- Cleavage of linear ether bonds is observed in both glycidyl ethers
- Deoxygenation of monomer takes also place, except phenyl glycidyl ether
- In the case of glycidyl ethers additional reactions occur leading to macromolecules, which do not possess mers of monomer used; this phenomenon needs further studies.

Acknowledgments The work was supported by Institutes' own funds.

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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