

Research article

Anionic ring-opening polymerization of isobutylene oxide initiated with potassium salts activated by 18-crown-6: Determination of mechanism and characterization of polyether monols and diols

Zbigniew Grobelny^{1*}, Justyna Jurek-Suliga², Sylwia Golba²

¹Institute of Chemistry, University of Silesia, 40-007 Katowice, Poland

²Institute of Materials Science, University of Silesia, 40-007 Katowice, Poland

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Abstract. Various potassium salts, *i.e.*, KOH, HOC₃H₆OC₃H₆OK, CH₃OK, *i*-PrOK, *t*-BuOK, CbK, and (Me₃Si)₂NK activated by 18-crown-6 appeared to be active initiators of first anionic polymerization of isobutylene oxide. The processes were performed in mild conditions, *i.e.*, tetrahydrofuran solution at room temperature under normal pressure. The polymers obtained are polyether-monols or -diols also containing macromolecules with starting groups having double bonds (12.5–46.6 mol%). It was stated that polymer unsaturation results not only from chain transfer reaction to monomer but mainly from deprotonation of monomer by an initiator, which behaves in the polymerizations as nucleophilic bases. In all systems, isomerization of the double bonds is also observed. Most of the obtained polymers are crystalline, insoluble materials with crystalline content up to 52.47% for a derived sample with potassium *i*-propoxide as initiator. The proneness of the polyisobutylene oxide to form crystal-type package is influenced by the average molar mass of the polymers. They are bimodal with $M_n = 400\text{--}1300$ ($M_{\text{calc}} = 1440$) and very low dispersities ($M_w/M_n = 1.01\text{--}1.12$). ¹³C NMR, MALDI-TOF, FTIR, SEC, XRD, and DSC techniques were used for polymers analysis. A mechanism of the processes studied was proposed.

Keywords: polymer synthesis, molecular engineering, anionic ring-opening polymerization, isobutylene oxide, potassium salts

1. Introduction

Polymerization of substituted oxiranes becomes more difficult as the number of substituted groups increases, and especially the polymerization of oxiranes such as isobutylene oxide (IBO), which has two methyl groups at one carbon atom, has been considered to be very difficult. Various single-component catalysts have been used ordinarily for the polymerization of isobutylene oxide [1]. Among these catalysts, there may be mentioned an iron compound, an organic acid salt of cobalt or manganese, an organometallic compound, or a sulfur-containing compound as dithiocarbamate. With a binary component catalyst system comprising an anionic compound and water,

the resulting polymer does not have a sufficiently high degree of polymerization [2]. All heretofore produced polymers have been too brittle and frail to serve in the fabrication of such useful products as fibers and film. These polymers have had melting points lower than 160 °C, generally in the range of 127–155 °C, and are soluble in hot tetrahydrofuran, dioxane, and dimethylformamide.

By proper selection of polymerization conditions, there can be obtained highly polymerized isobutylene oxide polymers which are highly crystalline polymers difficult soluble in most organic solvents. They show sufficient toughness for practical use, for example, as fibers and films. Isobutylene oxide can

*Corresponding author, e-mail: zbigniew.grobelny@us.edu.pl

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be effectively polymerized by a ternary-component catalyst system involving organozinc compounds represented by the formula $ZnRR'$, water, and monoamines at temperatures between 0 and 200 °C [2]. The polymerizations were carried out in a sealed tube made of stainless steel flushed by nitrogen gas in *n*-hexane for several hours. The yields of polymers were usually 60–90%. However, when the catalyst comprising diethylzinc, water, and an amine is used, longer periods of time are needed for polymerization, and the resulting polymer tends to have a very high viscosity. Such a polymer is poor in shape ability or moldability, and in many cases, has had stability unless a stabilizer is added thereto. Various other polymerization catalysts have been proposed, but they give polymers of low molar mass in poor yields. However, a novel ternary component catalyst consisting of an organozinc compound, water, and a sulfur-containing compound was applied for polymerization resulting in high molar mass polymers [3]. The polymerization is carried out in the absence of a solvent or in the presence of an inert solvent, for example, aliphatic and aromatic hydrocarbons or ethers, for example, tetrahydrofuran at –20 to 150 °C. Usually, the polymerization is carried out at atmospheric pressure, but if necessary, under high pressure. The high molar mass polymers that are obtained can find wide applications as fabricated articles such as films, fibers, plastics, etc. Still, for disubstituted oxirane monomers, yields and molecular weights for resultant polymers in the ROP were considerably lower than those in the polymerization of monosubstituted monomers [4]. Copolymerization and oligomerization of isobutylene oxide were proposed by Lee and Kim [5]. The authors used triisobutylaluminum as catalyst obtaining rather low molecular weights of hardly soluble products. Isobutylene oxide was subjected to radiation-induced polymerization [6]. The Polymerizability of isobutylene oxide synthesized with various catalysts was studied [7]. Polymers with high content of crystal phase were obtained, and it was proposed that it was symmetric structures of the monomer that was mainly responsible for this effect. Isobutylene oxide ring was used for the production of alternating copolymer with diglycolic anhydride (DGA) [8]. (BDI)ZnOAc (BDI = β -diiminato) catalysts were used reported to be highly active in reaction leading to new aliphatic polyesters with high number average molecular weight (M_n) values and low dispersity. The copolymerization of

IBO with isopropyl vinyl ethers (IPVE) successfully proceeded to a multiblock-like copolymer [9]. A Lewis acid catalyst, namely $B(C_6F_5)_3$, was used. A mechanism of the epoxide ring-opening with alcohols using heterogeneous Lewis acid catalysts was discussed [10]. Furthermore, the influence of the 2,2-disubstituted oxiranes on copolymerization with vinyl ethers by concurrent cationic vinyl-addition and the ring-opening mechanism was studied [11]. The authors focused on the influence of reactivities of monomers and propagating species. Hu *et al.* [12] described the alternating copolymerization of isobutylene oxide and cyclic anhydrides that resulted in semicrystalline polyesters. Polyisobutylene oxide was proposed as a promising photodegradable plastic material [13, 14]. The exposure of a thin film (25 μ m) under UV light at 60 °C resulted in rapid degradation with acetone, formic acid, and acetic acid formation as principal products, which can be included in the ecological cycle.

In the present work, we studied for the first time the course of anionic ring-opening homopolymerization of isobutylene oxide. Several metal salts with crownand 18-crown-6 (18C6) were used as initiators, *i.e.*, potassium hydroxide, monopotassium dipropylene glycoxide, potassium methoxide, potassium *i*-propoxide, potassium *t*-butoxide, carbazylpotassium, potassium bis(trimethylsilyl)amide. Crown ether activated anions by the complexation of K^+ , increasing the rate and yield of the reactions. All polymerizations were carried out in tetrahydrofuran solution at room temperature and normal pressure in an argon atmosphere. The polymers obtained were characterized by several techniques, namely ^{13}C NMR, MALDI-TOF, FTIR, SEC, XRD, and DSC techniques. The mechanism of the reactions was proposed and discussed.

2. Experimental

2.1. Materials

Isobutylene oxide (IBO) (Sigma aldrich, Poland) was dried over CaH_2 for 24 h under dry argon atmosphere and then distilled at 50 °C (purity 99.6%). Anhydrous tetrahydrofuran (THF) (Acros Organics, Poland) was kept over CaH_2 and distilled at 66 °C. Potassium hydride (KH) (Sigma Aldrich, Poland) was purified according to the procedure described by Brown [15]. A 35 wt% dispersion of KH in mineral oil (Sigma Aldrich, Poland) was mixed with *n*-pentane (Sigma Aldrich, Poland) in a dry argon atmosphere and then decanted. It was repeated three

times, followed by a three-fold washing with dry THF. Finally, the solvent was evaporated in a vacuum. Methanol, isopropanol, and dipropylene glycol (Sigma Aldrich, Poland) were dried over molecular sieves. Carbazole (Sigma Aldrich, Poland) was purified by sublimation. Potassium *t*-butoxide (1.0 M solution in THF) and potassium bis(trimethylsilyl) amide, as well as 18C6 (Sigma Aldrich, Poland) was used without purification.

2.2. Initiators synthesis and polymerization

Potassium hydroxide, potassium methoxide, potassium *i*-propoxide, monopotassium dipropylene glycolide, and carbazylpotassium were synthesized in the reaction of the appropriate substrate with KH activated 18C6 in THF solution at 20 °C. All syntheses were performed in a 50 cm³ reactor equipped with a magnetic stirrer and a Teflon valve, enabling substrates delivery and sampling under argon atmosphere. During the reactions, gaseous hydrogen was evolved. For example, KH (0.08 g, 2.0 mmol), 18C6 (0.53 g, 2.0 mmol), and THF (16.5 cm³) were introduced into the reactor, and then methanol (0.064 g, 2.0 mmol) was added by the use of microsyringe. The reaction mixture was then stirred for one hour until all H₂ (44.7 cm³) was evolved. This resulted in a fine dispersion of pure anhydrous potassium methoxide in the ether solution. That system was used as the initiator when isobutylene oxide (2.88 g, 40 mmol) was introduced into the reactor. Thus, the initial concentration of the monomer was 2.0 mol/dm³, and the initial concentration of the initiator was 0.1 mol/dm³. The reaction mixture was then stirred for several days. After almost complete conversion of the monomer, the reaction mixture was neutralized with HCl (2.0 mmol, 20 cm³, 0.1 mol/dm³)/H₂O (50 cm³) mixture and transferred to the separator containing chloroform (70 cm³). After shaking, two layers were formed, *i.e.*, an interior polyether layer and a superior layer containing water and potassium salt. These layers were separated, and a superior layer was removed. After three washing with fresh water, polyether was obtained by chloroform and water distillation in vacuum at 50 °C yielding a crystalline polymer. In all polymerizations, the concentration of the monomer during the process was monitored by the dioxane method [16]. The final conversion was usually 98–99% after ~4 weeks. The yields of the reactions were 96–99%. All polymerizations of isobutylene oxide were heterogeneous.



2.3. Measurements

Subsequently, 100 MHz, ¹³C NMR spectra were recorded in CDCl₃ (sample concentration 1 mg/ml) at 25 °C on a Bruker Avance 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 *i*-propanol. Data were analyzed using the LabSolutions program. Phase composition investigations of materials were performed by powder X-ray diffraction (XRD) method using an Empyrean Panalytical diffractometer and CuKα (λ = 0.1542 nm) radiation equipped with PIXcel3D detector. The data collection was over the 2θ range of 5 to 100° in of 0.02° steps. Calorimetric measurements (DSC) of the PIBOs were carried out by Mettler-Toledo DSC device equipped with liquid nitrogen cooling accessory and an HSS8 ceramic sensor (heat flux sensor with 120 thermocouples). The calibrations (temperature and enthalpy) were performed by use of standard (indium). The samples were weighed in an open aluminum crucible (40 μl) outside the DSC device and measured on two heating and cooling cycles in a range of (–80:200) °C at a constant heating rate (10 K/min). *T*_g was determined as values taken from the second heating cycle.

3. Results and discussion

¹³C NMR was used as the main technique for analysis of terminal groups present in polymers obtained and determination of the polymerization course. MALDI-TOF mass spectrometry was also applied as a supporting method. Molar masses and polydisper-

Table 1. Characterization of poly(isobutylene oxide)s synthesized with the use of potassium salts activated 18C6 in THF at room temperature; $[IBO]_0 = 2.0 \text{ mol/dm}^3$, $[I]_0 = 0.1 \text{ mol/dm}^3$.

No.	Initiator	MUSG ^a [mol%]	 [mol%]	 [mol%]	Yield [%]	M_n (SEC) [g/mol]	M_w/M_n (SEC)
1	$\text{HOC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}^- \text{K}^+$ ^b	12.5	6.0	6.5	98.3	1240 ^a (80%) 500 ^b (20%) 1092 (total)	1.08 1.03 1.07
2	$\text{K}^+ \text{OH}$	15.0	7.0	8.0	97.5	1100 ^a (80%) 500 ^b (20%) 980 (total)	1.08 1.02 1.07
3	$\text{Cb}^- \text{K}^+$	17.3	8.2	9.1	99.1	1050 ^a (75%) 550 ^b (25%) 925 (total)	1.06 1.03 1.05
4	$\text{MeO}^- \text{K}^+$	24.5	8.5	16.0	98.8	950 ^a (85%) 400 ^b (15%) 868 (total)	1.05 1.02 1.04
5	$i\text{-PrO}^- \text{K}^+$	26.7	10.0	16.1	96.5	900 ^a (88%) 500 ^b (12%) 852 (total)	1.04 1.01 1.04
6	$t\text{-BuO}^- \text{K}^+$	28.1	12.0	16.7	99.5	1000 ^a (80%) 450 ^b (20%) 890 (total)	1.12 1.03 1.10
7	$(\text{Me}_3\text{Si})_2\text{N}^- \text{K}^+$	46.6	13.3	33.2	99.0	1300 ^a (75%) 600 ^b (25%) 1125 (total)	1.06 1.05 1.06

^aMUSG – macromolecules with unsaturated starting groups; unsaturation of polymers were estimated by ¹³C NMR analysis

^ba circle denotes 18C6

sity indexes (M_w/M_n) of the polymers were estimated by SEC chromatography. Data characterizing the polymers obtained are presented in Table 1. They involve unsaturation, molar masses, and dispersities of PIBOs. From now on, we will refer to the No. 1 sample from Table 1 as PIBO (1) and so on.

It was observed that all prepared polymers consist of two fractions with different molar masses, dispersities, and yields. An exemplary chromatogram of PIBO (6) is shown in Figure 1.

¹³C NMR analysis of the polymers revealed high signals from CH₃, CH₂, and C present in the chain and also weak signals (at 23.20, 70.81, and 74.57,

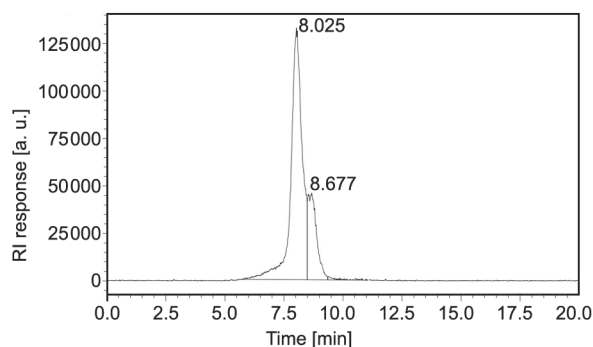


Figure 1. SEC of PIBO (6) prepared by use of $t\text{-BuO}^- \text{K}^+$ as initiator.

respectively) of starting groups derived from the initiator as well as two kinds of unsaturated starting groups resulting from chain transfer reaction to the monomer. However, the unsaturation of polymers obtained depends strongly on the initiator used. It indicates that the initiator also deprotonates the monomer. For example, Figure 2 shows an unsaturated region of the ¹³C NMR spectrum of PIBO (6).

In this region, four signals were observed. It was suggested that signals at 109.38 and 142.72 ppm derived from $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{O}-$ starting groups. Similarly, signals at 111.80 and 141.38 ppm belong to carbons of $(\text{CH}_3)_2\text{C}=\text{CH}-\text{O}-$ starting groups. Moreover, a signal of CH_3 groups derived from the initiator was identified at 27.65 ppm. Signal derived from terminal carbon atom of $\text{C}(\text{CH}_3)\text{OH}$ end group was found at 67.30 ppm.

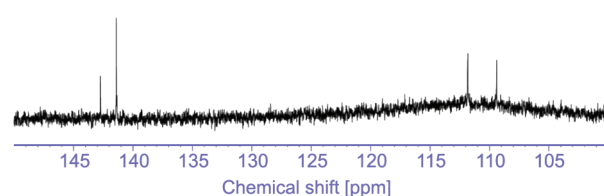


Figure 2. ¹³C NMR Signals of unsaturated starting groups present in PIBO (6) prepared with $t\text{-BuO}^- \text{K}^+$.

Based on these results, the course of polymerization of PIBO (3)–(7) refers to the synthesis listed in Table 1 initiated with potassium salts reacting as nucleophilic bases was proposed (Figure 3). Initiation starts by two different mechanisms, *i.e.*, oxirane ring-opening in the β -position and deprotonation of CH_3 group in monomer molecule. Moreover, isomerization of double bond primarily formed was mediated by initiator and active chain end all time during polymerization. A similar mechanism was proposed previously for the polymerization of propylene oxide, possessing one CH_3 group with acidic hydrogen atoms initiated by the same potassium salts [17, 18]. Oxirane ring-opening in the α -position and deprotonation of CH_2 group in the monomer was excluded in this system [19].

We were considering other possibilities of unsaturation formation observed in IBO polymerization; we have taken into account deprotonation of CH_2 group in the oxirane ring (Figure 4). However, in this case, isomerization is rather improbable.

Exemplary analysis of PIBO (7) by MALDI-TOF spectrometry confirmed its chemical structure (Figure 5).

The main series of signals at m/z 617.0 to 2258.1 belongs to macromolecules containing $(\text{Me}_3\text{Si})_2\text{N}^-$ starting groups and $-\text{OH}$ end groups. They form adducts with Na^+ ions. For example, signals at m/z 905.3, 1121.5, and 1410.3 represent macromolecules containing 10, 13, and 17 monomer units, respectively (the calculated, theoretic value of M_n , $M_{\text{calc}} = 905.5$, 1121.8, and 1410.3, respectively). The second series of peaks at m/z 528.2 to 959.4 belongs to macromolecules with unsaturated starting groups and $-\text{OH}$ end groups, which form adducts with Na^+ ions. For example, signals at m/z 528.2, 670.8, and 815.2 represent macromolecules containing 7, 9, and 11 monomer units, respectively ($M_{\text{calc}} = 527.8$, 672.0, and 816.2, respectively). The small signals of the third series involving signal at m/z 1137.8 belong to macromolecules represented by the first series but with K^+ ion. It was observed that unsaturated macromolecules have much lower molar masses than saturated ones. Their signals are placed in the left part of the spectrum. Therefore we concluded, that they form fraction (b) of polymer. A similar phenomenon was observed previously by us in the polymerization of propylene oxide initiated with various dipotassium glycoxides activated by 18C6 [20].

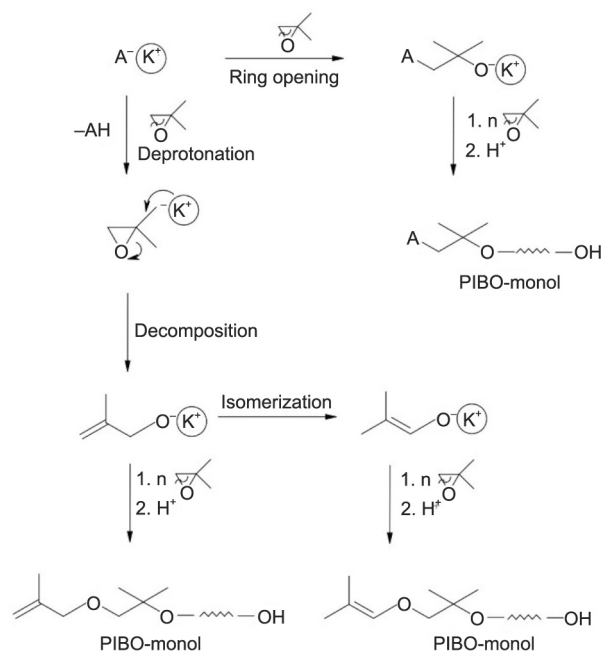


Figure 3. Polymerization of IBO initiated with potassium salts activated 18C6 (A^- : Cb^- , MeO^- , $i\text{-PrO}^-$, $t\text{-BuO}^-$, $(\text{Me}_3\text{Si})_2\text{N}^-$); chain transfer reactions to the monomer and AH were omitted.

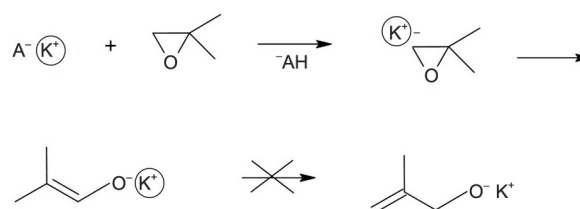


Figure 4. Possible way of unsaturated PIBO macromolecules formation through deprotonation of CH_2 groups in monomer by the initiator.

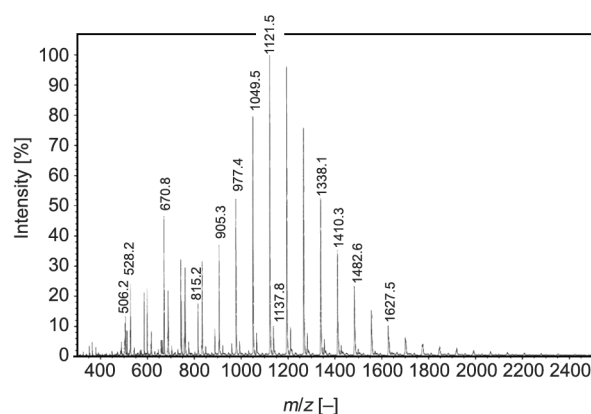


Figure 5. MALDI-TOF spectrum of PIBO (7) prepared with $(\text{Me}_3\text{Si})_2\text{N}^-(\text{K}^+)$ and quenched by $\text{HCl}/\text{H}_2\text{O}$.

Similar results were obtained in the case of PIBO (3)–(6). However, in PIBO (1) and (2), chain propagation takes place in two directions due to rapid cation exchange reaction resulting in polymers with two

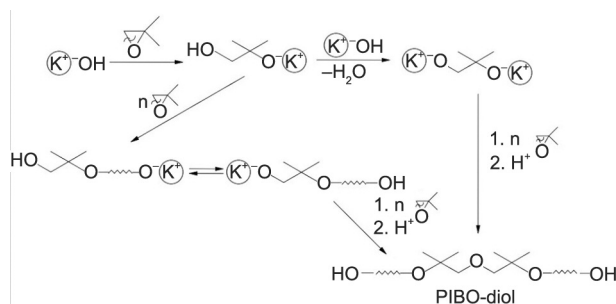


Figure 6. Polymerization of isobutylene oxide initiated with potassium hydroxide activated 18C6 2); monomer deprotonation by initiator and chain transfer reactions to monomer and water was omitted.

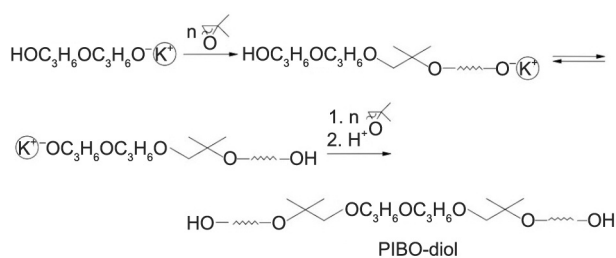


Figure 7. Polymerization of isobutylene oxide initiated with monopotassium dipropylene glycoxide (K-DPG) (1); monomer deprotonation by initiator and chain transfer reactions were omitted.

hydroxyl terminal groups (Figure 6 and 7). A distinct increase of polymer unsaturation was observed from PIBO (1) to (7) due to an increase of initiator basicity. Unsaturation of PIBO (1) and (2) is lower than that of other polymers. The presence of hydroxyl groups in initiators and growing chains is probably responsible for this phenomenon. Deprotonation of OH groups is much easier than CH₃ groups of the monomer due to the smaller acidity of the latter.

MALDI-TOF spectrum of PIBO (1) is shown in Figure 8.

The main series of signals at m/z 661.2 to 1816.3 belongs to macromolecules containing central part

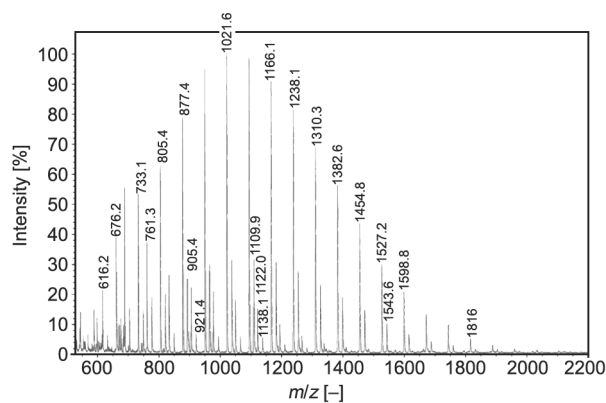


Figure 8. MALDI-TOF spectrum of PIBO (1) synthesized by use of $\text{HOC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}^- \text{K}^+$.

$-\text{OC}_3\text{H}_6\text{OC}_3\text{H}_6\text{O}-$ derived from initiator and two terminal $-\text{OH}$ groups. They form adducts with Na^+ ions. For example, signals at m/z 877.4, 1166.1, and 1454.8 represent macromolecules containing 10, 14, and 18 monomer units, respectively ($M_{\text{calc}} = 878.3$, 1166.7, and 1455.1, respectively). The second series of peaks at m/z 604.1 to 1832.4 represents the same macromolecules, which form adducts with K^+ ions. The third series at m/z 544.1 to 1510.4 represents macromolecules with starting unsaturated groups, which form adducts with K^+ ions. For example, signals at m/z 616.2, 761.3, and 1122.0 represent macromolecules containing 8, 10, and 15 monomer units, respectively ($M_{\text{calc}} = 615.9$, 760.1, and 1120.8, respectively).

A similar result was obtained for PIBO (2). Concluding, two series of macromolecules, *i.e.*, saturated and unsaturated ones, showed on MALDI-TOF spectra of all synthesized polymers concern well with two GPC fractions, *i.e.* (a) and (b) having various molar masses and yields. Additionally, ¹³C NMR analysis of the polymers confirms the formation of macromolecules with starting groups derived from initiators and unsaturated groups formed mainly by monomer deprotonation with the initiator. The presence of two polymer fractions is a consequence of the nucleophilic and basic character of potassium salts of anions used for initiation. The nucleophilicity of anions (*n*) is responsible for forming a saturated fraction of polymers, whereas the basicity of anions (*b*) is for unsaturated ones. Data presented in Table 1 show that *n/b* ratio of anions determines the yields of both fractions. Values of *n/b* diminish from K-DPG to $(\text{Me}_3\text{Si})_2\text{NK}$. In our opinion, the values of *n/b* can be determined by the saturated fraction [%]/unsaturated fraction [%] ratio. For example, for K-DPG and $(\text{Me}_3\text{Si})_2\text{NK}$ *n/b* ratios were 7.8/1 and 1.1/1, respectively.

For obtained polyethers, FTIR ATR spectra were recorded (Figure 9). Bands at 3000–2850 cm^{-1} reflect alkane-like fragments ($-\text{CH}_2-$) of the main chains together with bending and scissoring vibration of C–H in the range 1470–1450 cm^{-1} and rocking ones of C–H at 1370–1350 cm^{-1} . The band at appr. 1640 cm^{-1} results from stretching of alkenyl $-\text{C}=\text{C}-$ coupled together with low-intensity bands at 1430 and 1310 cm^{-1} from vinyl type C–H in-plane bending. For synthesized polymers, bands at 3492 cm^{-1} represent stretching vibration of associated $-\text{O}-\text{H}$. Furthermore, the broadness of these bands

indicates the presence of hydroxyl end groups. The position of the band is shifted for respective polyethers, which reflects the presence of hydrogen type of bonding involving protons of the hydroxylic group. The highest wavenumber of this band was detected for PIBO (7), followed by PIBO (2) and PIBO (1), and finally PIBO (6). This sequence represents the extent or strength of forming hydrogen bonds. Also, the low-intensity absorption peak at 1326 cm^{-1} is attributed to O–H bonding vibration. Complementary C–O stretching band is visible in the range $1210\text{--}1050\text{ cm}^{-1}$ with 1060 cm^{-1} band prescribed to stretching interaction of C–O for primary alcohol. It is accompanied by an ether C–O–C nonsymmetric broadband located at 1100 cm^{-1} characteristic for alkyl-substituted ether. Deconvolution of the complexed bands in this region reveals large diversity in the position of the peaks for polymer PIBO (7) and PIBO (6) and less intense for PIBO (2). This behavior reflects inter- and intrachain interaction presumably of

hydrogen bond type coming from lone pair of ether moiety oxygen.

Poly(isobutylene oxide) samples were insoluble in common organic solvents at room temperature. Similar insolubility was reported for PIBOs by Lee and Kim [5] and Kambara and Taskahashi [7]. It led to a suspect that the material is crystalline, which can be determined by recording an X-ray diffraction pattern. Crystallinity is an important materials parameter as it influences on *e.g.*, rate of polymer degradation – crystalline domains tend to degrade slower than the amorphous ones. Hence it is desirable to know the phase composition of PIBO samples, which was based on XRD analysis. The amorphous phase content was estimated by the area of the amorphous halo (Figure 10). The samples can be divided into two groups of various nature: amorphous (PIBO (3) and PIBO (4)) and semicrystalline (PIBO (1), PIBO (2), PIBO (5), PIBO (6), and PIBO (7)). The samples display an isotropic scattering profile with a diffused

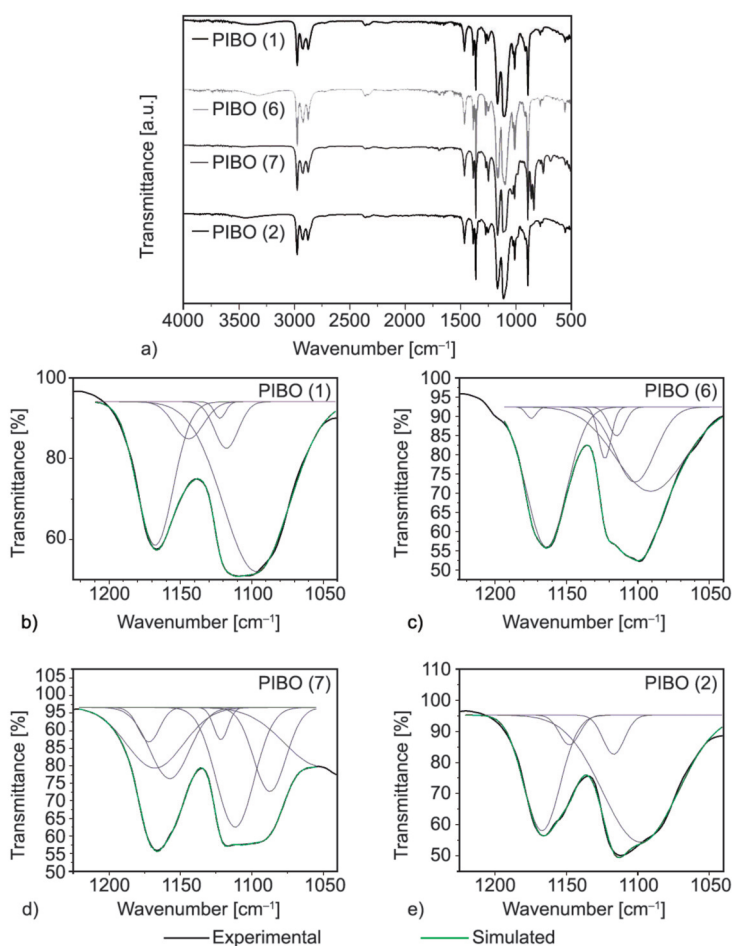


Figure 9. FTIR spectra of polyethers: (a) PIBO (1), PIBO (6), PIBO (7) and PIBO (2), and deconvoluted part of the spectra shown in (a) in a range $1225\text{--}1040\text{ cm}^{-1}$ (b) PIBO (1), (c) PIBO (6), (d) PIBO (7), (e) PIBO (2)).

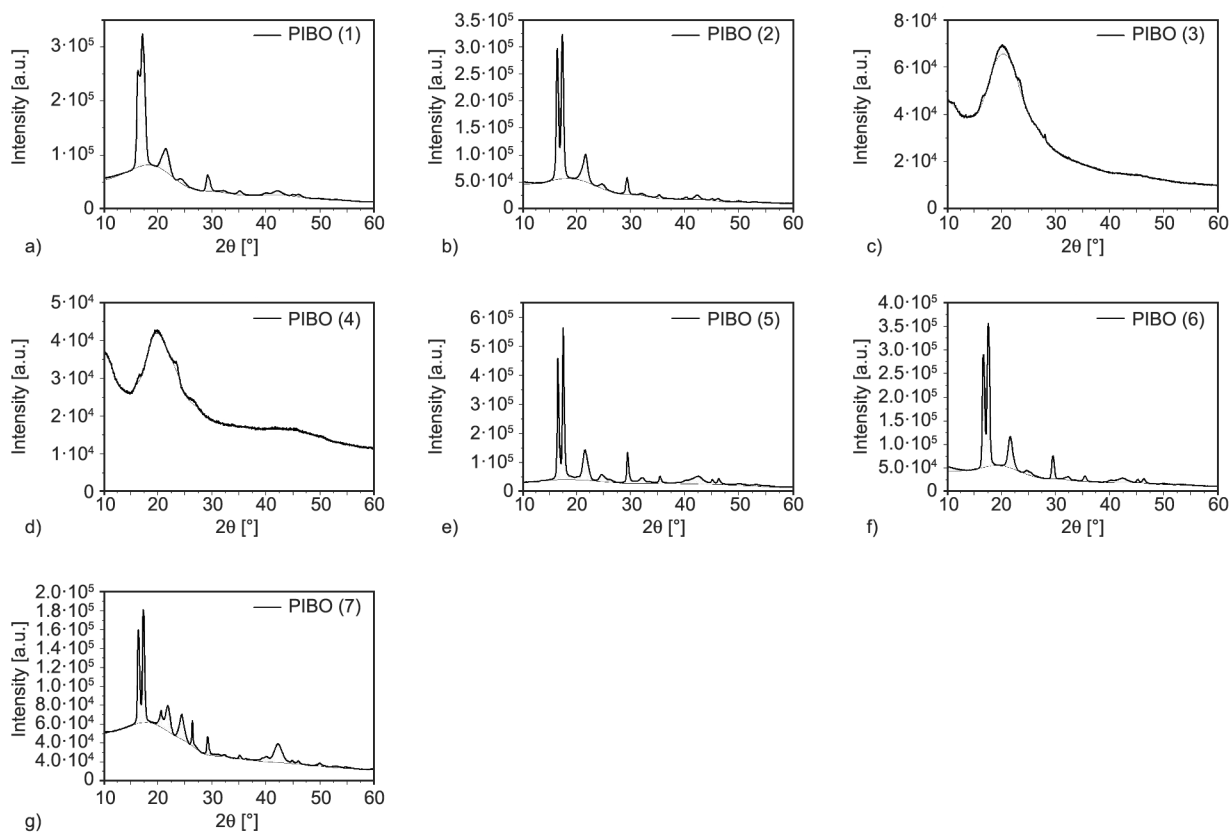


Figure 10. The integrated XRD profiles of polymers. a) (PIBO (1)), b) (PIBO (2)), c) (PIBO (3)), d) (PIBO (4)), e) (PIBO (5)), f) (PIBO (6)), e) (PIBO (7)).

amorphous halo and sharp crystalline peaks. Four peaks at 2θ values of 17.7, 18.6, 24.1, 26.8 are repeatedly observed in the samples (Figure 10), revealing their semicrystalline nature. They were already reported [12, 21] proclaimed for the orthorhombic unit cell containing four monomeric units – the chain twisted from the double zigzag structure.

The calculated crystalline content [%] derived from X-ray measurement is shown in Table 2. The crystalline content was the highest for PIBO (5) (52.47%), followed by PIBO (6) (49.43%), PIBO (2) (46.71%), PIBO (1) (36.43%) and PIBO (7) (30.42%). PIBO (3) and PIBO (4) are basically amorphous. By looking

at this sequence, one may indicate that in this series, the proneness of the PIBO to form crystal-type package is influenced by the average molecular weight of the polymer. The lowest value of M_n was reported for PIBO (5) (Table 2), while the highest was calculated for PIBO (7) (Table 2).

The thermal analysis of the PIBOs allowed determining the glass transition temperatures points (T_g), which are shown in Table 3. For all PIBOs T_g values were in a range of 11.0–27.3 °C with lower values prescribed to 3 and 4 samples. The energy required to move macromolecules being partially ordered is higher. It can be concluded that the presence of

Table 2. Phase content based on the quantitative structural analysis obtained by peak deconvolution of the integrated XRD scattering profiles for PIBOs.

No.	Peak 1 position, 2θ [°]	Peak 2 position, 2θ [°]	Peak 3 position, 2θ [°]	Peak 4 position, 2θ [°]	Peak 5 position, 2θ [°]	Crystalline content [%]	Amorphous content [%]
1	16.3338	17.1441	21.4809	×	29.2015	36.43	63.57
2	16.4651	17.3843	21.6910	×	29.3591	46.71	53.29
3	16.3601	×	20.1416	23.4242	28.0723	2.26	97.74
4	16.9378	×	×	24.0012	27.4946	1.81	98.19
5	16.5571	17.5287	21.5991	×	29.4510	52.47	47.53
6	16.7015	17.5681	21.6385	×	29.5166	49.43	50.57
7	16.3863	17.3055	21.8485	24.4221	29.1752	30.42	69.58

semi-crystallinity in the samples causes to increase in glass temperature transition. The recorded values of T_g are similar or higher in comparison to value of T_g for PIBO encountered in literature ($T_g^{\text{PIBO}} = -9^\circ\text{C}$ [18], $T_g^{\text{PIBO}} = -10^\circ\text{C}$ [5], $T_g^{\text{PIBO}} = 19^\circ\text{C}$ [22]). This shift is prescribed mainly to semicrystalline nature of prepared PIBOs, as shown in the XRD study.

The PIBO (1), (2) and (5)–(7) showed a melting endotherm due to the presence of crystalline micro-

domains. As an example, PIBO (1) synthesized with monopotassium dipropylene glyxide as an initiator (entry 1 in Table 3) exhibits a T_m at 87.23°C ($\Delta H_m = 57.69 \text{ J/g}$) (Figure 12). PIBO (3) and (4) phous (as detected with XRD analysis), and no melting phenomena were demonstrated on thermal curves. The DSC trace of PIBOs shows corresponding melting peaks (Figure 11) with melting enthalpies (ΔH_{melt}) of significantly different values (Table 3). This variation reflects the different amounts of crystalline

Table 3. DSC data of PIBO samples.

No.	Step 1 peak temperature [°C]	Step 1 onset temperature [°C]	Step 2 peak temperature [°C]	Step 2 onset temperature [°C]	T_g exp [°C]	ΔH_{melt} [J/g]
1	62.16	30.22	87.23	75.09	23.5	-57.69
2	113.52	97.86	×	×	24.6	-66.09
3	×	×	×	×	14.5	0
4	×	×	×	×	11.0	0
5	111.74	97.03	×	×	25.0	-76.28
6	115.26	101.60	×	×	27.3	-77.91
7	101.94	89.95	×	×	24.2	-43.29

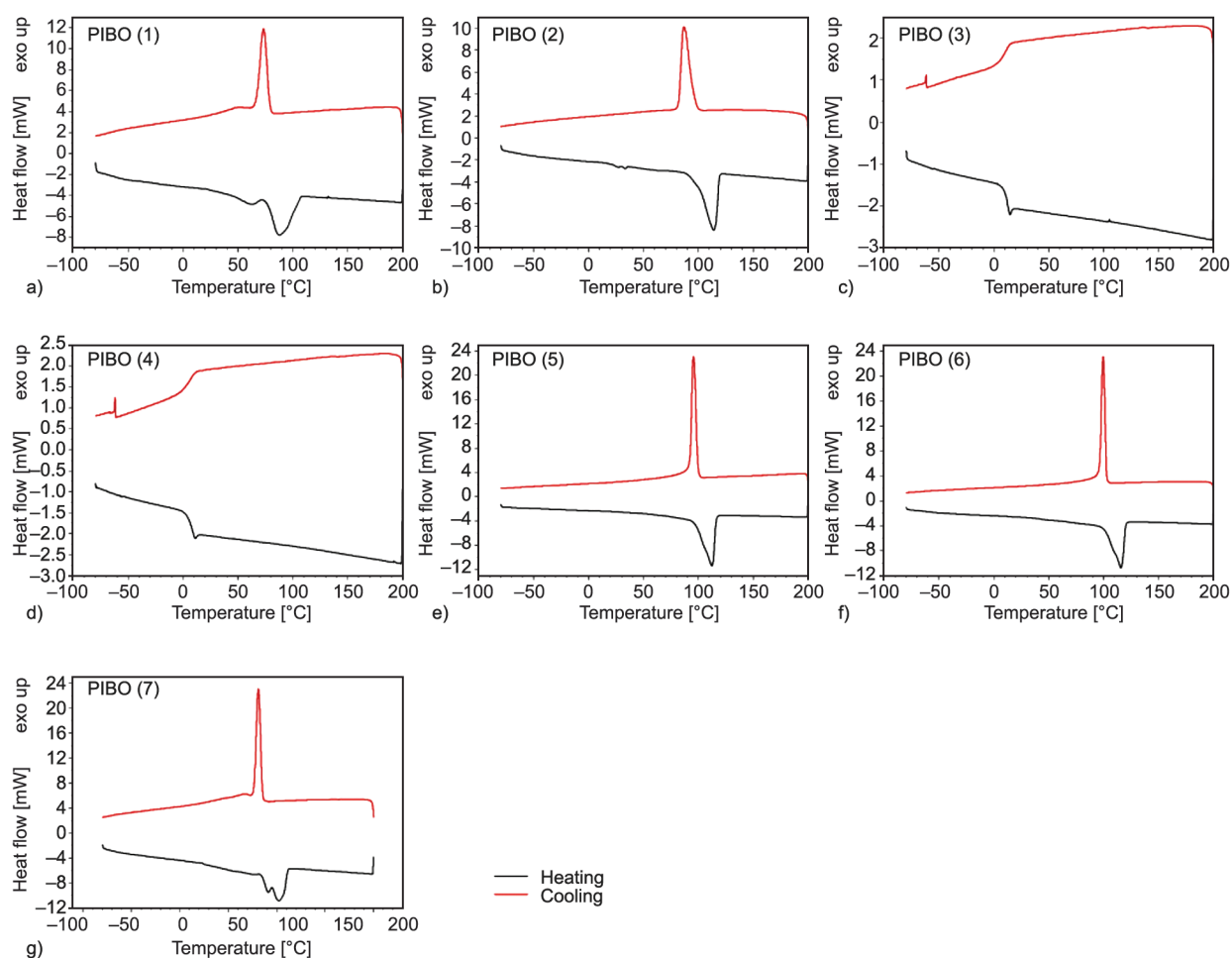


Figure 11. The DSC thermograms of polymers (the second heating/cooling cycle). a) (PIBO (1), b) (PIBO (2), c) (PIBO (3), d) (PIBO (4), e) (PIBO (5), f) (PIBO (6), e) (PIBO (7).

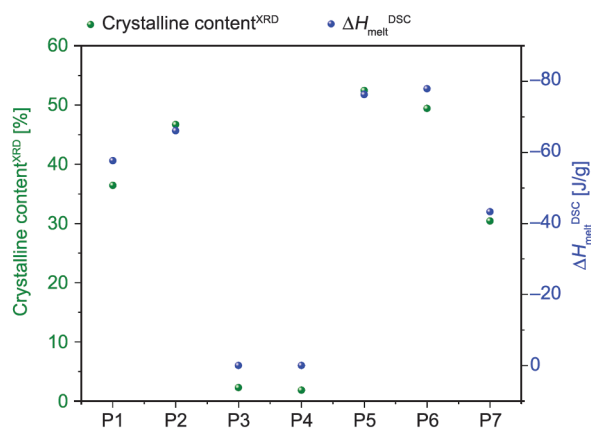


Figure 12. Comparison chart of the crystallinity content determined by XRD technique (●) with melting enthalpy values determined by DSC technique (●).

phase in the samples and can correlate well with XRD results (Figure 12). The melting temperatures are lower than the previously reported values (e.g., 127–155 °C [2], 173 °C [23]), which manifests an enhanced ability to transfer the crystalline phase into a disordered viscous liquid one. As reported, the PIBO crystals tend to grow in a lamellar form with chain folding [23] along with a radial arrangement of the lamellar crystals with respect to the center of the spherulite. It manifests that in the studied polymers, the crystal domains contain distorted regularity with more loose packaging.

4. Conclusions

In the present work, anionic ring-opening homopolymerization of isobutylene oxide was carried out for the first time by using various potassium salts activated 18-crown-6 in THF solution at room temperature. The polyethers obtained were characterized by several techniques, *i.e.*, SEC, ^{13}C NMR, MALDI-TOF, FTIR, XRD, and DSC. The most important conclusions to be drawn from the study are as follows:

- All initiators used to behave as nucleophilic bases, *i.e.*, open oxirane ring in the β -position and deprotonate monomer resulting in polymer unsaturation.
- The level of unsaturation depends strongly on the initiator used; the highest unsaturation (46.6 mol%) represented by two kinds of groups with double bonds has polymer obtained in the presence of potassium bis(trimethylsilyl)amide.
- Polymers prepared with monopotassium dipropylene glycoxide or potassium hydroxide possess the lowest unsaturation (12.5 and 15.0 mol%, respectively); these polymers have two reactive hydroxyl terminal groups.

- Molar masses of the polymer ($M_n = 900\text{--}1300$) are lower than theoretical ($M_{\text{calc}} = 1440$); dispersities are relatively low ($M_w/M_n = 1.04\text{--}1.10$).
- Several synthesized polymers are semicrystalline materials (crystalline content = 30.42–52.47%), with the melting temperature spanning from 87.23 to 115.26 °C.

References

- [1] Kambara S., Takahashi A.: Polymers from isobutylene oxide and its analogs. *Die Makromolekulare Chemie*, **58**, 226–231 (1962).
<https://doi.org/10.1002/macp.1962.020580116>
- [2] Kosaku K., Motoyuki K., Shigeo N.: Process for preparing highly polymerized isobutylene oxide polymers, and the polymers and articles thereof. U.S. Patent 3509074A, USA (1970).
- [3] Tanaka A., Sawada H., Kusumoto M., Sato K.: Process for polymerizing isobutylene oxide. U.S. Patent 3748286A, USA (1976).
- [4] Iwasa N., Miura K., Kan S., Furukawa Y.: Ring-opening polymerization of various oxirane derivatives using organotin phosphate condensate; Selective synthesis of the polyether containing oxirane ring in the side chain. *Polymer Bulletin*, **61**, 207–216 (2008).
<https://doi.org/10.1007/s00289-008-0949-z>
- [5] Lee Y. B., Kim S. K.: Copolymerisation and oligomerisation of isobutylene oxide. *Polymer (Korea)*, **24**, 124–127 (2000).
- [6] Bauer R. S., Spooncer W. W.: Radiation-induced polymerization of isobutylene oxide. *Journal of Polymer Science Part A-1: Polymer Chemistry*, **8**, 2971–2977 (1970).
<https://doi.org/10.1002/pol.1970.150081021>
- [7] Boor J., Bauer R. S.: Preparation and characterization of poly(isobutylene oxide). *Journal of Applied Polymer Science*, **18**, 3699–3721 (1974).
<https://doi.org/10.1002/app.1974.070181216>
- [8] Jeske R. C., DiCiccio A. M., Coates G. W.: Alternating copolymerization of epoxides and cyclic anhydrides: An improved route to aliphatic polyesters. *Journal of American Chemical Society*, **129**, 11330–11331 (2007).
<https://doi.org/10.1021/ja0737568>
- [9] Kanazawa A., Aoshima S.: Concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes. *Polymer Journal*, **48**, 679–687 (2016).
<https://doi.org/10.1038/pj.2016.27>
- [10] Deshpande N., Parulkar A., Joshi R., Diep B., Kulkarni A., Brunelli N. A.: Epoxide ring opening with alcohols using heterogeneous Lewis acid catalysts: Regioselectivity and mechanism. *Journal of Catalysis*, **370**, 46–54 (2019).
<https://doi.org/10.1016/j.jcat.2018.11.038>

- [11] Miyamae Y., Kanazawa A., Tamaso K-I., Morino K., Ogawa R., Aoshima S.: The influence of the substituents of oxiranes on copolymerization with vinyl ethers *via* concurrent cationic vinyl-addition and ring-opening mechanisms. *Polymer Chemistry*, **9**, 404–413 (2018).
<https://doi.org/10.1039/C7PY01292F>
- [12] Hu L., Zhang X., Cao X., Chen D., Sun Y., Zhang C., Zhang X.: Alternating copolymerization of isobutylene oxide and cyclic anhydrides: A new route to semicrystalline polyesters. *Macromolecules*, **54**, 6182–6190 (2021).
<https://doi.org/10.1021/acs.macromol.1c00793>
- [13] Kawai F.: Breakdown of plastics and polymers by microorganisms. in ‘Microbial and enzymatic bioproducts. Advances in biochemical engineering/biotechnology’ (ed.: Fiechter A.) Springer, Berlin, Vol 52, 151–194 (1995).
- [14] Kawai F.: Microbial degradation of polyethers. *Applied Microbiology and Biotechnology*, **58**, 30–38 (2002).
<https://doi.org/10.1007/s00253-001-0850-2>
- [15] Brown C. A.: Saline hydrides and superbases in organic reactions. VII. Potassium hydride, highly active new hydride reagent. Reactivity, applications, and techniques in organic and organometallic reactions. *The Journal of Organic Chemistry*, **39**, 3913–3918 (1974).
<https://doi.org/10.1021/jo00940a025>
- [16] Siggia S.: Quantitative organic analysis via functional groups. Wiley, New York (1963).
- [17] Grobelny Z., Matlengiewicz M., Jurek J., Michalak M., Kwapulińska D., Swinarew A., Schab-Balcerzak E.: The influence of macrocyclic ligands and water on propylene oxide polymerization initiated with anhydrous potassium hydroxide in tetrahydrofuran. *European Polymer Journal*, **49**, 3277–3288 (2013).
<https://doi.org/10.1016/j.eurpolymj.2013.06.035>
- [18] Grobelny Z., Matlengiewicz M., Jurek-Suliga J., Golba S., Skrzeczyna K.: The influence of initiator and macrocyclic ligand on unsaturation and molar mass of poly(propylene oxide)s prepared with various anionic system. *Polymer Bulletin*, **75**, 1101–1121 (2018).
<https://doi.org/10.1007/s00289-017-2078-z>
- [19] Grobelny Z., Jurek-Suliga J., Golba S.: 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. *Journal of Polymer Research*, **26**, 274 (2019).
<https://doi.org/10.1007/s10965-019-1943-x>
- [20] Grobelny Z., Matlengiewicz M., Golba S., Jurek-Suliga J., Swinarew A., Skrzeczyna K., Michalak M., Swinarew B.: Application of dipotassium glycoxides-activated 18-crown-6 for the synthesis of poly(propylene oxide) with increased molar mass. *International Journal of Polymer Analysis and Characterization*, **20**, 206–222 (2015).
<https://doi.org/10.1080/1023666X.2015.989379>
- [21] Kaji K., Sakurad I.: Crystal structure of poly(isobutylene oxide). *Die Makromolekulare Chemie*, **148**, 261–269 (1971).
<https://doi.org/10.1002/macp.1971.021480122>
- [22] Lubnin A., Kisliuk A., Sokolov A. P.: The puzzling role of symmetry: A tool for macromolecular engineering. in ‘Macromolecular engineering: Design, synthesis and application of polymers’ (eds.: Lubnin A., Erdodi G.) Elsevier, Amsterdam, Vol 1, 3–19 (2021).
<https://doi.org/10.1016/B978-0-12-821998-0.00001-6>
- [23] Mitsuhashi S.: Three dimensional shape of polyisobutylene oxide spherulites. *Journal of Polymer Science Part B: Polymer Letters*, **9**, 31–35 (1971).
<https://doi.org/10.1002/pol.1971.110090105>