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Application of cesium hydroxide monohydrate for ring opening polymerization of monosubstituted oxiranes: characterization of synthesized polyether-diols

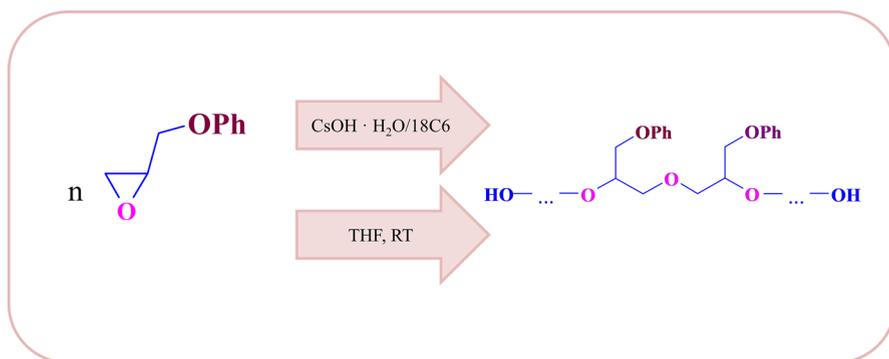
Zbigniew Grobelny¹ · Justyna Jurek-Suliga² · Sylwia Golba²

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Abstract

Cesium hydroxide monohydrate ($\text{CsOH} \cdot \text{H}_2\text{O}$) activated by cation complexing agents, i.e., 18C6 or C222 was applied as initiator of monosubstituted oxiranes polymerization. Propylene oxide (PO), 1,2-butylene oxide (BO), styrene oxide (SO) and some glycidyl ethers were used as monomers. All processes were carried out in tetrahydrofuran solution at room temperature. Such polymers, as PPO-diols, PBO-diols and PSO-diols, are unimodal and have molar masses $M_n = 2000\text{--}5100$. Their dispersities are rather high ($M_w/M_n = 1.17\text{--}1.33$). Moreover, PPO-diols and PSO-diols are not contaminated by monools with unsaturated starting groups. Poly(glycidyl ether)s are, in general, polymodal. For example, poly(isopropyl glycidyl ether)-diols are bi- or trimodal, whereas poly(allyl glycidyl ether)-diols possess two or even six fractions. Molar masses of main fraction are 4200–6400, and the second fraction is much lower, namely 600–2600. Dispersities of some fractions are very low ($M_w/M_n = 1.01\text{--}1.07$). Polymodality of polymers obtained was discussed in terms of the formation of two or more species propagating with different rate constants.

Graphic abstract

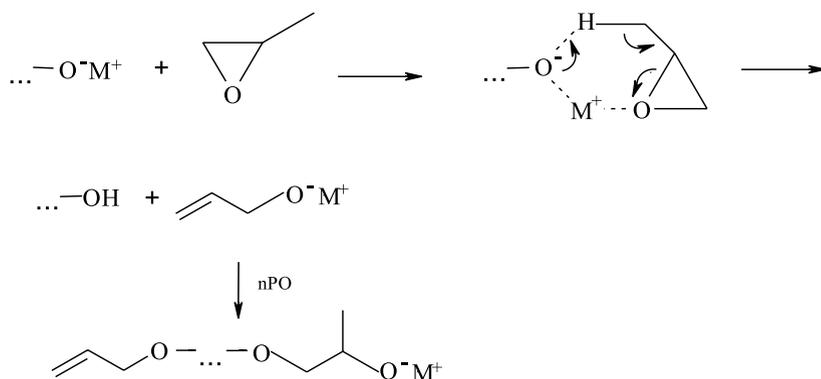


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Keywords Cesium hydroxide monohydrate · Ring opening polymerization · Monosubstituted oxiranes · Polyether-diol

Introduction

Polyethers are an important class of synthetic polymers, which have many applications, e.g., as impact modifiers, surfactants, de-emulsifiers, dispersant agents, fuel additives, lubricants, biomedical materials or adhesives [1–5]. Especially interesting are polyether- and copolyether-diols or triols prepared from oxiranes, i.e., ethylene oxide (EO), propylene oxide (PO) or 1,2-butylene oxide (BO), which are applied for fabrication of polyurethane elastomers or foams [6]. Many initiators were used for anionic ring-opening polymerization of oxiranes, e.g., potassium hydroxide [7, 8] or potassium alkoxides [9–15]. In industry, the most frequently used are KOH/1,2-propylene glycol or glycerol systems, which allow to obtain PPO-diols or PPO-triols with $M_n = 2000$ – 6000 at $110\text{ }^\circ\text{C}$ [6, 16]. The polymers possess low unsaturation due to excess of hydroxylic compound used, which strongly limited chain transfer reaction to monomer. On the other hand, PPOs with $M_n = 9000$ and high unsaturation were prepared in the polymerization initiated with anhydrous KOH in THF solution at room temperature [8]. It was proposed, that in this case deprotonation of the monomer by initiator and active centers of growing chains occur to a wide extend. KOH, RbOH and CsOH are effective catalysts, while LiOH and Na OH are ineffective [17, 18]. Unsaturation of PPOs depends strongly on the nature of alkoxide cation. The relative order of alkoxide reactivity in the transfer reaction with the monomer is: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ [19, 20]. This effect is rather unexpected and needs some comments. Basicity of hydroxides and alkoxides increases from Li^+ to Cs^+ [21]. Deprotonation of PO occurs in the complex involving monomer and active ion pair of growing chain [6, 10] (Scheme 1).



where M^+ denotes alkali metal cation

Scheme 1 Deprotonation of PO by E2 elimination during anionic polymerization (side reaction of chain transfer to monomer)

In our opinion, decreasing of deprotonation observed from Li^+ to Cs^+ could be explained by increasing of ionic radii of the metal cation (from 60 pm for Li^+ to 169 pm for Cs^+), which causes an increase in steric hindrance. On the other hand, in the polymerization initiated with potassium alkoxides and other salts activated coronand 18-crown-6 (18C6), formation of big $\text{K}^+18\text{C6}$ complexes results in direct deprotonation of the monomer and high unsaturation [15] (Scheme 2).

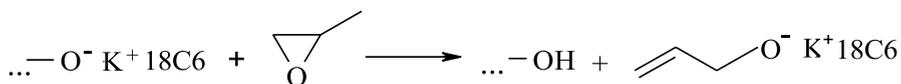
It was also worth noting that PPOs synthesized in the presence of $\text{KOH}/\text{H}_2\text{O}/18\text{C6}$ [8] or $t\text{-BuOK}/t\text{-BuOH}/18\text{C6}$ [14] systems have very low unsaturation and M_n due to chain transfer reaction to hydroxylic compound.

The aim of the present work was characterization of polyether-diols prepared by ring opening polymerization of several monosubstituted oxiranes initiated with cesium hydroxide monohydrate ($\text{CsOH}\cdot\text{H}_2\text{O}$). This reagent was useful for synthesis of dicesium 1,2-propanedioide, which was applied for some oxiranes copolymerization [22]. However, till now, it has not been used for initiation of oxiranes polymerization. Propylene oxide, 1,2-butylene oxide, styrene oxide, isopropyl glycidyl ether, allyl glycidyl ether and phenyl glycidyl ether were chosen as monomers for the study. Polymerizations were carried out in THF solution at room temperature. The influence of initial monomer concentration and kind of ligand complexing counterion (L), i.e., coronand 18C6 or cryptand C222 on molar mass (M_n), dispersity (M_w/M_n) and modality of the prepared polymers were studied and discussed. ^{13}C NMR, MALDI-TOF and SEC techniques were used for analysis of polymers.

Experimental

Materials

Monomers, i.e., propylene oxide, 1,2-butylene oxide, styrene oxide, isopropyl glycidyl ether, allyl glycidyl ether and phenyl glycidyl ether (from Aldrich) were dried over CaH_2 and distilled at 307 K (34 °C), 336 K (63 °C), 467 K (194 °C), 414 K (131 °C), 427 K (154 °C) and 518 K (245 °C), respectively. Anhydrous tetrahydrofuran (THF) (Acros Organics) was kept over CaH_2 and distilled at 339 K (66 °C). Coronand 18C6 (Merck), cryptand C222 (Merck) and $\text{CsOH}\cdot\text{H}_2\text{O}$ (Aldrich) were used without purification.



Scheme 2 Direct deprotonation of PO

Synthesis

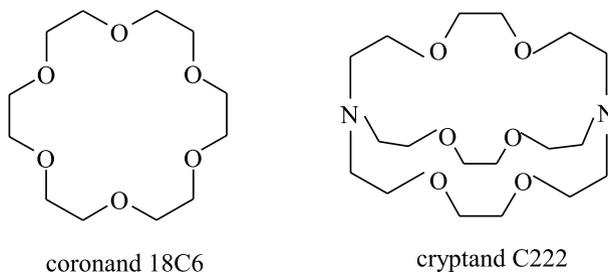
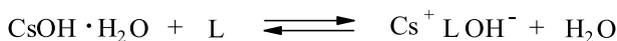
All syntheses were carried out at 20 °C in a 50 cm³ reactor equipped with a magnetic stirrer and a Teflon valve enabling substrates delivery and sampling under argon atmosphere. In the first series of polymerizations of propylene oxide, the initial concentration of the monomer was equal to 2.0 mol/dm³ and the initial amount of CsOH·H₂O (0.34 g, 2.0 mmol) and THF (17.0 cm³) was introduced into reactor and then 18C6 (0.53 g, 2.0 mmol) was added. The mixture was stirred during 30 min. That system was used as the initiator, when the monomer (2.8 cm³, 2.4 g, 40.0 mmol) was introduced into the reactor. The reaction mixture was then stirred during 170 h. After this time complete conversion of the monomer occurred and the reaction mixture was neutralized with HCl/H₂O system (0.1 mol/dm³, 50 cm³) and transferred to the separator containing chloroform (70 cm³). After shaking during 5 min, two layers were obtained, i.e., inferior polyether layer and superior layer containing water and the cesium salt. These layers were separated, and the superior layer was removed. After three washings with distilled water, polyether was obtained by evaporating of chloroform and water in vacuum at elevated temperature. In the next series, polymerizations were performed in the presence of other ligand C222 and higher initial concentration of the monomer, i.e., 5.0 mol/dm³. Similar procedure was applied for polymerization of other oxiranes. The concentration of monomer during the polymerizations was monitored by the 1,4-dioxane method [23]. The final conversions were ~99%. The yields of the reactions were 97–99%. All studied processes were heterogeneous and part of initiator remained at the end of polymerization.

Measurements

100 MHz ¹³C NMR spectra were recorded in CDCl₃ at 25 °C on a Bruker Avance 400 pulsed spectrometer equipped with 5 mm broad-band probe and applying Waltz16 decoupling sequence. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. To obtain a good spectrum of the polymer main chain exhibiting its microstructural details, about 3000 scans were sufficient but in order to observe the signals of the polymer chain terminal groups 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 THF as a solvent. Polystyrenes were used as calibration standards. MALDI-TOF spectra were recorded on a Shimadzu AXIMA Performance instrument. Dithranol was used as a matrix.

Results and discussion

It was observed, that CsOH·H₂O is practically insoluble in THF at room temperature and does not initiate polymerization of oxiranes. Therefore, all processes were carried out with this initiator, which is activated by macrocyclic ligands complexing


Scheme 3 Ligands (L) for metal cations

Scheme 4 Equilibrium involving complexation of initiator by ligand

metal cations, i.e., 18C6 or C222 (Scheme 3). It allowed to increase the reactions rate and yield of the polymers.

Both ligands cause ionization of initiator, which results in the formation of ligand separated ion pairs existing in equilibrium with solid salt. Thus, the concentration and reactivity of initiator increase markedly in the presence of ligand and initiator of the polymerization occurs in the solution (Scheme 4).

Due to the ratio of the ionic cesium cation radius to the 18C6 cavity radius ≈ 1.2 [24], it is theoretically possible to exist in equilibrium two kinds of complexes, i.e., flat (1/1) and sandwich (1/2) ones [25]. Cryptand C222 is able to form exclusive and inclusive complexes being in equilibrium, but in THF the formation of the inclusive complex was hindered by the strong cation–anion interaction [26].

Table 1 Characterization of PPO-diols, PBO-diols and PSO-diols obtained in the polymerization of oxiranes initiated with CsOH·H₂O activated by complexing agent (L); [CsOH·H₂O]₀=[L]₀=0.1 mol/dm³

No	Initiating system	[Monomer] ₀ (mol/dm ³)	Time (h)	Yield (%)	M _n (SEC)	M _w /M _n (SEC)
1	CsOH·H ₂ O/18C6	PO (2.0)	170	99	2000	1.29
2	CsOH·H ₂ O/18C6	PO (5.0)	390	99	5100	1.20
3	CsOH·H ₂ O/C222	PO (2.0)	140	99	1800	1.22
4	CsOH·H ₂ O/C222	PO (5.0)	350	98	4900	1.17
5	CsOH·H ₂ O/18C6	BO (2.0)	250	97	2700	1.25
6	CsOH·H ₂ O/18C6	BO (5.0)	460	98	4200	1.19
7	CsOH·H ₂ O/C222	BO (2.0)	220	97	2500	1.20
8	CsOH·H ₂ O/C222	BO (5.0)	415	99	4000	1.26
9	CsOH·H ₂ O/18C6	SO (2.0)	490	99	3000	1.28
10	CsOH·H ₂ O/18C6	SO (5.0)	610	98	4600	1.30
11	CsOH·H ₂ O/C222	SO (2.0)	460	99	2700	1.24
12	CsOH·H ₂ O/C222	SO (5.0)	595	97	4000	1.33

Table 2 Characterization of polyether-diols obtained in the polymerization of glycidyl ethers initiated with CsOH-H₂O activated by complexing agent (L); [CsOH-H₂O]₀ = [L]₀ = 0.1 mol/dm³

No	Initiating system	[Monomer] ₀ (mol/dm ³)	Time (h)	Yield (%)	M_n (SEC)	M_w/M_n (SEC)
13	CsOH-H ₂ O/18C6	PGE (2.0)	130	99	2700	1.27
14	CsOH-H ₂ O/18C6	PGE (5.0)	270	(a) 60 (b) 40	6400 600	1.23 1.29
15	CsOH-H ₂ O/C222	PGE (2.0)	115	99	2500	1.21
16	CsOH-H ₂ O/C222	PGE(5.0)	250	98	5000	1.29
17	CsOH-H ₂ O/18C6	IPGE (2.0)	110	(a) 24 (b) 50 (c) 26	5400 2500 800	1.03 1.10 1.11
18	CsOH-H ₂ O/18C6	IPGE (5.0)	245	(a) 57 (b) 43	5200 2400	1.04 1.12
19	CsOH-H ₂ O/C222	IPGE (2.0)	100	(a) 75 (b)25	4700 2100	1.03 1.09
20	CsOH-H ₂ O/C222	IPGE (5.0)	230	(a) 60 (b) 40	4800 2300	1.08 1.17
21	CsOH-H ₂ O/18C6	AGE (2.0)	105	(a) 70 (b) 30	5300 2400	1.04 1.15
22	CsOH-H ₂ O/18C6	AGE (5.0)	225	(a) 65 (b) 35	5200 2600	1.07 1.14
23	CsOH-H ₂ O/C222	AGE (2.0)	95	(a)20 (b)57 (c)23	5300 2400 600	1.02 1.08 1.09
24	CsOH-H ₂ O/C222	AGE (5.0)	215	(a)7 (b) 13 (c) 42 (d) 30 (e) 5 (f) 3	18,000 10,500 5000 2300 750 450	1.01 1.03 1.05 1.09 1.03 1.02

Molar masses (M_n) of PPO-diols (1–4), PBO-diols (5–8), PSO-diols (9–12) and their dispersities (M_w/M_n) are collected in Table 1.

It was suggested, that initiation occurs exclusively in liquid phase, i.e., it is mediated by the part of initiator, which is soluble in the reaction mixture. It causes increase of M_n . Polarity of the medium depends on the kind and initial concentration of the monomer, which also influences M_n of polymers. Moreover, chain transfer to water results in decrease of M_n . Polymers synthesized in the presence of C222 has a little lower M_n than obtained with 18C6 at the same monomer concentration. It may result from slight increase in initiator concentration in the reaction mixture containing C222 ligand. Relatively high dispersity of the polymers obtained ($M_w/M_n = 1.17–1.34$) results from chain transfer reaction to water and slow solubilization of initiator during the polymerization. It was established, that PPO-diols and PSO-diols obtained in this work do not contain macromolecules with unsaturated starting groups. Signals in unsaturated region,

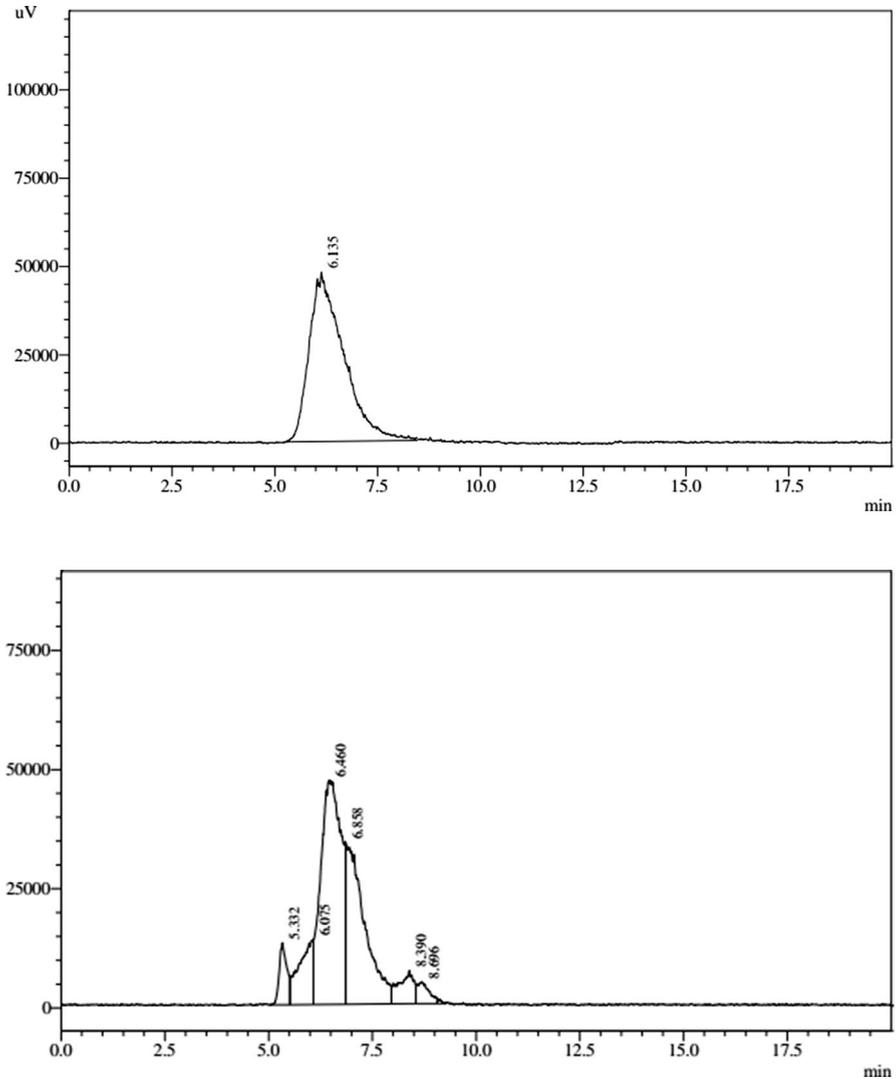


Fig. 1 Modality of polyether-diols prepared by anionic ring opening polymerization of glycidyl ethers initiated with CsOH·H₂O activated by complexing agent; (1) PPGE-diol (16); (2) PAGE-diol (24)

i.e., at 116.7 and 134.9 ppm for PPO-diols as well at 133.2 and 159.7 ppm for PSO-diols were not observed in ¹³C NMR spectrum. FTIR analysis of PPOs and PSOs did not indicate signals of C=C bonds in their spectra neither at 1600–1680 (C=C bond stretching) or at 3300–3200 cm⁻¹ (sp² C–H bond stretching). However, such signals were detected in other systems with K⁺ counterion [8, 26, 27]. It indicates, that the presence of Cs⁺ ions and high amount of water completely

eliminate unsaturation in these polymers, due to chain transfer reaction to water. In the studied systems, the rate of this reaction is evidently much more higher, than the rate of chain transfer to monomer.

Polyether-diols (1–12) are unimodal. Unexpectedly, polymers synthesized from glycidyl ethers are, in general, bimodal (13–24) (Table 2). One of them, i.e., (24) consists even six fractions.

It is worth noting, that dispersities of fractions (a) are lower than (b). Dispersities of some fraction are extremely low (1.01–1.05). Figure 1 shows SEC chromatograms of two exemplary polyether-diols.

M_n of main fraction (a) of PIPGE-diol (18) obtained at $[M]_0 = 2.0 \text{ mol/dm}^3$ is about two-fold higher than M_n of fraction (b). Similar effect is observed for PIPGE (20) prepared at $[M]_0 = 5.0 \text{ mol/dm}^3$. Unexpectedly, M_n of fractions do not increase at much higher initial concentration of monomer. In the presence of C222, molar masses are lower. Similar phenomenon occurs in the case of PAGE-diols. The same heterogeneity and dissolving of the initiator with the course of polymerization may be responsible for the not observed increase of M_n of the product with increasing concentration of monomer (more initiator in the ionic form—smaller M_n).

MALDI-TOF spectrum of polymer (24) (Fig. 2) reveals one series of signals at m/z 954.2–6775.3. These signals represent macromolecules which consist central oxygen atom and two terminal hydroxyl groups. For example, peaks at m/z 1981.7, 3808.7 and 4379.0 belong to macromolecules possessing 17, 33 and 38 monomer units ($M_{\text{calc}} = 1981.4, 3809.1$ and 4378.6 , respectively). These macromolecules form adducts with sodium ions.

Basing on the results obtained, the course of polymerization is proposed in Scheme 5.

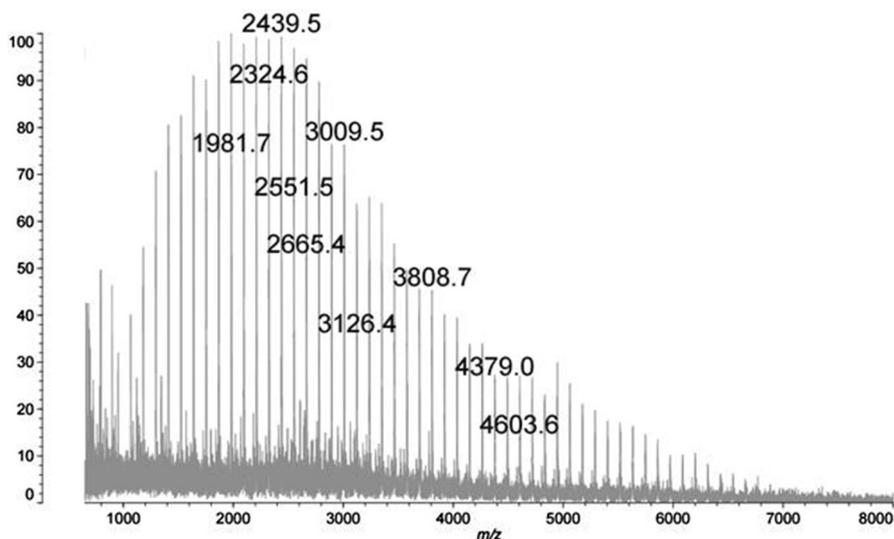
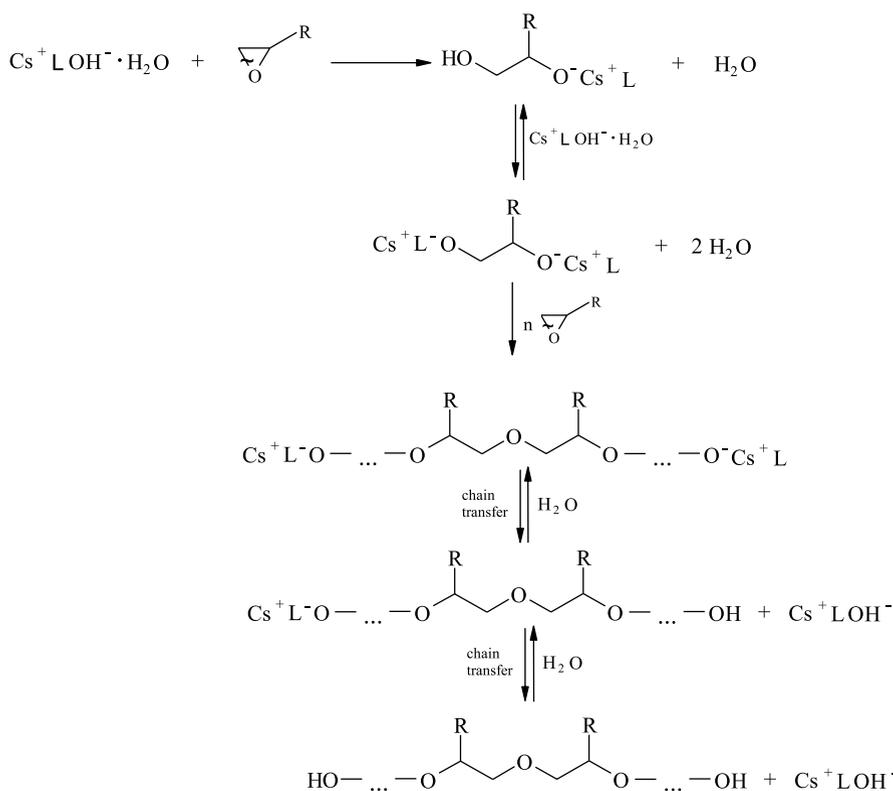


Fig. 2 MALDI-TOF spectrum of PAGE-diol (24) prepared by use of CsOH·H₂O activated by C222

Formation of two or more fraction in the polymerization of some oxiranes needs some comments. It is generally accepted, that in the polymerization process bimodality exclusively appears, when there are two species, propagating with different rate constants and that these species do not exchange fast enough [28]. According to this statement, it was proposed, that in the studied systems various kinds of anionic centers with different reactivity in growing polymer chains should be formed and be responsible for polymodality of some polymers (Scheme 6).

On the other hand, the heterogeneity of the system (transfer of an initiator from solid state to liquid followed by its ionization) may be consider as a reason of polymodality. However, unimodality observed in some polyethers indicates, that formation of two or more fractions in other polymers depends also on the kind of monomer. Explanation of this phenomenon needs further investigations.



Scheme 5 Polymerization of monosubstituted oxiranes in the presence of CsOH·H₂O activated by complexing agent (L)

References

1. Zhang ZQ, Xu GY, Wang F, Dong SL, Li Y (2004) Characterization and demulsification of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) copolymers. *J Colloid Interface Sci* 277:464–470. <https://doi.org/10.1016/j.jcis.2004.04.035>
2. Gosa KI, Uricanu V (2002) Emulsions stabilized with PEO–PPO–PEO block copolymers and silica. *Colloids Surf A* 197:257–269. [https://doi.org/10.1016/S0927-7757\(01\)00902-5](https://doi.org/10.1016/S0927-7757(01)00902-5)
3. Izukawa T, Kunihiro T, (1999) Nishikawa A (Eds.), M.C.I. US Patent 5,916,994
4. Jeong B, Bae YH, Lee DS, Kim SW (1997) Biodegradable block copolymers as injectable drug-delivery systems. *Nature* 388:860–862. <https://doi.org/10.1038/42218>
5. Mathur AM, Drescher B, Scranton AB, Klier J (1998) Polymeric emulsifiers based on reversible formation of hydrophobic units. *Nature* 392:367–370. <https://doi.org/10.1038/32856>
6. Ionescu M (2008) Chemistry and technology of polyols for polyurethanes. Rapra Technology Limited, Shropshire
7. Steiner EC, Pelletier RR, Trucks RO (1964) A Study of the Polymerization of Propylene Oxide Catalyzed by Anhydrous Potassium Hydroxide. *J Am Chem Soc* 86:4678–4686. <https://doi.org/10.1021/ja01075a031>
8. Grobelny Z, Matlengiewicz M, Jurek J, Michalak M, Kwapińska D, Swinarew A, Schab-Balcerzak E (2013) The influence of macrocyclic ligands and water on propylene oxide polymerization initiated with anhydrous potassium hydroxide in tetrahydrofuran. *Eur Polymer J* 49:3277–3288. <https://doi.org/10.1016/j.eurpolymj.2013.06.035>
9. Becker H, Wagner G (1984) Zur Übertragungsreaktion bei der anionischen Polymerisation von Oxiranen VI. Zum Einfluß von Kronenetherzusätzen auf die Polymerisation von Propylenoxid. *Acta Polym* 35:28–32. <https://doi.org/10.1002/actp.1984.010350106>
10. Becker H, Wagner G, Stolarzewicz A (1982) Zur Übertragungsreaktion bei der anionischen Polymerisation von Oxiranen. III. Zur Dynamik der Doppelbindungsbildung bei der Propylenoxid-polymerisation. *Acta Polym* 33:34–37. <https://doi.org/10.1002/actp.1982.010330107>
11. Yu GE, Heatley F, Booth C, Bleas TG (1994) Anionic polymerization of propylene oxide: isomerization of allyl ether to propenyl ether end groups. *J Polym Sci Part A Polym Chem* 32:1131–1135. <https://doi.org/10.1002/pola.1994.080320615>
12. Ding J, Price C, Booth C (1991) Use of crown ether in the anionic polymerization of propylene oxide–1 Rate of polymerization. *Eur Polym J* 27:891–894. [https://doi.org/10.1016/0014-3057\(91\)90028-M](https://doi.org/10.1016/0014-3057(91)90028-M)
13. Ding J, Heatley F, Price C, Booth C (1991) Use of crown ether in the anionic polymerization of propylene oxide–2. Molecular weight and molecular weight distribution. *Eur Polymer J* 27:895–899. [https://doi.org/10.1016/0014-3057\(91\)90029-N](https://doi.org/10.1016/0014-3057(91)90029-N)
14. Grobelny Z, Swinarew A, Jurek-Suliga J, Skrzeczyna K, Gabor J, Łęźniak M (2016) The influence of crown ether and alcohol on unsaturation and molar mass of poly(propylene oxide)s prepared by use of potassium *t*-butoxide: reinvestigation of chain transfer reactions. *Int J Anal Chem*. <https://doi.org/10.1155/2016/3727062>
15. Grobelny Z, Matlengiewicz M, Jurek-Suliga J, Golba S, Skrzeczyna K (2018) The influence of initiator and macrocyclic ligand on unsaturation and molar mass of poly(propylene oxide)s prepared with various anionic system. *Polym Bull* 75:1101–1112. <https://doi.org/10.1007/s00289-017-2078-z/>
16. Wegener G, Brandt M, Duda L, Hofmann J, Kleczewski B, Koch D, Kumpf R-J, Orzesek H, Pirkel H-G, Six Ch, Steinlein Ch, Weisbech M (2001) Trends in industrial catalysis in the polyurethane industry. *Appl Catal A* 221:303–335. [https://doi.org/10.1016/S0926-860X\(01\)00910-3](https://doi.org/10.1016/S0926-860X(01)00910-3)
17. PierrePrice LESTChC (1956) The room temperature polymerization of propylene oxide. *J Am Chem Soc* 78:3432–3436. <https://doi.org/10.1021/ja01595a047>
18. Snyder Jr W.H., Ph. D. Thesis, University of Pennsylvania, 1961
19. Freidly HR (1992) Reaction Polymers. In: WF Gum, W Riese, H Ulrich (Eds), Hanser Publishers: NY p. 66
20. Curtis CJ, Levis Jr WW, Pizzini LC inventors, BASF Wyandotte Corporation, assignee US Patent 4,487,853, 1984
21. Exner JH, Steiner EC (1974) Solvation and ion pairing of alkali-metal alkoxides in dimethyl sulfoxide. *J Am Chem Soc* 96:1782–1787. <https://doi.org/10.1021/ja00813a022>

22. Dimitrov P, Rangelov S, Dworak A, Tsvetanov ChB (2004) Synthesis and associating properties of poly(ethoxyethylglycidyl ether)/poly(propylene oxide) triblock copolymers. *Macromolecules* 37:1000–1008. <https://doi.org/10.1021/ma0354039>
23. Siggia S (1963) *Quantitative organic analysis via functional groups*. Wiley, USA, p 241
24. Lamb JD, Izatt RM, Christensen JJ, Eatough DJ (1979) Coordination chemistry of macrocyclic compounds. In: Melson GA (Ed.), Plenum Press, New York, p. 145–218
25. Issa D, Ellaboudy A, Janakiraman R, Dye JL (1984) Magnetic-susceptibilities and electron-paramagnetic resonance-spectra of a ceside and an electride. *J Phys Chem* 88:3847–3851. <https://doi.org/10.1021/j150661a032>
26. Kauffmann E, Dye JL, Lehn JM, Popov AI (1980) A study of the inclusive and exclusive cesium cryptates in nonaqueous solvents by cesium-133 NMR. *J Am Chem Soc* 102:2274–2278. <https://doi.org/10.1021/ja00527a023>
27. Grobelny Z, Matlengiewicz M, Jurek-Suliga J, Golba S, Skrzeczyna K, Kwapulińska D (2017) Ring opening polymerization of styrene oxide initiated with potassium alkoxides and hydroxy-alkoxides activated by 18-crown-6: determination of mechanism and preparation of new poly-ether-polyols. *Polym Bull* 74:4763–4780. <https://doi.org/10.1007/s00289-017-1976-4/>
28. Penczek S, Cypryk M, Duda A, Kubisa P, Słomkowski S (2007) Living ring-opening polymerizations of heterocyclic monomers. *Prog Polym Sci* 32:247–282. <https://doi.org/10.1016/j.progpolymsci.2007.01.002>

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