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Cationic oligomerization of α-hydroxy-γ-butyrolactone

Summary — Cationic polymerization of 5-membered cyclic ester α-hydroxy-γ-butyrolactone (BL-OH) proceeds according to activated monomer (AM) mechanism and leads to low molecular weight polymers. Elimination of water from growing macromolecules occurs during the polymerization process. The extent of dehydration depends on the catalyst and is the lowest in the case of scandium triflate [(CF$_3$SO$_3$)$_3$Sc] catalyst. Spontaneous polymerization of BL-OH, occurring during vacuum distillation, leads to the oligomeric product without dehydration.
Key words: branched polymers, polyesters, cationic polymerization, ring-opening polymerization, MALDI-TOF method.

KATIONOWA OLIGOMERYZACJA α-HYDROKSY-γ-BUTYROLAKTONU
Streszczenie — Kationowa polimeryzacja 5-członowego cyklicznego estru α-hydroksy-γ-butyrolaktonu (BL-OH) zachodzi według mechanizmu aktywowanego monomeru (AM) i prowadzi do produktów o niewielkich ciężarach cząsteczkowych (tabela 1). W wyniku analizy produktów polimeryzacji metodą MALDI-TOF (rys. 1) stwierdzono, że w trakcie polimeryzacji prowadzonej w obecności kwasów protonowych lub w obecności kwasów Lewisa zachodzą reakcje odwodnienia prowadzące m.in. do powstawania wiązań podwójnych. Udział reakcji odwodnienia zależy od użytego katalizatora i jest najmniejszy w przypadku polimeryzacji katalizowanej za pomocą triftanalu skandu [(CF$_3$SO$_3$)$_3$Sc] prowadzonej w temperaturze 40 °C (rys. 3). Stwierdzono, że podczas destylacji próżniowej BL-OH zachodzi spontaniczna polimeryzacja monomeru bez udziału reakcji odwodnienia (rys. 2).
Słowa kluczowe: polimery rozgałęzione, poliestry, polimeryzacja kationowa, polimeryzacja z otwarciem pierścienia, MALDI-TOF.

Heterocyclic monomers containing hydroxyl group in the substituent constitute an interesting class of monomers that can be used for the syntheses of highly branched or hyperbranched polymers. Those monomers can be treated as latent AB$_2$ monomers [1]. Typical example of latent AB$_2$ monomer is hydroxymethyloxirane (glycidol) that can polymerize by ionic mechanism (both anionic or cationic) to highly branched polyethers containing multiple terminal hydroxyl groups [2—4]. Syntheses and possible applications of such polymers have been described in a few recent reviews [1, 5—9].
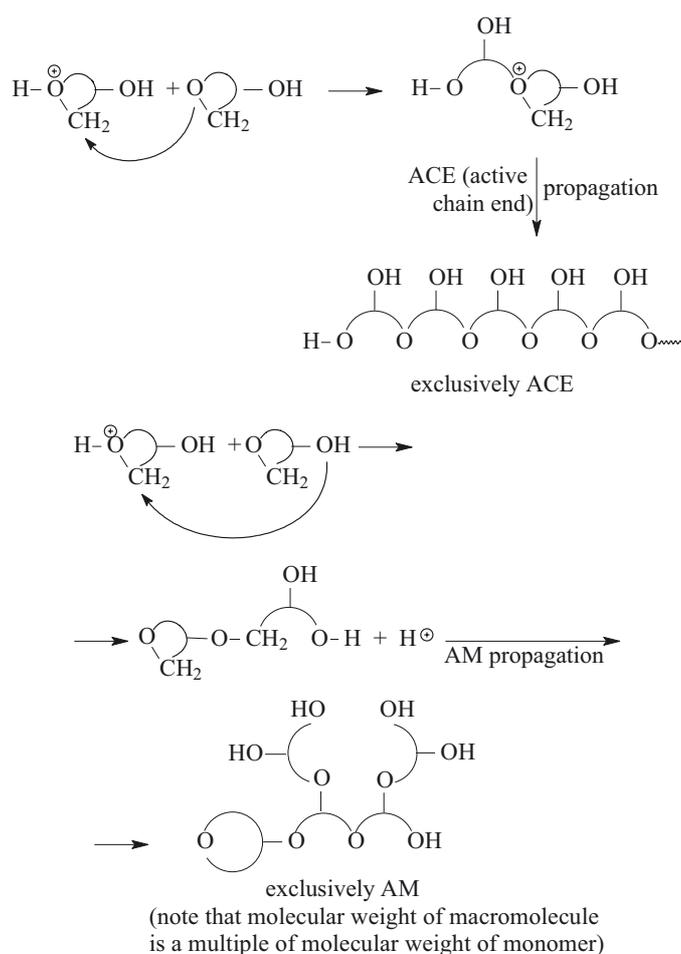
Cationic polymerization of glycidol proceeds by activated monomer (AM) mechanism [3, 4]. Polymerization of heterocyclic monomers by AM mechanism has also been reviewed [10]. In the cationic polymerization of heterocyclic monomers containing hydroxyl group in the substituents, a contribution of AM mechanism should lead to branching, as shown schematically below (Scheme A) using hydroxyl substituted cyclic ether as an example.

In a series of reports from our laboratory the cationic AM polymerization of 3- and 4-membered cyclic ethers substituted with hydroxymethyl groups was described

[3, 11—15]. There is, however, the number of easily available heterocyclic compounds (cyclic ethers, cyclic esters) containing hydroxymethyl or hydroxyl substituents attached to 5- or 6-membered rings.

It is known, that the thermodynamic polymerizability of weakly strained 5- and 6-membered cyclic ethers or esters is limited, due to the low enthalpy of polymerization [16]. Substitution typically decrease further the thermodynamic polymerizability (to linear polymers) [16] but there is practically no information on the thermodynamics of polymerization leading to highly branched polymers. Because in such case macromolecules may be built from short chain fragments connected by branching units, the thermodynamic limitations of polymerization leading to highly branched polymers may not be the same as the thermodynamic limitations of polymerization leading to linear polymers.

Indeed, it has been shown recently that 5-membered cyclic ether — tetrahydrofuran, substituted with hydroxymethyl or hydroxyl groups, undergoes cationic polymerization although the molecular weights of products are rather limited (M_n up to 3000). Polymerization was

Scheme A. *Two possible mechanisms of cationic polymerization of heterocyclic monomers containing hydroxyl groups in the substituents*
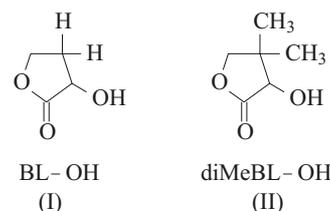
accompanied by dehydration and possible mechanisms of these processes were discussed [17].

In order to explore further the possibility of using weakly strained heterocyclic monomers substituted with hydroxyl groups for the syntheses of branched polymers (oligomers), in this article the behavior of 5-membered cyclic ester substituted with hydroxyl group, namely α-hydroxy-γ-butyrolactone at the conditions of cationic polymerization is reported. Frechet *et al.* [18] reported on anionic polymerization of 4-(2-hydroxyethyl)-ε-caprolactone leading to highly branched polymers but till now there is no report in the literature on the cationic polymerization of hydroxy- substituted lactones.

EXPERIMENTAL

Materials

α-Hydroxy-γ-butyrolactone [BL-OH, formula (I), Aldrich] was distilled under vacuum. Dihydro-3-hydroxy-4,4-dimethyl-2(3H)-furanone [diMeBL-OH, formula (II), Aldrich] was used after drying in vacuum. Trifluo-

romethanesulfonic acid (CF_3SO_3H), boron trifluoride etherate ($BF_3 \cdot Et_2O$), tetrafluoroboric acid etherate ($HBF_4 \cdot Et_2O$) and tin tetrachloride ($SnCl_4$) (all from Aldrich) were distilled before use. Scandium triflate [$(CF_3SO_3)_3Sc$, Aldrich] was used after drying in vacuum. Solvents were purified by distillation.

Polymerization procedure

0.5 g of BL-OH (4.9 mmol) was placed in an ampoule together with 0.24 mmol of catalyst (it corresponds for example to 0.12 g of scandium triflate) and with stirring bar. In the case of liquid catalyst, the appropriate amount — 0.24 mmol was added with syringe to the cooled BL-OH. The ampoule was connected to vacuum line and sealed under vacuum. Sealed ampoule was placed in an oil bath preheated to the desired temperature. After predetermined time it was opened and the polymerization mixture was analyzed.

Methods of testing

^{1}H and ^{13}C NMR spectra were recorded using 200 MHz Bruker spectrometer [deuterated dimethyl sulfoxide (DMSO) was used as a solvent].

Conversion of monomer was determined by comparison of the intensity of corresponding signals present in ^{1}H NMR spectrum recorded for polymerization mixture (without neutralization). With opening of the cyclic monomer ring, the magnetic nonequivalency of the protons in β position disappears and both protons present in an oligomer give the signals at the same region of the spectrum (the signal corresponding to one proton at 2.33—2.48 ppm is shifted to the region of the second proton at 1.85—2.10 ppm).

SEC (size exclusion chromatography) analyses were carried out using a ConstaMetric 4100 pump, Refracto-Monitor IV (both from Thermo Separation Products, USA) and two Phenogel columns: 5 50A and 5 500A. THF was used as an eluent at a flow rate 0.70 cm^3/min, and polystyrene standards were used for calibration.

For the SEC analyses the products were first dissolved in DMSO and the samples were next diluted with tetrahydrofuran (THF). When $(CF_3SO_3)_3Sc$ was used as a catalyst, it was separated from polymeric product by precipitation of the salt from DMSO solution into THF. In the case of the other catalysts, polymerization mixture was neutralized by adding of about 0.1 g of CaO to the reaction mixture (~0.5 g) diluted with DMSO and subsequently filtered.

MALDI-TOF (Matrix-Assisted Laser Desorption/Ionization Time-of-Flight) spectra were recorded using Voyager Elite apparatus, using dihydroxybenzoic acid as a matrix and NaI as cationating agent in THF solution. Polymeric samples were dissolved in DMSO. Nitrogen laser desorption at a wavelength equal to 337 nm was applied.

RESULTS AND DISCUSSION

When BL-OH is distilled under vacuum (60 °C at 10^{-2} mm Hg), about 30 % of the initial mass of BL-OH remains in the flask in form of viscous liquid that solidifies to glassy, colorless solid at room temperature. This residue is insoluble in typical solvents like chloroform, methylene chloride, poorly soluble in THF and soluble in DMSO. When DMSO solution is injected into SEC apparatus with THF as eluent the broad signal is observed corresponding to $M_n \approx 1000$ (polystyrene calibration). Analysis of the product by MALDI-TOF indicates the presence of series of oligomers with molecular weights corresponding to $n \times 102.09 + 23$ (102.09 is molecular weight of BL-OH and 23 is molecular weight of Na^+ used as cationating agent) with n up to 20. This indicates that spontaneous polymerization of BL-OH occurs at the conditions of vacuum distillation. Because possible impurities in crude BL-OH should be acidic rather than basic ones, acid catalysis can be assumed. In order to exclude the possibility that polymerization is catalyzed by basic impurities the distillation was conducted in the presence of ~1 % of $HBF_4 \cdot Et_2O$. The amount of solid residue was higher than in the absence of acid and this residue was no longer soluble even in DMSO.

T a b l e 1. The effects of conditions of bulk polymerization of α-hydroxy-γ-butyrolactone (BL-OH) on the conversion and molecular weights of products

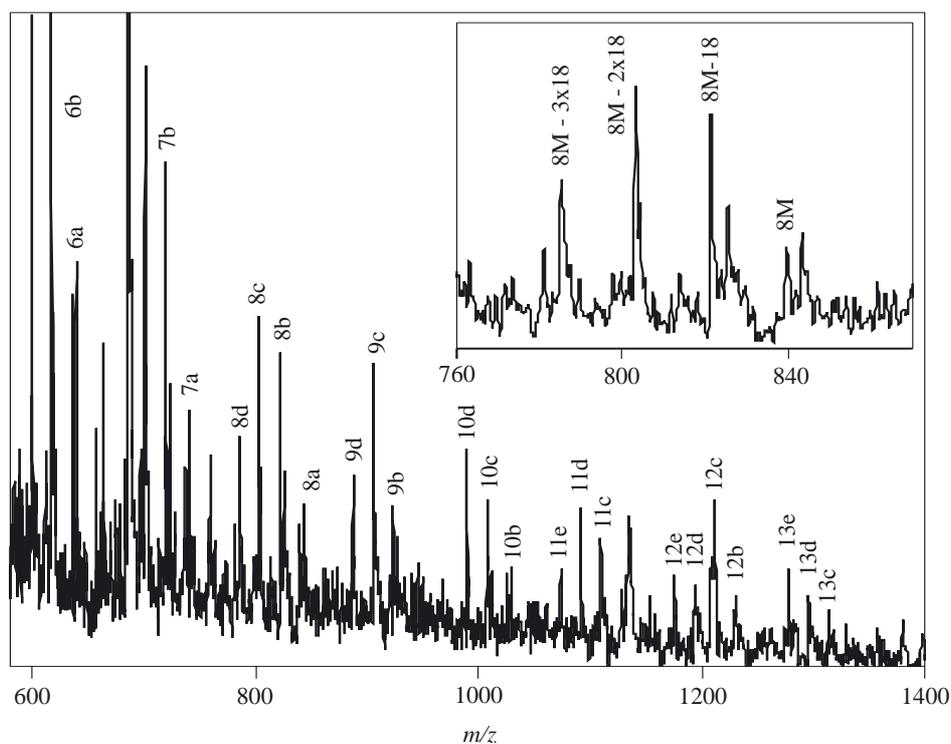| No	Catalyst	Tempe-rature, °C	[BL-OH]/[cat]	Time h	Conver-sion, %	M_n (by SEC)
1	CF_3SO_3H	90	20	24	56	n.d.[a]
2	$HBF_4 \cdot Et_2O$	60	40	24	48	1290
3	$BF_3 \cdot Et_2O$	60	20	72	42	640
4	$SnCl_4$	70	20	24	55	690
5		60 (in Ar atmo-sphere)	20	72	35	n.d.
6		25	20	72	30	n.d.
7		60	40	72	12	n.d.
8	$(CF_3SO_3)_3Sc$	60	20	24	35	n.d.
9		80	20	72	53	570
10		40	20	72	39	730
11		60	20	72	43	600
12		60	20	240	42	n.d.

[a] n.d. — not determined.

Fig. 1. MALDI-TOF mass spectrum of poly(BL-OH) obtained in the presence of CF_3SO_3H (number 1 in Table 1); the signals correspond to the following series (number indicates the length of oligomer): a) $m/z = n \times 102.09 + 23$, b) $m/z = n \times 102.09 - 1 \times 18 + 23$, c) $m/z = n \times 102.09 - 2 \times 18 + 23$, d) $m/z = n \times 102.09 - 3 \times 18 + 23$, e) $m/z = n \times 102.09 - 4 \times 18 + 23$, in the inlet the region corresponding to octamers is presented

The apparent conclusion is that this spontaneous polymerization is acid catalyzed and thus proceeds by cationic mechanism. Therefore the series of experiments were conducted in order to reproduce this process under controlled conditions.

All polymerizations of BL-OH were performed in sealed ampoules under vacuum. After defined time of heating in an oil bath ampoules were opened and polymerization mixtures (after removing of acid catalyst) were analyzed by ^{1}H and ^{13}C NMR and MALDI-TOF methods. Results are summarized in Table 1.

In all cases relatively low molecular weight oligomers with up to 50 % yield were obtained.

The information on the nature of products may be obtained from MALDI-TOF analysis. In Figure 1 MALDI-TOF spectrum of the product obtained in polymerization performed with CF_3SO_3H as a catalyst (number 1 in Table 1) is shown. Signals of oligomers with degree of polymerization (DP_n) up to 13 can clearly be detected. Only however, for oligomers with DP_n up to 8, the signals corresponding to multiple of molecular weight of monomer unit ($m/z = n \times 102.09 + 23$) are present. Those signals are accompanied by the signals appearing at $m/z = n \times 102.09 - k \times 18 + 23$) indicating that in the course of polymerization the elimination of one or more water molecules occurs. For higher oligomers ($DP_n > 8$) the signals at $m/z = n \times 102.09 + 23$ can no longer be detected and the only signals are those corresponding to dehydrated macromolecules.

This observation is similar to reported earlier elimination of water molecules in the course of cationic AM

$$-CH_2-OH + HO-CH_2- \longrightarrow -CH_2-O-CH_2- + H_2O \quad (1)$$

polymerization of tetrahydrofuran derivatives substituted with hydroxymethyl or hydroxyl groups [17].

There are two possible mechanisms of water elimination. One involves condensation of two hydroxyl groups
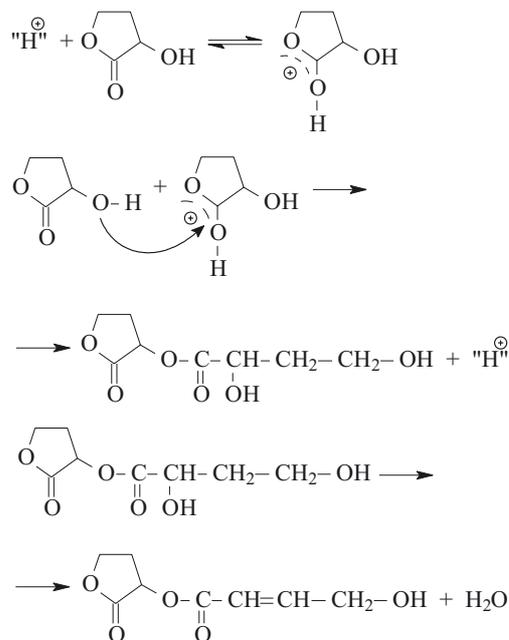
Scheme B. Elimination of water with formation of double bonds
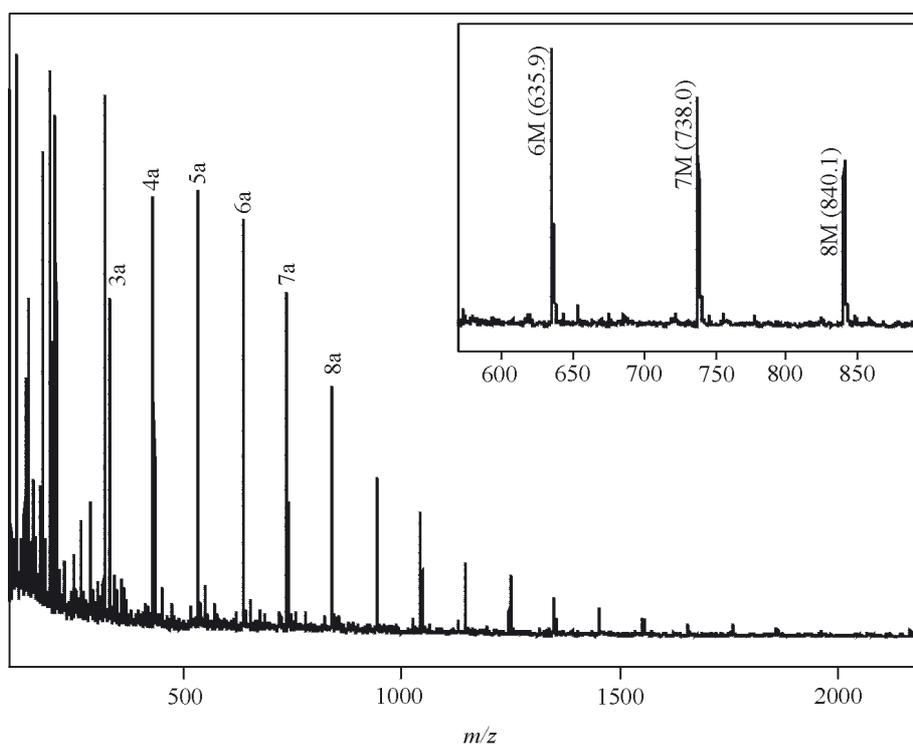

Fig. 2. MALDI-TOF mass spectrum of poly(BL-OH) obtained as a result of spontaneous polymerization; the signals correspond to oligomers being a multiple of monomeric unit (without any terminal groups; $m/z = n \times 102.09 + 23$)
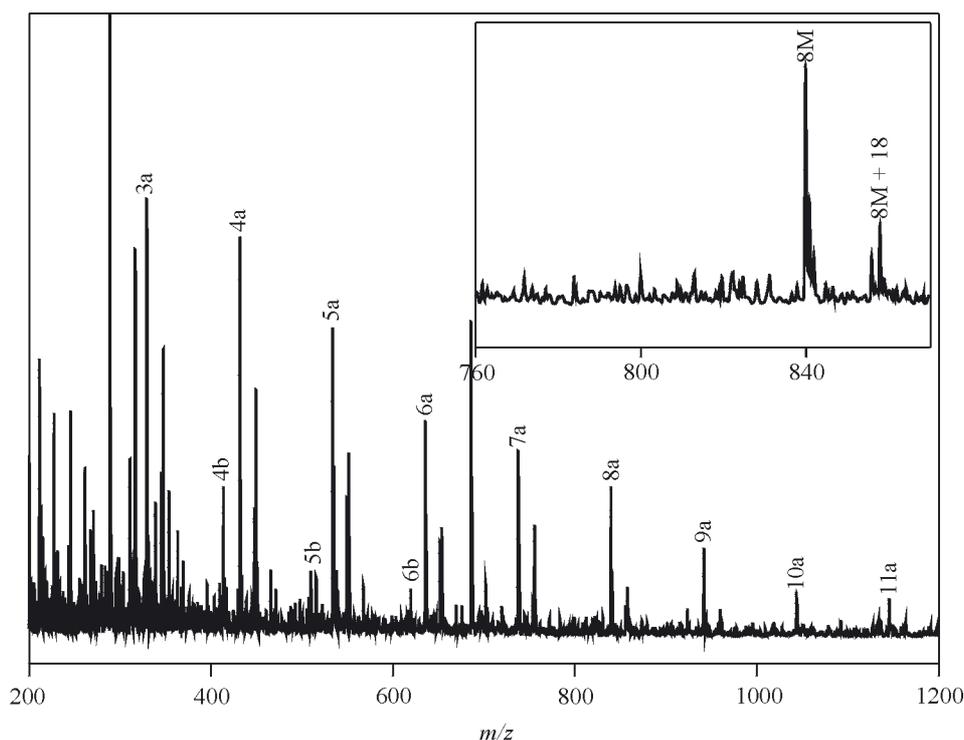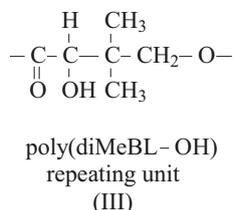
Fig. 3. MALDI-TOF mass spectrum of poly(BL-OH) obtained in the presence of (CF₃SO₃)₃Sc (number 10 in Table 1); two major series are: a (m/z = n × 102.09 + 23), and series of macromolecules with additional water (m/z = n × 102.09 +18 + 23)

as shown in equation (1) while the other involves elimination of water molecule with formation of double bond as shown in Scheme B.

In the formerly studied polymerization of hydroxy-substituted tetrahydrofuran derivatives both reaction pathways were found to operate. In order to check whether in the polymerization of cyclic ester dehydration occurs also in the case when there is no hydrogen atoms in α-position to carbon bearing HO- substituent, MALDI-TOF spectra of products obtained at identical conditions from BL-OH analogue substituted at β position with two methyl groups (dihydro-3-hydroxy-4,4-di-methyl-2(3H)-furanone; diMeBL-OH) were analyzed [formula (III)].

$$- \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{||}}{C}} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - O -$$

poly(diMeBL–OH)
repeating unit
(III)

Although the spectra were more complex, indicating additional side reactions, the presence of signals at $m/z = n \times 130.15 - k \times 18 + 23$ (130.15 is the molecular weight of diMeBL-OH unit) could clearly be detected, indicating that even when reaction pathway shown in Scheme B is eliminated, dehydration still occurs by condensation as shown in eq. (1). Apparently in the polymerization of BL-OH, when reaction pathway shown in Scheme B is possible, an elimination of water molecules occurs also

by this mechanism because the signals corresponding to double bonds can be detected in ^{13}C NMR spectra of the products at 117.5 and 129.9 ppm. Thus one has to conclude that both mechanisms of water elimination occur in the system studied.

It is interesting to note, that spontaneous polymerization of BL-OH during vacuum distillation leads to oligomeric product without dehydration. In Figure 2 MALDI-TOF spectrum of the product of spontaneous polymerization is shown. In the spectrum only the signals appearing at $m/z = n \times 102.09 + 23$ are observed. This indicates that at certain conditions polymerization of BL-OH may proceed without dehydration.

In order to establish whether the extent of dehydration depends on the nature of catalyst, MALDI-TOF spectra of the products obtained with use of different catalysts (listed in Table 1) were analyzed. It turned out that (CF₃SO₃)₃Sc gives the lower extent of dehydration. MALDI-TOF spectrum of the product obtained with this catalyst at 40 °C (number 10 in Table 1) is shown in Figure 3. In the spectrum the signals corresponding to $m/z = n \times 102.09 - k \times 18 + 23$ are of much lower intensity as compared to the product of polymerization initiated by CF₃SO₃H (shown in Fig. 1) and additionally the signals at $m/z = n \times 102.09 + 18 + 23$ appear, indicating that some macromolecules are initiated by water molecules that is formed in the system.

SEC curves for the products obtained with use of different catalysts, shown in Figure 4, indicate that the nature of catalyst has some, although not significant, effect on molecular weight.
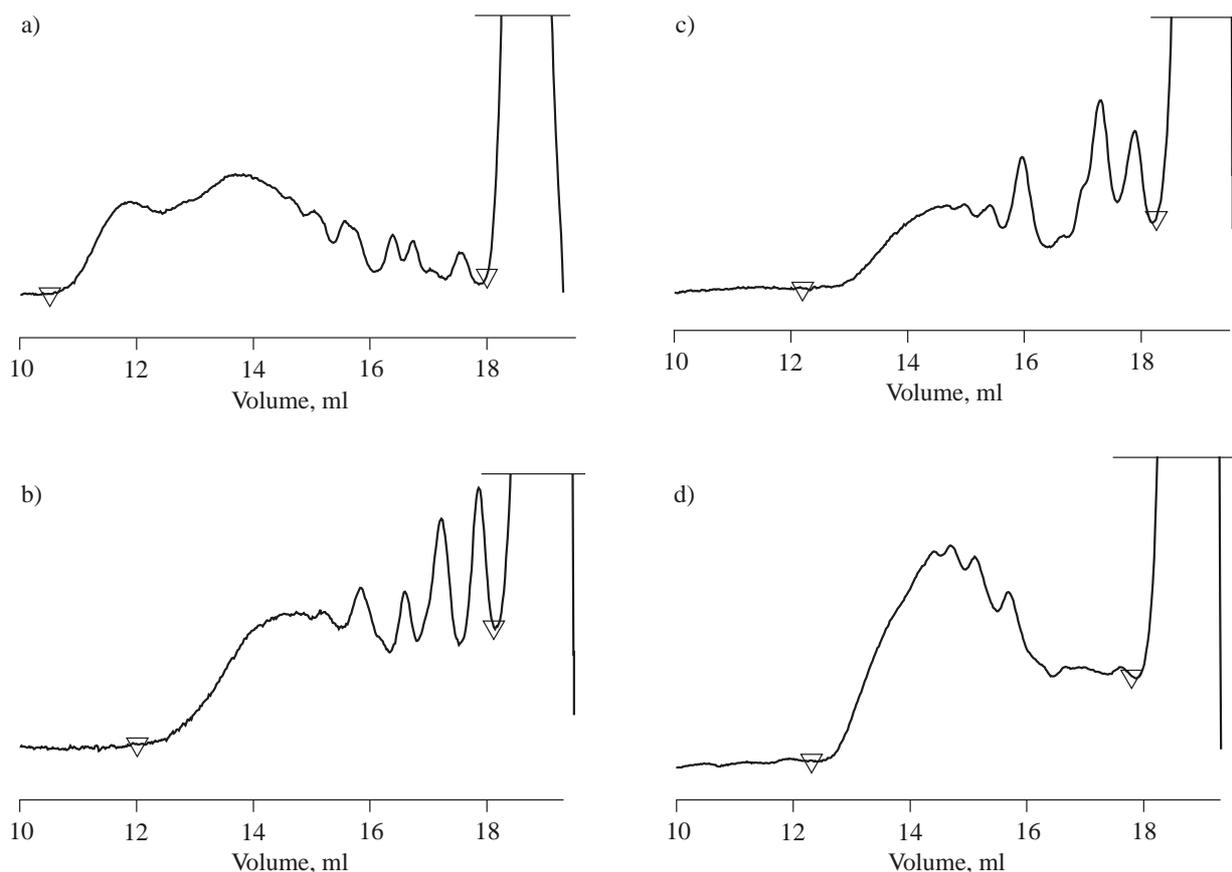
Fig. 4. SEC traces of poly(BL-OH) obtained at different conditions of polymerization defined in Table 1 for number: a) 2, b) 3, c) 4, d) 10

Molecular weights of the products obtained with protic acids as catalysts are higher than those of products obtained with use of Lewis acids. Because, as evidenced from analysis of MALDI-TOF spectra, protic acids favor dehydration, the difference in molecular weights may be attributed to further oligomerization through double bonds.

CONCLUSIONS

It has been observed that 5-membered cyclic ester substituted with hydroxyl group: α-hydroxy-γ-butyrolactone (BL-OH) undergoes spontaneous polymerization during vacuum distillation. The product is low molecular weight polymer and according to MALDI-TOF analysis the molecular weights of oligomers correspond to $n\times$ molecular weight of BL-OH unit. Most probably this process is catalyzed by acidic impurities in crude BL-OH. Attempts to conduct this process in controlled manner were only partly successful. In contrast to spontaneous polymerization, during polymerization catalyzed by added protic or Lewis acids, elimination of water molecules occurs leading to macromolecules with molecular weights equal to $n \times$ molecular weight of BL-OH unit — $k \times 18$. The extent of dehydration depends on the nature of catalyst and is lower for polymerization conducted with Lewis acid — scandium triflate at relatively low temperature (40 °C).

Similar dehydration was observed earlier for cationic polymerization of 5-membered cyclic ether — tetrahydrofuran substituted with hydroxyl or hydroxymethyl substituent.

Unsubstituted 5-membered cyclic ester is difficult to polymerize because of unfavorable thermodynamics (low enthalpy of polymerization due to the low ring-strain) [19]. Typically, the substitution decreases the thermodynamic polymerizability even further. Therefore, an observation that BL-OH undergoes spontaneous polymerization during distillation, without any side reactions as evidenced by MALDI-TOF spectra of the product, is rather unexpected. Apparently this process requires specific reaction conditions because in the presence of added acid catalyst, the polymerization is accompanied by elimination of water from growing macromolecules. Thus it may be concluded that oligomers are formed by combination of polymerization and condensation reaction.

Further work is in progress to optimize the reaction conditions in order to make in a controlled manner the product similar to that formed by spontaneous polymerization during distillation.

REFERENCES

1. Sunder A., Heinemann J., Frey H.: *Chem. Eur. J.* 2000, **6**, 2499.
2. Sunder A., Mülhaupt R., Haag R., Frey H.: *Adv. Mater.* 2000, **12**, 235.
3. Tokar R., Kubisa P., Penczek S., Dworak A.: *Macromolecules* 1994, **27**, 320.
4. Dworak A., Walach W., Trzebicka B.: *Macromol. Chem. Phys.* 1995, **196**, 1963.
5. Kim Y. H.: *J. Polym. Sci. Part A: Polym. Chem.* 1998, **36**, 1685.
6. Voit B.: *J. Polym. Sci. Part A: Polym. Chem.* 2000, **38**, 2505.
7. Voit B.: *J. Polym. Sci. Part A: Polym. Chem.* 2005, **43**, 2679.
8. Kubisa P.: *J. Polym. Sci. Part A: Polym. Chem.* 2002, **41**, 457.
9. Bednarek M.: *Polimery* 2003, **48**, 163.
10. Kubisa P., Penczek S.: *Prog. Polym. Sci.* 1999, **24**, 1409.
11. Bednarek M., Biedroń T., Heliński J., Kałużyński K., Kubisa P., Penczek S.: *Macromol. Rapid Commun.* 1999, **20**, 369.
12. Bednarek M., Kubisa P., Penczek S.: *Macromolecules* 2001, **34**, 5112.
13. Bednarek M., Penczek S., Kubisa P: *Macromol. Symp.* 2002, **177**, 155.
14. Chen Y., Bednarek M., Kubisa P., Penczek S.: *J. Polym. Sci. Part A: Polym. Chem.* 2002, **40**, 1991.
15. Bednarek M.: *Polimery* 2006, **51**, 727.
16. "Ring-opening Polymerization", (Eds. Ivin K. J., Saegusa T.), Elsevier Publishers, London, New York 1984, Chap. 1, p. 1.
17. Bednarek M., Kubisa P.: *J. Polym. Sci. Part A.: Polym. Chem.* 2006, **44**, 6484.
18. Liu M., Vladimirov N., Fréchet J.: *Macromolecules* 1999, **32**, 6881.
19. Penczek S., Biela T., Duda A.: *Macromol. Rapid Commun.* 2000, **21**, 941.