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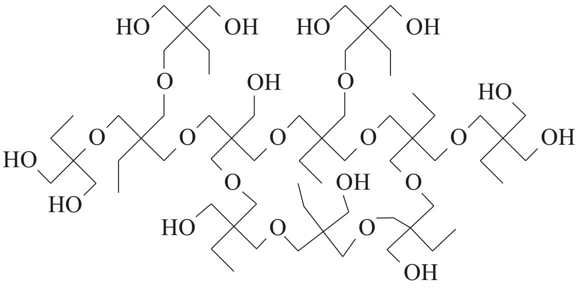
Application of poly(3-ethyl-3-hydroxymethyloxetane) as macroinitiator for the synthesis of star polymers of ethylene oxide. Efficiency of initiation

RAPID COMMUNICATION

Summary — Macromolecules of poly(3-ethyl-3-hydroxymethyloxetane) (poly-EHMOX) may act as convenient multifunctional initiators for the synthesis of star polymers in polymerizations initiated by -OH (or -O$^-$) groups. It is desirable, that all functional groups of the initiator are indeed involved in initiation because in such case the number of arms is equal to the number of functional groups. We have used poly-EHMOX as macroinitiator for anionic and cationic polymerization of ethylene oxide (EOX) leading to star polymers containing poly-EHMOX core and poly-EOX arms. Using ^{1}H NMR method it has been shown that the efficiency of initiation of anionic polymerization by -O$^-$ groups derived from poly-EHMOX is not quantitative. On the other hand, in the cationic polymerization of EOX in the presence of poly-EHMOX (proceeding by Activated Monomer mechanism) efficiency of initiation is quantitative and the number of arms is equal to the number of functional groups in poly-EHMOX even at the early stages of reaction.

Key words: star polymers, poly(3-ethyl-3-hydroxymethyloxetane), macroinitiator, poly(ethylene oxide), ionic polymerization, initiation efficiency.

Cationic polymerization of 3-ethyl-3-hydroxymethyloxetane (EHMOX) leads to branched, multihydroxyl polyethers showing medium molecular weights (M_n ~ 2000) [1—3]. Intramolecular chain transfer, resulting in cyclization, is a factor that limits $\overline{M}_n$ [3, 4]. An average macromolecule has therefore a compact structure shown schematically below:



(I)

Such compact, multihydroxyl macromolecule may be used as a precursor for a core of star polymers in the processes in which HO- groups may act as groups initiating the polymerization of other monomer forming the arms. This approach was used recently for the synthesis of star polymers of lactide [5]. In the synthesis of star polymers it is essential that the number of arms is known and preferably that each functional group in the core is indeed involved in initiation of the chain.

The subject of this work is the method of synthesis of star polymers containing poly-EHMOX core and poly(ethylene oxide) (poly-EOX) arms; we report here the method of determination of initiation efficiency based on the results from the following model systems:

a) cationic copolymerization of EHMOX with EOX

b) cationic polymerization of EHMOX having attached short poly-EOX chains

c) anionic polymerization of EOX initiated by alkoxide anions derived from poly-EHMOX

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d) cationic polymerization of EOX initiated by poly-EHMOX by Activated Monomer mechanism [6] (AM mechanism)

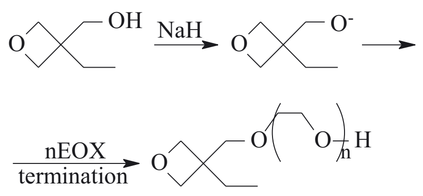
EXPERIMENTAL

Materials

3-Ethyl-3-hydroxymethyloxetane (EHMOX) was synthesized from trimethylolpropane as described earlier [1, 3] and was dried over molecular sieves before use. Ethylene oxide (Petrochemia Płock, Poland) was dried under CaH_2, CH_2Cl_2 was purified by distillation, monomethoxy polyethylene glycol (PEG 500, Fluka), was vacuum-dried at 60 °C for 4 h, $BF_3 \cdot Et_2O$ (Aldrich), *N*,*O*-bis(trimethylsilyl)acetamide (BSA, POCh Gliwice, Poland), phenyl isocyanate (Aldrich) and trifluoroacetic anhydride (Aldrich) were used as supplied. Poly-EHMOX was obtained as described previously [1, 3].

Synthesis of EHMOX-nEOX macromonomer (MM)

Equation (1) illustrates the above-mentioned synthesis.



(1)

In an ampoule fitted with Teflon stopcock 4 g (0.035 mol) of dry EHMOX and 0.1 g (0.0042 mol) of NaH were placed under argon atmosphere. Then 20 mL of THF stored over sodium-potassium alloy was distilled in. The content of the ampoule was mixed and was stored for 24 h at room temperature with degassing under vacuum from time to time. Next 9.62 g (0.219 mol) of EOX was distilled in and the reaction was conducted for two days at room temperature. To stop the reaction a few drops of 5 % solution of CH_3COOH in CH_3OH were added. Solution was filtered, solvent was evaporated and the product was dried under vacuum; 8.17 g of product (oil) was obtained (about 60 % yield). On the basis of ^1H NMR spectrum it was found that all oxetane rings were preserved and the proportion of EHMOX to EOX units was about 2.4. In MALDI-TOF spectrum of the product only one series of signals with molecular weights corresponding to the structure shown in equation (1) were present.

Polymerization of MM

1 g of EHMOX-nEOX was placed in a flask (containing stirring bar) which, after filling with argon, was closed with rubber septum. In the bulk polymerization 0.030 mL (0.24 mmol) of $BF_3 \cdot Et_2O$ was added by syringe, in the solution polymerization first 12 mL of CH_2Cl_2 was added followed by addition of 0.150 mL (1.05 mmol) of $BF_3 \cdot Et_2O$. The reaction mixture was stirred for 12 days at room temperature. After that time polymerization was stopped by adding of 5 % CH_3ONa solution in CH_3OH to pH ~6. After evaporation of the solvent (in the solution polymerization) polymers were dried under vacuum. About 100 % yields were achieved.

Copolymerization of EHMOX with EOX

In an ampoule fitted with two inlets (one closed with Teflon stopcock) and equipped with stirring bar, 1 g (0.0086 mol) of EHMOX was placed. After closing the second inlet with rubber septum, the ampoule was connected to the vacuum line and 2.5 mL of CH_2Cl_2 and 1.32 g (0.0300 mol) of ethylene oxide were distilled in under vacuum. After mixing the components 0.01 mL (0.08 mmol) of $BF_3 \cdot Et_2O$ was added by syringe through the rubber septum. The solution was stirred for 24 h at room temperature. After that time polymerization was stopped by adding of a few drops of 5 % CH_3ONa solution in CH_3OH. The content of ampoule was filtered, and polymer obtained after evaporation of solvent was dried under vacuum (2.30 g; yield: ~100 %).

Anionic polymerization of EOX with poly-EHMOX as macroinitiator

0.5 g of poly-EHMOX ($\overline{M}_n$ ~1200; 0.0043 mol of -OH groups) together with 0.041 g (0.0017 mol) of NaH were placed in an ampoule under argon atmosphere. Then 10 mL of THF stored over sodium-potassium alloy was distilled in under vacuum. The content of the ampoule (poly-EHMOX was not dissolved completely at the beginning) was stirred with magnetic stirrer for 3 days at 35 °C. Then about 7 mL of THF was distilled off and 2.3 g (0.052 mol) of EOX was distilled into the mixture. The polymerization was conducted for 24 h at 35 °C and 24 h at 25 °C with vigorous stirring. Polymer was not quite dissolved from the beginning but after one day homogenous solution was obtained. Polymer was separated by solvent evaporation and was dried under vacuum. About 2 g of product was obtained (yield: 71 %).

Cationic (AM mechanism) polymerization of EOX with poly-EHMOX as macroinitiator

0.5 g of poly-EHMOX ($\overline{M}_n$ ~1200; 0.0043 mol of -OH groups) was dissolved in 20 mL of CH_2Cl_2 under reflux, 0.025 mL (0.2 mmol) of $BF_3 \cdot Et_2O$ was added, after mixing the content, an ampoule was cooled and was connected to the vacuum line. Next 0.53 g (0.012 mol) of EOX was distilled into ampoule during about 20 minutes from another container. Polymerization was continued for 24 h, then it was stopped by stirring the reaction mixture with about 0.5 g of CaO. After half an hour the solution was filtered, solvent was evaporated and polymer was dried under vacuum. To 0.5 g of this product, after dissolving in 20 mL of CH_2CH_2 and after introducing 0.025 mL of $BF_3 \cdot Et_2O$, next portion (0.52 g) of EOX was added. After 24 hours of mixing the polymerization was stopped and polymer was separated the same way as after the first portion of EOX. Next, to 0.5 g of the product, the third portion (0.65 g) of EOX was added. Copolymer was separated as previously. After every stage of polymerization product was analyzed by ^1H NMR, GPC and after second stage — by MALDI-TOF methods.

Esterification with trifluoroacetic anhydride, silylation and the reaction of polymers with phenyl isocyanate

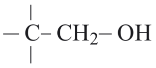
The above-mentioned reactions were performed as follows: 0.5 g of monomethoxy polyethylene glycol (PEG 500) (0.001 mol of -OH groups) or the sample of copolymer with the same amount of hydroxyl groups was dissolved in 5 mL of $CHCl_3$ (THF in the case of the reaction with isocyanate) and was stirred for one hour with 0.42 g of $(CF_3CO)_2O$ (0.002 mol) or 0.24 g (0.002 mol) of phenyl isocyanate or 0.41 g (0.002 mol) of BSA. Product was separated by evaporating of solvent and drying at vacuum line.

Measurements

^1H and ^{13}C NMR spectra were recorded using 200 MHz Bruker spectrometer. MALDI-TOF spectra were recorded by Voyager Elite apparatus, using dihydroxybenzoic acid as a matrix and NaI as cationating agent. Nitrogen laser desorption at a wavelength equal to 337 nm was applied. GPC analysis was carried out using ConstaMetric 4100 pump equipped with Phenogel 5 500A and Phenogel 5 50A columns, with RI detector, THF as a solvent, against polystyrene standards.

RESULTS AND DISCUSSION

In any of the studied systems, two types of hydroxyl groups may be present, namely HO- groups attached to EHMOX unit (II) and HO- groups attached to EOX unit (III):



$$-\overset{|}{\underset{|}{C}}-CH_2-OH \quad (II) \qquad -CH_2-CH_2-OH \quad (III)$$

In order to estimate what extent of HO- groups of poly-EHMOX participated in the reaction it is necessary to distinguish between both types of groups. In both ^1H and ^{13}C NMR spectra of the products of reactions a—d the signals of -C-$\mathbf{CH_2}$-OH (from EOX unit) and -CH_2-$\mathbf{CH_2}$-OH are overlapping and therefore the ratio of both groups cannot be determined (Fig. 1). In order to select the shifting reagent allowing to observe the signal corresponding to -$OCH_2\mathbf{CH_2}OH$, hydroxyl groups were converted into other functional groups in reaction with silylating agent (BSA), phenyl isocyanate and trifluoroacetic anhydride. As shown in Fig. 1a (I—IV) only in the last case the signals were sufficiently well separated.

Figure 1b shows the relevant regions of ^1H NMR spectra of hydroxyl terminated poly-EHMOX containing exclusively -CH_2CH_2OH groups (1bII), poly-EOX containing exclusively -C-CH_2OH groups (1bIII) and copolymer containing both types of groups (1bIV), all of them functionalized with trifluoroacetic anhydride.

Results show that functionalization of HO- groups with trifluroacetic anhydride allows to draw the distinction between both structures.

Results of the polymerizations carried out in the systems a)—d) are listed in Table 1.

Table 1. Molecular weights and end-groups of EHMOX/EOX copolymers

Method	Conditions	Yield %	$\overline{M}_n$ (calculated from conversion)	$\overline{M}_n$ found from NMR	$\overline{M}_n$ found GPC	[EOX]/[EHMOX] (NMR)	Fraction of EHMOX terminal units
Copolymerization of EHMOX with EOX (a)	CH_2Cl_2, $BF_3 \cdot Et_2O$, 25 °C, 24 h, [EOX]/[EHMOX] = 3.5	~100	—	—	1600	3.2	13
Polymerization of EHMOX-nEOX macromonomer (MM) (b) [EOX]/[EHMOX] ≈ 2.4	bulk, $BF_3 \cdot Et_2O$, 25 °C, 12 days	~100	—	—	1110	2.5	60
	CH_3Cl_2, $BF_3 \cdot Et_2O$, 25 °C, 12 days	~100	—	—	500	2.6	59
Anionic polymerization of EOX with poly-EHMOX (c)	CH_2Cl_2, NaH, 35 °C, 24 h + 25 °C, 24 h, [EOX]/[EHMOX] = 12.1	71	7280	5100	3280	7.1	15
Cationic polymerization of EOX with poly-EHMOX (d)	CH_2Cl_2, $BF_3 \cdot Et_2O$, 25 °C, 24 h, [EOX]/[EHMOX] = 2.7	—	2520	2580	2580	2.8	18
	[EOX]/[EHMOX] = 8.3	—	5200	4610	4000	7.1	0
	[EOX]/[EHMOX] = 21.7	—	11 580	8380	6050	15.0	—

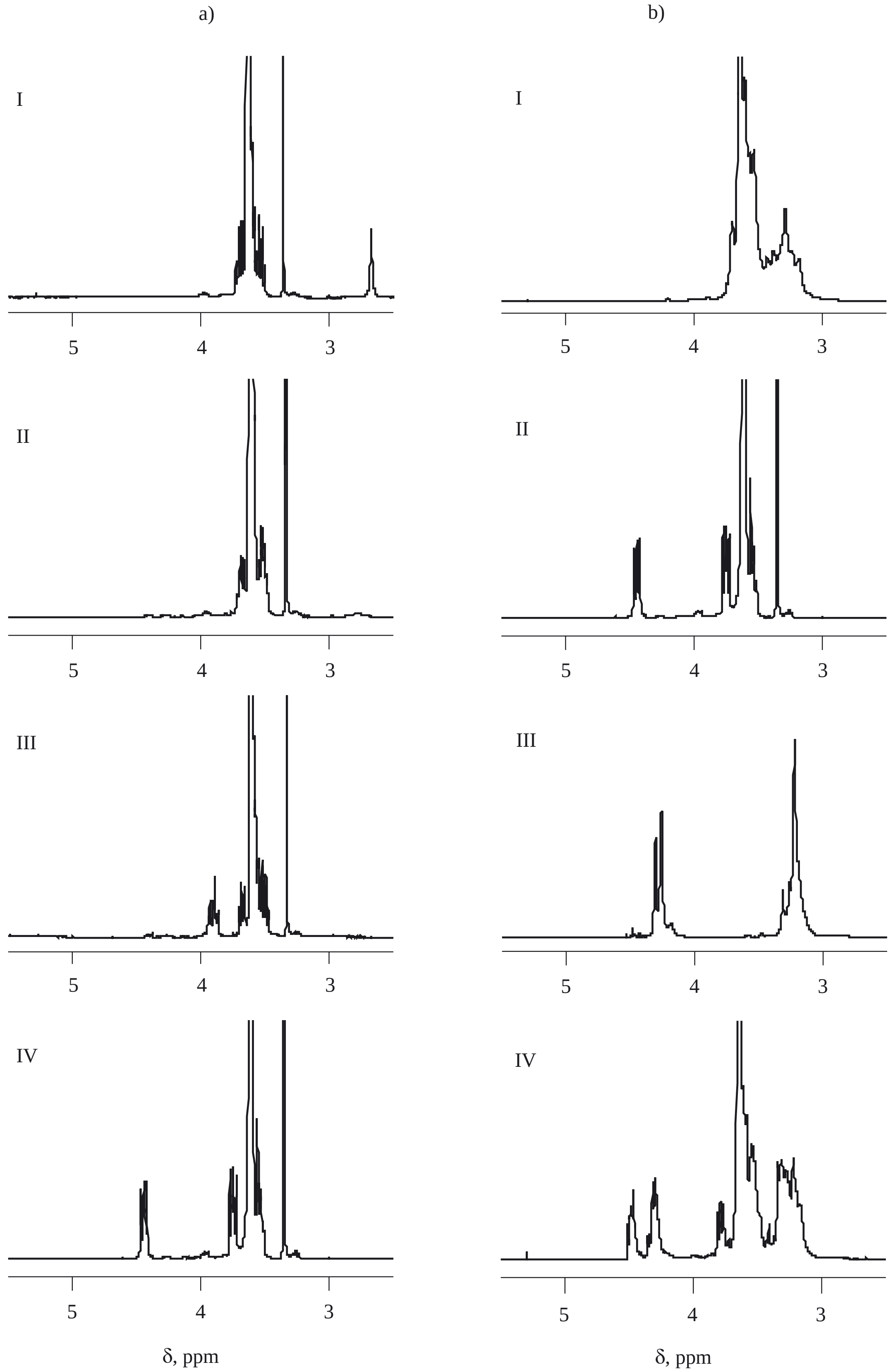
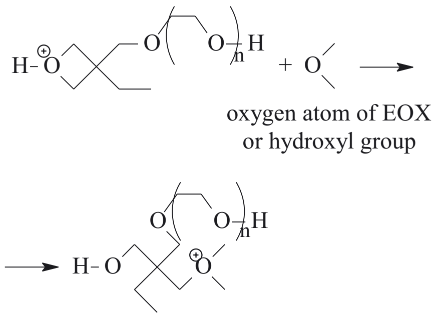
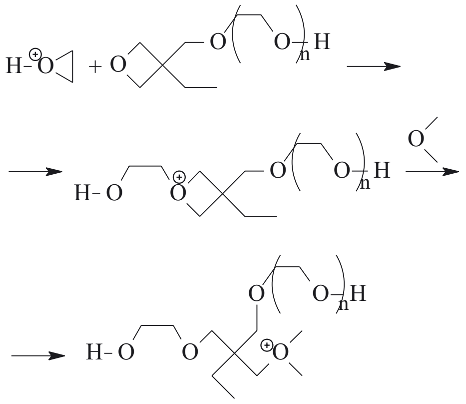


Fig. 1. The relevant regions of ^{1}H NMR spectra (CDCl$_3$ as solvent) in which the signals corresponding to -$\mathbf{CH_2}$-O- groups appear: a) poly-EOX (monomethoxy polyethylene glycol, $\overline{M}_n$ ~500) (I), poly-EOX after treatment with phenyl isocyanate (II), after silylation with BSA (III), after esterification with (CF$_3$CO)$_2$O (IV); b) copolymer (method b) without transformation of -OH groups (I), poly-EOX after esterification (II), poly-EHMOX after esterification (III), copolymer after esterification (IV). The high intensity signal between 3.45—3.75 ppm δ corresponds to -$\mathbf{CH_2}$O- groups from poly-EOX backbone or ether linkages (-C-$\mathbf{CH_2}$-O-) from poly-EHMOX, signal at 3.35 ppm δ corresponds to $\mathbf{CH_3}$O- group from poly-EOX (monomethoxy polyethylene glycol)

The following conclusion, casting some light on the polymerization mechanism may be drawn from the data presented in Table 1. The overall composition of the products of reactions a) and b) (the ratio of EOX and EHMOX units) is practically the same. The fraction of two types of hydroxyl groups is, however, distinctly different. In the product of homopolymerization of EHMOX containing short EOX chains, *i.e.* MM, HO- groups come mainly from EHMOX units while in the product of copolymerization of EHMOX with EOX, HO- groups are attached mainly to EOX units. This indicate, that in the polymerization of MM an opening of the oxetane ring is a result of protonation [eq. (2a)] while in the copolymerization of EOX with EHMOX, EOX is protonated predominantly and oxetane ring undergoes ring-opening upon attack by protonated EOX [eq. (2b)]:



(2a)



(2b)

This observation is in line with observed differences in $\overline{M}_n$ of both products. In the product of MM polymerization the average length of EOX sequences is 2.6. Although the number of EOX units per one EHMOX unit in EHMOX-EOX copolymers is slightly higher (3.2), EOX units in the product form shorter sequences because they are more randomly distributed. Reaction limiting the molecular weight is an intramolecular chain transfer to polymer (cyclization) [3, 4]. Apparently, this reaction is facilitated by the presence of longer EOX sequences increasing the chain flexibility. Therefore, the molecular weight of MM homopolymer is lower than that of EHMOX-EOX copolymer, in spite of the similar overall composition (ratio of [EHMOX]/[EOX] units). The cyclic structure of MM homopolymer is confirmed by MALDI-TOF analysis.

Intramolecular reaction should be more pronounced in more diluted solution. Indeed, as shown in Table 1, molecular weight of homopolymer of MM is considerably lower for solution polymerization than for bulk polymerization.

All presented results are coherent and indicate that some conclusions concerning the mechanism of the process can be drawn on the basis of the determination of ratio of two types of HO- groups that may be present in corresponding polymers.

The determination of the ratios of both types of HO- groups is even more important in the case of the synthesis of star polymers [systems c) and d)]. Each -C-CH_2--OH group in poly-EHMOX macromolecule that is involved in initiation of the growth of poly-EOX chain is transformed into -$(CH_2$-CH_2-$O)_n$-H group. Therefore, determination of their ratios provide a direct information on the efficiency of initiation, *i.e.* on the number of HO- groups, from which poly-EOX chain grow, and thus on the real number of arms. This type of analysis leads to the conclusion, that efficiency of initiation of anionic EOX polymerization is not quantitative and cationic AM polymerization of EOX with poly-EHMOX initiator seems to be a method of choice for the synthesis of star polymers.

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