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Functionalization of multihydroxyl branched poly(3-ethyl-3-hydroxymethyloxetane). Synthesis of star poly(ethylene oxide)

Summary — The synthesis of star polymers containing poly(ethylene oxide) (PEOX) arms connected to poly(3-ethyl-3-hydroxymethyloxetane) (PEHMOX) core is described. The medium molecular weight (M_n ~$2 \cdot 10^3$) branched multihydroxyl polyether — PEHMOX — was functionalized by acrylate groups. Polyethers with different functionalization degree were obtained using different molar excess of (meth)acryloyl chloride as esterification agent. Functionality of polymers was analyzed by ^{1}H NMR and MALDI TOF MS methods. PEHMOX samples with different number of acrylate groups (PEHMOX-Acrylate functionalized in 55 % and 80 %) were further applied to the synthesis of star polymers using "grafting onto" method. Thus, star copolyethers with hydrophobic PEHMOX core and hydrophilic arms PEOX were obtained by Michael addition of α-amino-ω-methoxy-poly(ethylene oxide) (PEOX-NH_2). Complete conversion of acrylate groups was confirmed on the basis of ^{1}H NMR analysis. From the overall composition of star polymers it was concluded that PEOX arms were attached to the PEHMOX core either through one or two acrylate groups, which means that Michael addition proceeded with involvement of one or two protons of primary end-amine groups of the PEOX-NH_2 chain. Star PEOX polymers with PEHMOX core not fully functionalized, *i.e.* still containing reactive hydroxyl groups, are potential precursors for miktoarm star polymers.

Key words — polyethers, star polymers, esterification, functionalization of polymers, Michael addition.

FUNKCJONALIZACJA WIELOHYDROKSYLOWEGO ROZGAŁĘZIONEGO POLI(3-ETYLO-3-HYDROKSYMETYLOOKSETANU). SYNTEZA GWIAŹDZISTEGO POLI(TLENKU ETYLENU).

Streszczenie — Opracowano syntezę polimerów gwiaździstych zawierających hydrofilowe ramiona z poli(tlenku etylenu) (PEOX) połączone z rdzeniem zawierającym jednostki powtarzalne 3-etylo-3-hydroksymetylooksetanu. W tym celu najpierw wielohydroksylowy, rozgałęziony poli(3-etylo-3-hydroksymetylooksetan) (PEHMOX) o średnim ciężarze cząsteczkowym (M_n ~$2 \cdot 10^3$) poddano funkcjonalizacji w wyniku, której grupy hydroksylowe przekształcono w grupy akrylanowe. Stosując różne molowe nadmiary chlorku akryloilu (metakryloilu) jako środka estryfikującego, otrzymano PEHMOX o różnym stopniu funkcjonalizacji (tabela 1, rys. 1 i 2). Funkcyjność polimerów analizowano stosując metody spektroskopowe — ^{1}H NMR i MALDI TOF MS. Próbki PEHMOX zawierające różną ilość grup akrylanowych (PEHMOX-Acrylate, zestryfikowane w 55 % lub 80 %) użyto następnie do syntezy polimerów gwiaździstych metodą „*grafting onto*", w wyniku addycji Michaela α-amino-ω-metoksy-poli(tlenku etylenu) (PEOX-NH_2) (schemat A). Opierając się na wynikach analizy ^{1}H NMR potwierdzono pełną konwersję grup akrylanowych (rys. 3, schemat B). Na podstawie sumarycznego składu polimerów gwiaździstych wywnioskowano, że ramiona poli(tlenku etylenu) są przyłączone do rdzenia PEHMOX z udziałem jednej albo dwóch grup akrylanowych, co oznacza, że addycja Michaela przebiegała z zaangażowaniem jednego lub dwóch protonów pierwszorzędowej końcowej grupy aminowej łańcucha PEOX-NH_2. Częściowo funkcjonalizowane polimery gwiaździste poli(tlenku etylenu) zawierające rdzeń poli(3-etylo-3-hydroksymetylooksetanu), tzn. takie, jakie zawierają jeszcze wolne grupy hydroksylowe, są potencjalnymi prekursorami polimerów gwiaździstych o ramionach mieszanych (tzw. „*miktoarm star*").

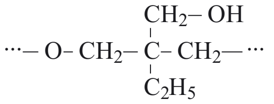
Słowa kluczowe: polietery, polimery gwiaździste, estryfikacja, funkcjonalizacja polimerów, addycja Michaela.

In the series of previous papers from our laboratory the mechanism of cationic polymerization of 3-ethyl-3-hydroxymethyloxetane (EHMOX) leading to multihydroxyl branched polyethers was described [1—4]. The microstructure of polymers and its dependence on the polymerization conditions were examined [1, 2]. The intramolecular hydrogen bonding facilitating chain transfer reactions was found responsible for the limited molecular weights of the final products (M_n up to $2 \cdot 10^3$) [2, 5] containing known number of hydroxyl groups.

Highly branched polymers containing large number of functional groups can be used for building more complicated polymer architectures [6]. Multifunctional macromolecules may serve as a core for the synthesis of star polymers in which the arms may be built from chains varying in nature (*e.g.* hydrophobic or hydrophilic), depending on possible applications.

Multihydroxyl polyether — polyglycidol — was used for example as macroinitiator for the synthesis of star polymers having poly(ethylene oxide), poly(propylene oxide), poly(methyl methacrylate) or poly(ε-caprolactone) arms [7].

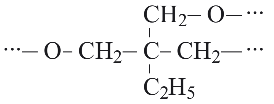
Multifunctional branched polyether investigated by our group — poly(3-ethyl-3-hydroxymethyloxetane) (PEHMOX), as opposed to polyglycidol containing both primary and secondary hydroxyl groups [7, 8], has an advantage of having exclusively primary hydroxyl functional groups. In such case the macromolecules are composed of the following unit:



$$\cdots-\mathrm{O}-\mathrm{CH_2}-\underset{\mathrm{C_2H_5}}{\overset{\mathrm{CH_2-OH}}{\mathrm{C}}}-\mathrm{CH_2}-\cdots$$

(I)

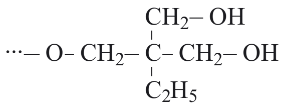
linear



$$\cdots-\mathrm{O}-\mathrm{CH_2}-\underset{\mathrm{C_2H_5}}{\overset{\mathrm{CH_2-O}-\cdots}{\mathrm{C}}}-\mathrm{CH_2}-\cdots$$

(II)

branched



$$\cdots-\mathrm{O}-\mathrm{CH_2}-\underset{\mathrm{C_2H_5}}{\overset{\mathrm{CH_2-OH}}{\mathrm{C}}}-\mathrm{CH_2-OH}$$

(III)

terminal

Hydroxyl groups in PEHMOX may be used to initiate the polymerization, *e.g.* after converting into alkoxide groups, or may be transformed into groups initiating the polymerization by other mechanism. Therefore, PEHMOX may be considered as convenient precursor for miktoarm type star polymers ("mikto" coming from Greek, means mixed) containing both hydrophobic and hydrophilic arms.

In the earlier paper from our laboratory the synthesis of ATRP (Atom Transfer Radical Polymerization) macroinitiators by reaction of PEHMOX with 2-bromoisobutyryl bromide was described and resulting macroinitiators were characterized [9]. Those macroinitiators were successfully applied for the synthesis of star polystyrene by ATRP process [10]. Because functionalization of PEHMOX may be conducted in such way that only part of HO- groups is reacted, the remaining HO- groups could be used to attach the hydrophilic poly(ethylene oxide) (PEOX) chains.

To find the most efficient method of attachment of PEOX chains to PEHMOX, the anionic polymerization of EOX initiated with PEHMOX (after converting some of HO- groups in PEHMOX into alkoxide groups) and cationic polymerization of EOX initiated with PEHMOX (by Activated Monomer Mechanism [11]) were investigated [12]. It was found that both systems have some disadvantages. Initiation of anionic polymerization is not quantitative while in cationic polymerization it is difficult to built longer PEOX chains (probably because of cyclization being the side reaction in the competing ACE (Active Chain End) propagation [11].

Star polymers, in general, may be synthesized by two approaches, corresponding to "grafting from" and "grafting onto" techniques of the synthesis of graft copolymers. The method, in which polymerization of the arm-forming monomer is initiated from hydroxyl groups of multihydroxyl polyether as starter molecule, is essentially a "grafting from" approach. The efficiency of this method depends on the quantitative initiation that is not always easily achieved. If proper reaction conditions are selected, "grafting onto" method may allow better control over the number and length of arms.

In this paper the "grafting onto" approach to a synthesis of star poly(ethylene oxide), using PEHMOX as a core, is described. In the first step hydroxyl groups in PEHMOX were converted into acrylate groups. Functionalized PEHMOX then reacted with amino-terminated poly(ethylene oxide) (PEOX-NH_2). Michael addition led to the attachment of PEOX chains onto PEHMOX core. If this approach was effective it could open a way of synthesis of star polymers containing PEHMOX core with hydrophobic (polystyrene) and hydrophilic [poly(ethylene oxide)] arms. Although this general approach to the synthesis of star polymers is known [6, 13-15], multihydroxyl branched PEHMOX was used for the first time as a core in the "*grafting onto*" method.

EXPERIMENTAL

Materials

PEHMOX was obtained as described earlier [1, 2]. Acryloyl and methacryloyl chloride (Aldrich) were purified by distillation. α-Amino-ω-methoxy poly(ethylene oxide) (PEOX-NH_2; M_n = 500) (BASF, USA) was dried under vacuum. Solvents — CH_2Cl_2 and methanol (Chempur, Poland) — were purified by distillation. CaO was used without purification.

Transformation of -OH groups into (meth)acrylate groups

Typical procedure (No 4 in Table 1) is described below:

I. PEHMOX (M_n = 1400, 1 g, 0.0086 mol of -OH groups) was dissolved in 50 mL of CH_2Cl_2 under reflux. The solution was cooled to room temperature and about 1.5 g of dry CaO was added followed by the drop-wise addition of acryloyl chloride (1.4 mL, 0.017 mol) (or methacryloyl chloride) under argon atmosphere. The mixture was stirred overnight. The solution was filtered from CaO and washed 3 times with water. After drying in vacuum the product was obtained with the yield 80 %. At those conditions ~80 % of hydroxyl groups was converted into acrylate groups, as determined by ^{1}H NMR.

II. In the reaction leading to the product in which intentionally about half of all -OH groups was transformed into acrylate groups 0.84 mL (0.010 mol) of acryloyl chloride was used. Product obtained with the yield of 90 % had functionality 55 % (^{1}H NMR).

Synthesis of star polymers

I. PEHMOX-Acrylate (80 %) (0.5g, 0.0025 mol of acrylate groups) was dissolved in the mixture methanol/CH_2Cl_2 (5/10 mL) and 1.38 g PEOX-NH_2 (M_n=500) dissolved in 5 mL of methanol was added (10 % excess with respect to acrylate groups). The solution was stirred 4 days at room temperature under argon atmosphere. Then solvents were evaporated, crude product was dried under vacuum and was analyzed by GPC and ^{1}H NMR methods. To remove unreacted PEOX-NH_2, the product was purified by twofold ultrafiltration in 50 % aqueous solution of ethanol with Amicon Ultrafiltration Stirred Cell (200 mL), using membrane with molar mass 1000 cut-off ("Diaflo®" ultrafiltration membranes).

II. The same procedure was applied for the reaction of PEHMOX-Acrylate (55 %) with PEOX-NH_2: to the 0.5 g of PEHMOX-Acrylate (55 %, 0.0019 mol of acrylate groups) 1.04 g of PEOX-NH_2 was added.

Measurements

— ^{1}H NMR spectra were recorded using 200 MHz Bruker spectrometer. — MALDI TOF (Matrix-Assisted Laser Desorption/Ionization Time-of-Flight) mass 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.

— IR spectra were recorded using ATI Mattson Infinity Series 60 AR FTIR (Fourier Transformation Infra-Red) instrument. Samples were analyzed in KBr cells with a path length of 0—5 in films.

— SEC (Size Exclusion Chromatography) analysis was carried out using KNAUER HPLC PUMP 64 equipped with Phenogels 5 50A and 5 500A columns, with RI detector, THF as a solvent, against polystyrene standards. Independently, for star polymers SEC analyses were performed using MALLS (MultiAngle Laser Light Scattering) Wyatt Technology DAWN® EOS™) and RI (Wyatt Optilab Rex) detectors and Agilent 1100 Series Pump, set of columns 2 x PL Gel 5 microns MIXED-C against polystyrene standards, in CH_2Cl_2 solvent, using the ASTRA v 4.70 program (Wyatt Technology Corp.).

RESULTS AND DISCUSSION

Transformation of -OH groups into (meth)acrylate groups

Transformations of hydroxyl groups into acrylate or methacrylate groups were performed with acryloyl (methacryloyl) chlorides as esterification agents. Typically, in such esterifications, triethylamine is used for trapping of HCl formed. First attempts with triethylamine revealed that it remained in functionalization product in spite of several washings operations. Triethylamine probably interacts with the remaining -OH groups through strong hydrogen bonds. Thus, CaO was used instead of triethylamine, similarly to performed earlier synthesis of ATRP macroinitiators [9]. In spite of 2-fold excess of acryloyl chloride, complete functionalization was not achieved as it is evident from Table 1.

Table 1. Esterification reactions leading to PEHMOX-(Meth)Acrylates with different functionalization degrees

No	Acyl chloride	HCl trap	Molar excess of acyl chloride	Degree of functionalization % (^{1}H NMR)
1	Methacryloyl chloride	Et_3N	1.5	79
2	Acryloyl chloride	CaO	0.85	45
3	-"-	CaO	1.2	55
4	-"-	CaO	2	81

Degree of functionalization was determined on the basis of ^{1}H NMR analysis. In the ^{1}H NMR spectrum the signals corresponding to protons from methylene groups connected with -OH groups are shifted towards lower field after esterification (from 3.45÷3.65 ppm to 4.00÷4.25 ppm) and signals corresponding to double bonds appear at 5.75÷6.50 ppm.

^{1}H NMR analysis gives only an average degree of polymer sample functionalization. It should be remembered that polymer consists of macromolecules of different length (different number of monomer units) which may be esterified to different degree. In order to analyze the degree of functionalization more precisely, MALDI TOF method which enables to identify individual macromolecules, was used. Fig. 1 shows MALDI TOF spectra of two polymer samples — PEHMOX esterified in 55 % (a; number 3 in Table 1) and PEHMOX esterified in 80 % (b; number 4 in Table 1).

In both spectra the same signals, appearing at the same *m/z* values may be found differing, however, in relative intensity. The identified signals correspond to the macromolecules containing both non-esterified $-CH_2-C(C_2H_5)(CH_2OH)-CH_2-O-$ (M = 116.16) and esterified $-CH_2-C(C_2H_5)$ $[CH_2OC(O)CH=CH_2]-CH_2-O-$ (M = 170.19) EOX units in different proportions. Molecular weights of these macromolecules may be expressed by

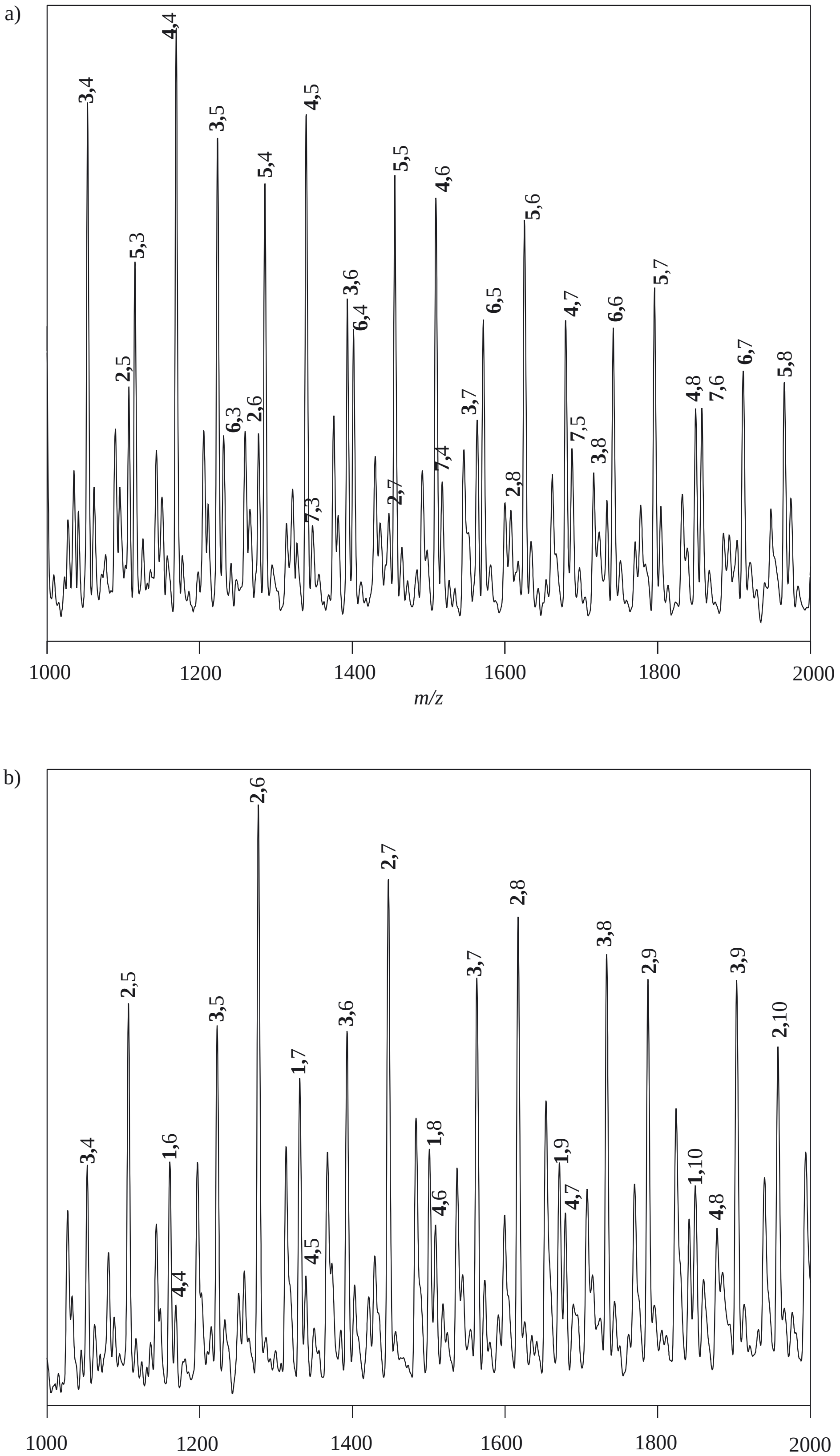


*Fig. 1. MALDI TOF mass spectra of PEHMOX-Acrylate (55 %) (a) and PEHMOX-Acrylate (80 %) (b); the signals correspond to macromolecules with **n** non-esterified (first digit of the label of the signal) and m esterified (second digit) EHMOX units*

the formula: $M = \boldsymbol{n} \times 116.16 + m \times 170.19$ (PEHMOX macromolecules are cyclic as it was shown in our previous papers [1, 2]). Consequently *m/z* values at which signals appear are equal $n \times 116.16 + m \times 170.19 + 23$ (*M* of Na^+ used as cationating agent). In the spectra the signals assigned to macromolecules containing non-esteri-

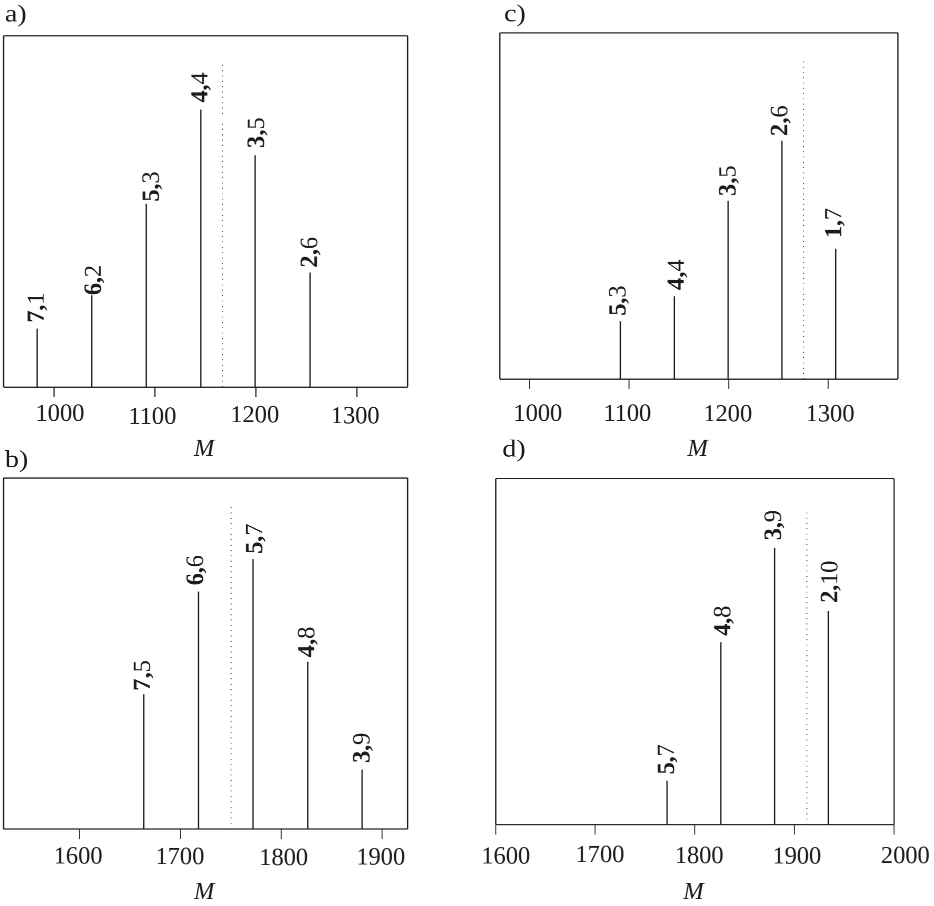


Fig. 2. Distribution of non-esterified and esterified groups in two populations of PEHMOX macromolecules and two different PEHMOX samples:
a) n + m = 8; PEHMOX-Acrylate (55 %) b) n + m = 12; PEHMOX-Acrylate (55 %)
c) n + m = 8; PEHMOX-Acrylate (80 %) d) n + m = 12; PEHMOX-Acrylate (80 %)
Dashed lines correspond to the average degree of functionalization

fied and esterified EHMOX units are marked as ***n***, *m* where ***n*** gives the number of non-esterified and *m* the number of esterified units.

The homologous series: $M = \boldsymbol{n} \times 116.16 + m \times 170.19$ may be identified in the spectra. MALDI TOF analysis unambiguously indicates that functionalized polymers are not uniform and that functionalization degree determined by other methods represents only average value. This statistical character of functionalization must be taken into account when further application of functionalized polymer is considered. As it is evident from Fig.1, in the sample with average degree of esterification equal to 80 % (1 b) the macromolecules with two and three non-esterified units prevail, in the sample with average degree of esterification equal to 55 % the macromolecules with four and five non-esterified units are the main fraction.

Different degrees of esterification lead to different overall contents of the remaining hydroxyl groups in the products obtained. That should result in different extent of hydrogen bonding in the polymer samples with different degree of esterification. The involvement of PEHMOX macromolecules in hydrogen bonding was proved by us during our earlier studies of this polymer [5]. To confirm the relationship between number of remaining free hydroxyl groups and the extent of hydrogen bonding, IR spectra of PEHMOX esterified in 80 % and PEHMOX esterified in 55 % were recorded. The position of maximum of -OH groups absorption in IR depends on the extent of hydrogen bonding [16].

According to the literature, signals of "free" hydroxyl groups (gas phase) appear in IR spectra at 3580—3650 cm^{-1} while for hydrogen bonded systems these signals are observed at the region 3200—3550 cm^{-1} [16], depending on the extent and strength of hydrogen bonds. In the spectrum of PEHMOX with 55 % of HO- groups esterified (more remaining hydroxyl groups) the signal is present at 3509 cm^{-1} and in the spectrum of PEHMOX with 80 % of HO- groups esterified (less remaining hydroxyl groups) at 3523 cm^{-1}. For comparison, the maximum of absorption for non-esterified PEHMOX appear at 3413 cm^{-1} [5]. Thus the relation between the degree of functionalization and hydrogen bonding was confirmed.

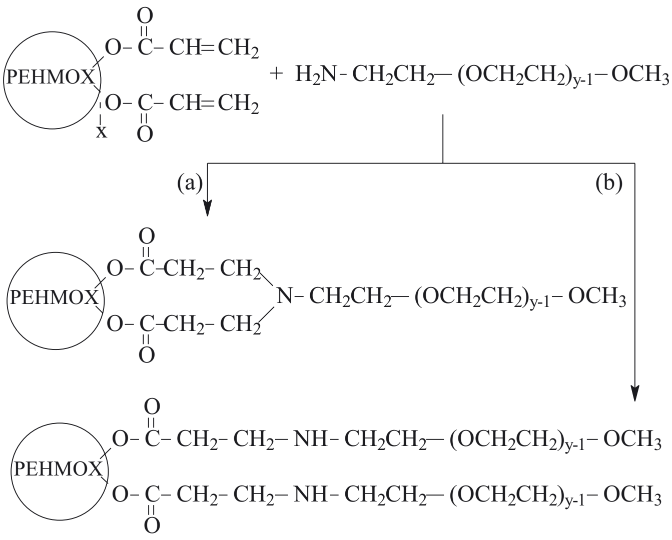
Involvement of HO- groups in PEHMOX in hydrogen bonding may affect their reactivity. Because

PEHMOX is composed of macromolecules containing different number of repeating EHMOX units and therefore different number of hydroxyl groups, macromolecules differing in size may be to different extent involved in hydrogen bonding. This in turn may lead to different reactivity of HO- groups in PEHMOX macromolecules of different size. To check whether this is indeed the case, the distribution of non-esterified and esterified groups was compared for two population of PEHMOX macromolecules differing in size. In Fig. 2 the intensities of signals corresponding to $n \times 116.16 + m \times 170.19$ series are compared for $n + m$ (DP_n of PEHMOX macromolecule) equal to 8 and to 12 for the samples with the average degree of functionalization = 55 % and 80 %. Dashed lines correspond to the average degree of functionalization.

Although it is difficult to analyze the results in a quantitative way, because in MALDI TOF spectra the intensity of signal is not necessarily strictly proportional to the concentration, it may be assumed that for macromolecules having similar structure and similar polymerization degree the intensity of signal is proportional to concentration. If both distributions are compared on this assumption, it may be concluded that the fractions of non-esterified and esterified groups in the macromolecules differing in size are very similar, indicating that there is no significant difference in reactivity of HO-groups in PEHMOX macromolecules differing in size.

Syntheses of star polymers using of PEHMOX containing (meth)acrylate groups

Star polymers with PEHMOX core and poly(ethylene oxide) arms were obtained in the Michael addition of PEOX-NH_2 to acrylate or methacrylate groups connected to PEHMOX macromolecules as shown in the Scheme A.



$x_{average}$ (number of acrylate groups) = 9.6 when functionalization degree is 80 %
= 6.6 when functionalization degree is 55 %
$y_{average}$ = 10
(only two groups are shown for simplicity)

Scheme A

Reactions were monitored by ^1H NMR. After 4 days of reaction, almost complete conversion of acrylate groups (> 98 %) was observed in the case of reaction with PEHMOX-Acrylate (80 %) (number 4 in Table 1) and in the case of reaction with PEHMOX-Acrylate (55 %) (number 3 in Table 1). Fig. 3 presents NMR spectra before and after coupling reaction performed with PEHMOX-Acrylate (55 %) (see also Scheme B). In the case of using PEHMOX with methacrylate groups after 4 days of stirring with PEOX-NH_2 only 30 % of methacrylate groups reacted, probably due to the higher steric hindrance (this product was not further investigated).

Nearly quantitative conversion of acrylate groups (at 10 %-mol excess of PEOX-NH_2) could indicate the efficient attachment of PEOX arms. SEC analysis showed, however, that there was unreacted PEOX-NH_2 in the product and the amount of unreacted PEOX-NH_2 was apparently larger than expected on the basis of its known excess. Product was therefore purified by ultrafiltration using membrane with a cut-off at M_n = 1000. SEC analysis confirmed quantitative removal of unreacted PEOX-NH_2. From ^1H NMR spectra of purified

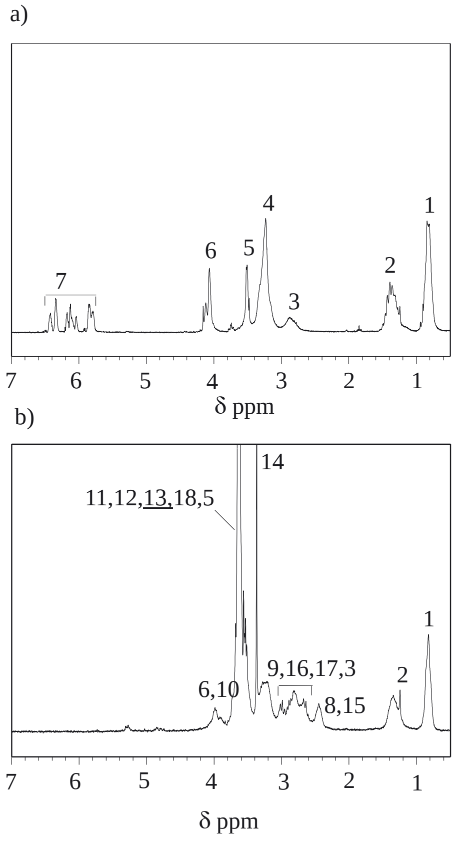
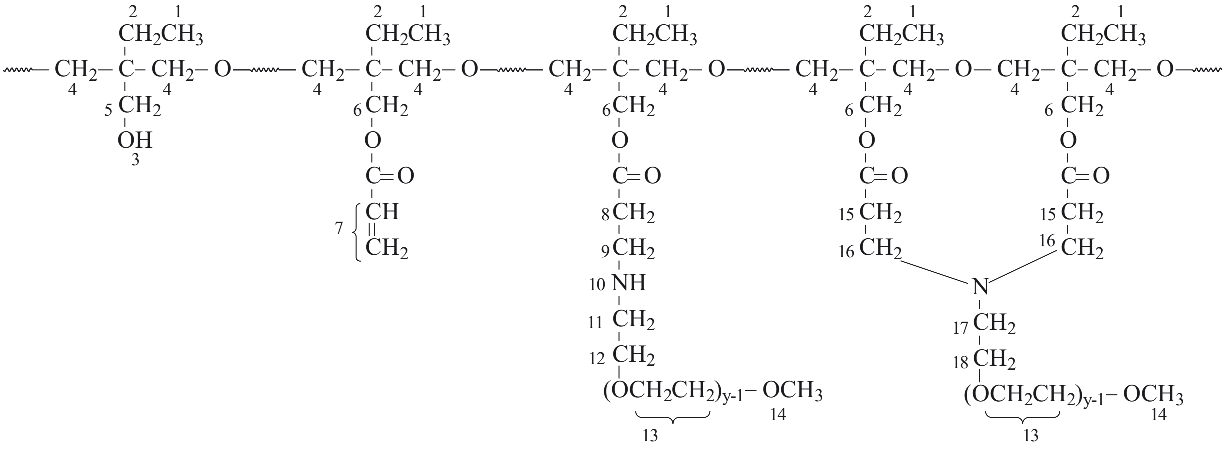


Fig. 3. ^1H NMR spectra of PEHMOX-Acrylate (55 %) (a) and star polymer obtained after coupling reaction performed with PEOX-NH_2 (b). The assignments of signals are shown in the Scheme B



Scheme B

products the overall compositions of star polymers were determined from the ratio of integration of signals corresponding to PEHMOX core and PEOX arms. Thus, 6.6 arms (on average) were attached to PEHMOX-Acrylate (80 %), and 5.0 arms were attached to PEHMOX-Acrylate (55 %). This means that in the first case the number of attached PEOX-NH_2 macromolecules corresponds to 66 mol % of all consumed acrylate groups and in the second case to 78 mol %. That, in turn means that in both cases some of PEOX-NH_2 arms are connected to the PEHMOX core through two acrylate groups (with participation of two protons from amine group in Michael addition as shown in Scheme A), and some of the arms are attached through one acrylate group (with participation of one proton from amine group in Michael addition, as shown in Scheme B).

Typically, Michael addition of primary amines to acrylate groups involves both protons of amino group [17] (although the rates of reaction of primary and secondary groups may be different). In the studied case, acrylate groups are immobilized on the polymer and therefore some products of reaction of the first proton may have no acrylate group in close vicinity and reaction of the second proton may be prohibited.

In star macromolecule with PEHMOX-Acrylate (55 %) core, there is more arms connected through one acrylate group than in PEHMOX-Acrylate (80 %). This is logical because it is more probable that one PEOX-NH_2 chain reacts with two acrylate groups that are located close to each another (higher degree of esterification) than if they are further apart from each other (lower degree of esterification).

Different number of arms in both star polymers was reflected in SEC analysis with RI and MALLS detectors. Fig. 4 presents the dependence of actual molecular weight of the polymer fraction eluted at given elution volume on this elution volume.

The higher the elution volume of macromolecules, the lower their hydrodynamic volume. It is evident from Fig. 4 that for the set of polymer with different structure (linear or star), for the same elution volume the highest molecular weight is for the most compact structure (star polymer with higher number of arms). Presented dependence is in agreement with the known rule that with increasing number of arms, the macromolecules of star polymers become more compact which results in their lower hydrodynamic volume (if polymers of the same molecular weight are compared).

Determination of absolute value of M_n of star polymer by SEC is difficult due to the missing corresponding standards. If, however linear polystyrene calibration was used, the value M_n = 5200 was obtained for star polymer with PEHMOX-Acrylate (80 %) core. Theoretical M_n was calculated as 5300 taking into account 65 %

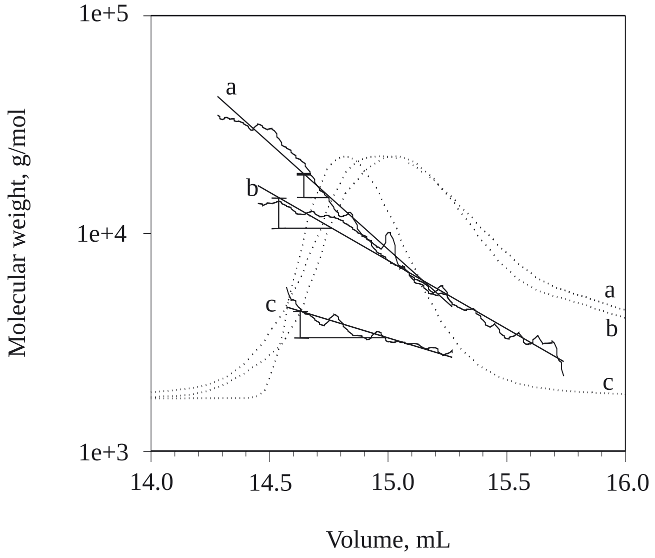


Fig. 4. Dependence of actual molecular weight of the polymer fraction eluted at given elution volume on this elution volume (solid lines) and SEC curves (dashed lines) for star polymer with PEHMOX-Acrylate (80 %) as a core (a), for star polymer with PEHMOX-Acrylate (55 %) as a core (b) and for linear PEOX (M_n=5000) (c) presented for comparison

conversion of PEOX-NH_2 used (as indicated by ^1H NMR analysis and gravimetric determination). M_n can be more reliably estimated on the basis of MALDI TOF analysis. It is difficult to assign the signals to the particular macromolecules because several different distributions of macromolecules are overlapping, namely those due to the different degree of functionalization of PEHMOX with acrylate groups, different number of PEOX-NH_2 arms in stars formed and polydispersity of PEOX-NH_2. In MALDI TOF spectrum the broad distribution of oligomers with maximum at m/z value about 4500 is present. Thus M_n of the product estimated on the basis of MALDI TOF spectrum is not far from the calculated value (5300).

CONCLUSIONS

Although experimental procedure outlined in this paper has some shortcomings, it still offers a synthetic route to star PEOX. Reaction is not quantitative at the stage of functionalization (conversion of hydroxyl group into acrylate groups) and at the stage of Michael addition, due to the possibility of reaction involving either one or two protons of primary amino group; number of attached PEOX chains is lower that the number of acrylate groups. On the other hand well defined PEOX chains may be attached to the PEHMOX core and their number can easily be determined. More efficient procedures should, however, be developed for successful synthesis of miktoarm star polymers based on PEHMOX core.

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