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Functionalized star-shaped polymers having PEO and/or polyglycidyl arms and their properties

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ABSTRACT

The introduction of methacrylic, carboxylic and phosphate functional groups on the core and at the end of the poly(ethylene oxide) (PEO) arms in the PEO star-shaped polymers is described. In the polyglycidol (PGL) star-shaped polymers phosphate groups were attached to the PGL arms as side groups. Polymers were characterized by NMR and SEC analysis with triple detection. The conversion of the unsubstituted star-shaped polymers into functionalized has been confirmed by ^1H and ^{13}C NMR spectra. The influence of the length of arms, their structure and the presence of functional groups on melting (T_m) and crystallization (T_c) temperatures and the degree of crystallinity (X_c) by differential scanning calorimetry (DSC) has been studied.

1. Introduction

A large number of papers were devoted to the synthesis of dendrimers, star-shaped and branched polymers containing various functional groups. Predominantly –OH, $-NH_2$, –COOH, and unsaturated groups were introduced. These functional polymers have been described in several review papers [1–7].

In our laboratory a new method of the synthesis of star-shaped polymers has been elaborated, based on reactions of the –OH ended oligomers with dicyclic compounds.

Previously star-shaped polymers having PEO [8–12] or PGL [13] arms and containing hydroxyl groups placed at the end of arms and/or on the core were described.

Introduction of the functional groups into these, new type – fully hydrophilic, star polymers can be very useful for their presumable applications as e.g. polymeric carriers for biologically active molecules or components of solid polymer electrolytes.

2. Experimental

2.1. Materials

The procedure of purification of ethylene oxide (EO), Ar, THF, NaH (Fluka), and diglycidyl ether of neopentyl glycol (DGNG) (Aldrich technical product, purity ~50%) was described previously [11].

Triethylamine after typical drying procedure was kept in a closed vacuum ampoule over calcium hydride.

Methacryloyl chloride (Aldrich) was distilled under vacuum before use.

Triethyl phosphate (Aldrich) was dried over P_2O_5 at 25 °C for 24 h, filtered, and distilled under reduced pressure. A fraction boiling at 90 °C/10 mmHg was collected.

Ethyl bromoacetate (Fluka) was distilled and dried with molecular sieves before use.

$POCl_3$ (Aldrich) and other reagents were used as received.

2.2. Synthesis of star-shaped polymers with functional groups

A few examples of the synthesis of PEO star-shaped polymers with methacrylic and carboxylic groups and PGL star polymers with phosphate groups placed on polyglycidyl chains, as side groups, are given below.

2.2.1. Synthesis of PEO star polymer having methacrylic groups

1.01 g of the purified (after ultrafiltration) PEO star polymer, prepared according to the procedure described previously [11], and having arms with hydroxyl end groups (Table 1, entry 1; $M_n = 37400$; 3.75×10^{-4} mol of hydroxyl groups) was placed in a vacuum glass ampoule closed with Rotaflo stopcock and dried for 5 h at 75 °C in high vacuum. Then to this ampoule 3.3 mL of dry THF was distilled and 22 μL of dry triethylamine (1.58×10^{-4} mol) and 8 μL of methacryloyl chloride (8.19×10^{-5} mol) were added. The ratio of [methacryloyl chloride]/[–OH groups] was equal to 0.22. The reaction mixture was stirred for 5 h at room temperature. Then the mixture was poured into ~150 mL of distilled water and purified by ultrafiltration. The resulting solution was liophilized on the vacuum

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Table 1
Star-shaped polymers with functional groups.

No.[a]	M_n[b] (I arm)	$[DGNG]_o/[MPEG]_o$	M_n[b] (II arm)	M_n[c] (star)	f[d]	Functional groups	DS[e] [%]
1	550	1.59	1800	37400	2 × 13.9	–OH	~100
2	550	1.59	1800	37400[f]	2 × 13.9	Methacrylate[g]	14.4
3	2000	2.10	–	37500	14.8	–OH	~100
4	2000	2.10	–	48800[h]	(19.3)[h]	–C(=O)ONa	~70
5	2000	2.10	2400	73300	2 × 14.8	–C(=O)ONa	~53
6	2450	2.92[i]	–	55200	17.9	–OH	~100
7	2450	2.92[i]	–	57800	17.9[j]	$–OP(=O)(ONa)_2$	24.0
8	2450	2.92[i]	–	63500	17.9[j]	$–OP(=O)(ONa)_2$	57.9
9	2450	2.92[i]	–	68400	17.9[j]	$–OP(=O)(ONa)_2$	74.5

[a] Star-shaped polymers with PEO arms (entries 1–5) and with PGL arms (entries 6–9).
[b] M_n of the first (I arm) and second (II arm) generation of arms.
[c] Determined by SEC (TriSEC software).
[d] Number of arms – determined from comparison of M_n of star polymer with M_n of precursor.
[e] Degree of substitution by functional groups.
[f] M_n is the same as for the starting polymer, entry 1.
[g] $–OC(=O)C(CH_3)=CH_2$.
[h] M_n and f should be the same as for the starting polymer, entry 3.
[i] $[DGNG]_o/[PGL]_o$; PGL – polyglycidol.
[j] f is the same as for the starting polymer, entry 6.

line. Yield: 0.99 g of star polymer having 14.4 mol% of methacrylate groups and 85.6 mol% of hydroxyl groups (Table 1, entry 2). The degree of substitution was determined by ^{1}H NMR spectrum.

2.2.2. *Synthesis of PEO star-shaped polymers having carboxylic groups*

2.10 g of dry MPEG 2000 (1.05×10^{-3} mol) and 26.7 mg NaH (1.11×10^{-3} mol) were placed in a vacuum glass ampoule closed with Rotaflo stopcock together with ~5.5 mL of THF ($[RO^{\ominus}] = 100\%$). In the next stage to this reaction mixture 0.483 g of DGNG (2.24×10^{-3} mol) was added ($[DGNG]_o/[\text{active centers}]_o = 2.13$; concentration of reagents: 37.2 wt%). Then, the reaction mixture was kept at 70 °C for 164 h. From time to time small amount of samples were taken from the reaction mixture for the determination of the presence of epoxy groups (^{1}H NMR) and the overall progress of reaction (^{1}H NMR and SEC). After quantitative conversion of precursor and diepoxide (cf. Table 1, entry 3), the reaction mixture was divided into two parts: A and B. To sample A (~70 wt% of the reaction mixture) 78 μL (7.01×10^{-4} mol) of ethyl bromoacetate was added (21 mol% excess to the amount of alcoholate) and the reaction mixture was stirred for 2 days at 25 °C. Then the reaction mixture was dissolved in ~10 mL of methanol, 5 mL of 0.5 molar NaOH solution was added and the mixture was heated under reflux for 32 h. From time to time small amount of samples were taken off, solvent removed under vacuum, dissolved in D_2O, and ^{1}H NMR spectra were recorded. When no presence of ester group was detected, the sample was dissolved in water, neutralized by diluted HCl and purified by ultrafiltration. Finally the product was concentrated and dried under vacuum. Yield: 1.19 g; ~70% of substitution with carboxymethyl groups (Table 1, entry 4).

To the ampoule with sample B (~30 wt% of the reaction mixture) 0.63 g of EO (1.43×10^{-2} mol) was distilled and polymerization was carried out for 2 days at 25 °C and next for 4 days at 45 °C. Then 40 μL (3.60×10^{-4} mol) of ethyl bromoacetate (37 mol% excess to the amount of alcoholate) was added to the reaction mixture. The further procedure was identical to that described above. Yield: 1.27 g; ~53% of substitution with carboxymethyl groups (Table 1, entry 5).

The degree of substitution was determined by ^{13}C (inverted gate) NMR spectra.

2.2.3. *Phosphorylation of the PGL star polymers*

The synthesis of the PGL star polymers with the first generation of arms built from polyglycidol (containing primary hydroxyl groups distributed along the arms) was described previously [13].

2.2.3.1. *Example of the synthesis.*

0.29 g of dry PGL star polymer (Table 1, entry 6; $M_n = 49\,000$; 3.10×10^{-3} mol of primary hydroxyl groups) was dissolved in 3 mL of dry triethyl phosphate and then 0.29 mL of $POCl_3$ (3.15×10^{-3} mol) was added to the reaction mixture. The mixture was stirred at room temperature for 1 h and poured into aqueous solution of 3.2 g $NaHCO_3$ (twofold molar excess for neutralization of acids formed from $POCl_3$), then stirred for 2 h and finally purified by ultrafiltration to remove low molecular salts and other impurities. The degree of phosphorylation: 74.5%, was determined by ^{13}C (inverted gate) NMR spectrum (Table 1, entry 9).

2.3. *Purification of the products*

Products were purified by ultrafiltration in water with Amicon Ultrafiltration Stirred Cell (200 mL), using membrane with a molar mass equal to 1000 cut off (Diaflo ultrafiltration membranes).

2.4. *Analysis of the products*

The ^{1}H and ^{13}C (inverted gate) NMR spectra were recorded on a Bruker AC-200 apparatus operating at 200 MHz.

The primary –OH (–OH in precursor) and the secondary –OH (–OH on the core of stars) were determined in the form of their trifluoroacetic esters $\cdots\!-\!\underline{CH_2}OC(=O)CF_3$ ($\delta = \sim 4.50$ ppm) and $\cdots\!>\!\underline{CH}OC(=O)CF_3$ ($\delta = \sim 5.30$ ppm) respectively, converted with trifluoroacetic anhydride (TFAA), according to the procedure described earlier [14].

SEC chromatography with triple detection was carried out on the chromatograph composed of LKB 2150 HPLC pump or Knauer K-501 HPLC pump with LDC RI detector and Viscotek T60A dual detector (right angle laser light scattering, at $\lambda = 670$ nm (RALLS) and differential viscometer). Detectors were connected in parallel. Three Suprema columns (30 + 100 + 3000 Å; 8 × 300 mm; Polymer Service Standard) were used in a series. Aqueous solution of NaN_3 (0.1%) was degassed (4-Channel Degasser; K-5004, Knauer) and used as a mobile phase at the flow rate of 1.0 mL / min. Samples (concentration of polymers: ~7 mg / mL) were filtered through 0.2 μm pore size membrane filters. Injection volumes of the sample solutions were 100 μL. TriSEC software (Viscotek) was used to treat the data. The whole procedure of calculation based on RALLS measurements and viscometry is given in one of the recently published papers, where a large part of Viscotek manual is quoted [15].

Differential scanning calorimetry (DSC) was carried out with a DSC TA Instrument 2920 Modulated. Specimens weighing ∼8 mg were heated and cooled at the rate of 10 or 5 °C/min in nitrogen atmosphere. Samples, after reaching 100 °C were annealed for 3 min at this temperature, then cooled to 0 °C and reheated again. Such protocol was used to erase thermal history of samples. Glass transition temperature (T_g) was determined from the second heating thermogram as the temperature of an inflection point.

Thermogravimetric analysis (TGA) was carried out with a Hi-Res TGA 2595 Thermogravimetric Analyzer (TA Instrument), at the heat up rate of 10 °C/min in nitrogen atmosphere in the range from ambient temperature to 500 °C.

3. Results and discussion

3.1. Synthesis of the star-shaped polymers

The method of the preparation of the star-shaped polymers having PEO arms and containing hydroxyl attached to the ends of arms and/or to the core was previously described [8–12].

In this paper the synthesis of PEO star polymers with methacrylic and carboxylic end groups and PGL stars with polyglycidyl arms having phosphate groups, placed along chains as side groups, is reported. The schematic structures of functionalized PEO star-shaped polymers, on the core (**$A_xB_y(Y)_x$**) and at the end of the arms (**$A_xB_y(CY)_x$**) are shown in Scheme 1, where R = –OCH$_3$, **A** and **C** stand for PEO chains and **B** corresponds to polymer unit created from diepoxide molecule (present in the core).

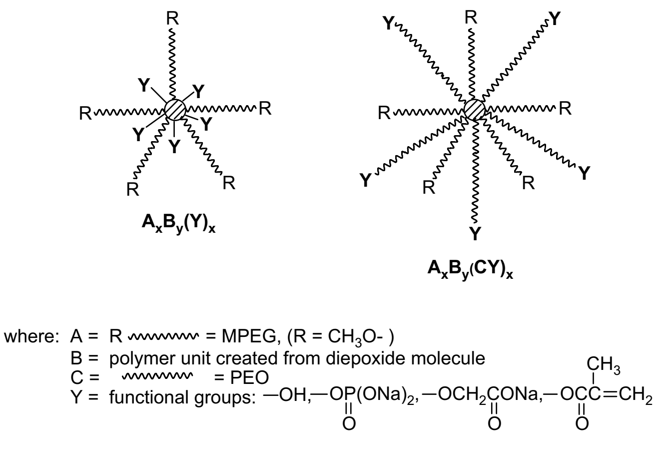
In Table 1 the summarized data of the properties of the functionalized star-shaped polymers (described below in the text) are collected.

3.2. PEO star polymers having methacrylic groups

Methacrylic groups were introduced at the end of the second generation of PEO arms e.g. star polymer having $f = 13.9$ arms (MPEG 550; the first generation) and $f = 13.9$ PEO chains with –OH end groups (the second generation) (Table 1, entry 1) was reacted with methacryloyl chloride.

In Figs. 1 and 2 ^{1}H NMR spectra of star polymers before and after functionalization are shown, respectively.

The degree of substitution was determined from ^{1}H NMR spectra (Fig. 2) by comparison of the intensity of signals k derived from protons in methacrylic groups ($=\underline{CH_2}$; $\delta = 6.10$ and 5.55 ppm) with protons from $-O\underline{CH_3}$ end groups ($\delta = 3.35$ ppm) in MPEG arms (the first generation of arms), equal to the number of starting hydroxyl groups. Star PEO molecules having ∼2 methacrylic, ∼12 hydroxyl, and ∼14 methoxy end groups were obtained, that agrees with the ratio of reagents used in the synthesis (Table 1, entry 2). Changing the ratio of [methacryloyl chloride]/[–OH groups] the different number of methacrylic groups could be introduced.



where: A = R ∿∿∿ = MPEG, (R = CH$_3$O-)
B = polymer unit created from diepoxide molecule
C = ∿∿∿ = PEO
Y = functional groups: $-OH, -OP(=O)(ONa)_2, -OCH_2C(=O)ONa, -OC(=O)C(CH_3)=CH_2$

Scheme 1.

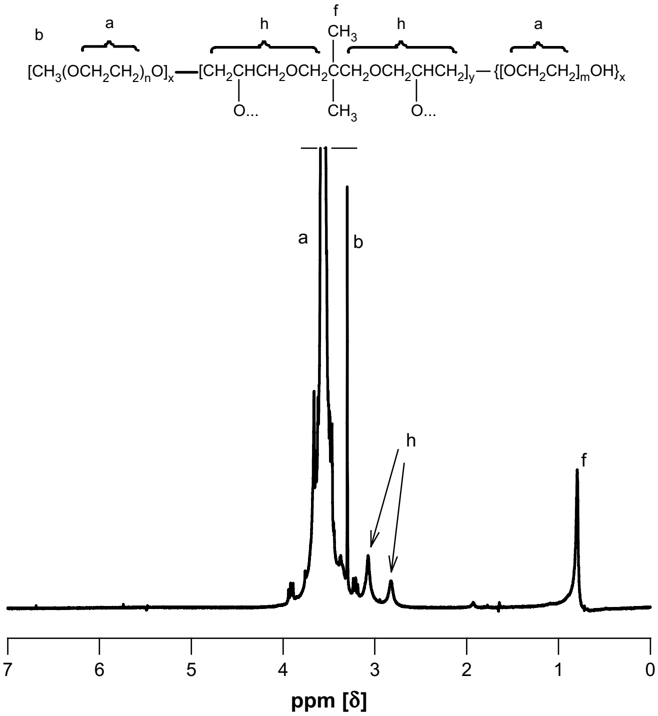


Fig. 1. ^{1}H NMR spectrum of PEO star polymer before functionalization (**$A_xB_y(CY)_x$**, **Y** = OH, Table 1, entry 1) in CDCl$_3$. Structure of star molecule is shown schematically.

3.3. PEO star polymers having carboxylic groups

Carboxymethyl groups (**Y** = $-OCH_2C(=O)ONa$) were introduced on the core (**$A_xB_y(Y)_x$**) and/or at the end of PEO arms (**$A_xB_y(CY)_x$**) in

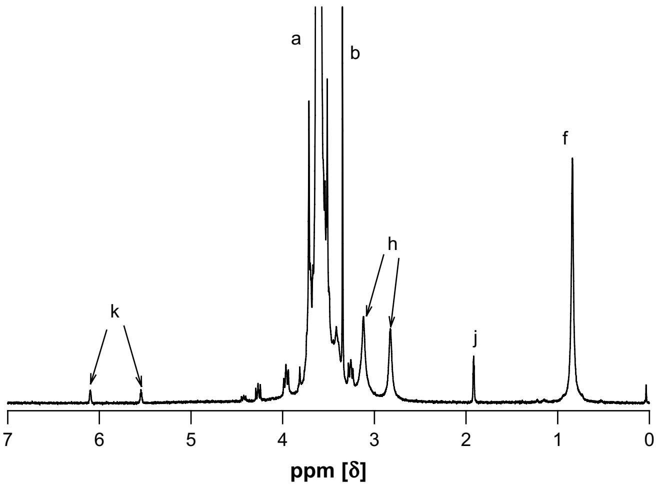
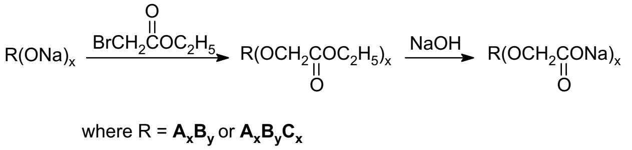


Fig. 2. ^{1}H NMR spectrum of PEO star polymer containing methacrylic groups (**$A_xB_y(CY)_x$**, **Y** = $-OC(=O)C(CH_3)=CH_2$, Table 1, entry 2) in CDCl$_3$. Description of signals are the same as in Fig. 1. Signals j and k are derived from methacrylic group; j: $-\underline{CH_3}$ and k: $=\underline{CH_2}$ atoms.



Scheme 2.

the star polymers (Scheme 1), according to the procedure described previously [16] and as shown in Scheme 2.

Star-shaped polymers with alkoxide groups were reacted with ethyl bromoacetate. The resulted products were hydrolyzed by 0.5 M sodium hydroxide solution and refluxed until hydrolysis was complete. The progress of reaction was monitored by ^{1}H NMR. The absence of signals of the –OCH$_2$CH$_3$ group indicated that hydrolysis was complete. Then the product was purified by ultrafiltration, concentrated and finally dried under vacuum. The degree of carboxymethylation was determined by the quantitative analysis of ^{13}C (inverted gate) NMR spectra (Fig. 3). Intensity of signals derived from the introduced >C=O groups (signal m; $\delta = 176.24$ ppm) and –OCH$_3$ groups at the end of the MPEG arms (signal b; $\delta = 58.02$ ppm) was compared. The highest degree of substitution on the core attained ∼70 mol% (Table 1, entry 4) and ∼53 mol% at the end of arms (Table 1, entry 5). This may result from kinetic restriction in the crowded areas.

3.4. Phosphorylation of the PGL star polymers

Phosphorylation of the polyglycidol arms (shown in Scheme 3) was carried out according to the procedure described by us previously [16].

The use of triethyl phosphate as solvent in phosphorylation reaction with POCl$_3$ excluded formation of the crosslinked products, since in this solvent only one of three P–Cl bonds is reacting. Hydrolysis (in aqueous solution of NaHCO$_3$) yielded soluble products, consisting mainly of monoesters of phosphoric acid, with a low content of pyrophosphates and diesters. Products **2**, with various degrees of phosphorylation (24.0, 57.9, and 74.5 mol%), were prepared this way (Table 1, entries 7–9). The values of *z*/*y* ratios for these products (**2**) were equal to: 0.32, 1.38, and 2.92, respectively. Typical ^{31}P NMR spectrum of the phosphorylated PGL star is shown in Fig. 4 indicating the presence of monoesters ($\delta = 4.74$ ppm; 89.5 mol%), diesters ($\delta = 1.76$ and 0.85 ppm; 5.2 mol%), and pyrophosphates ($\delta = -10.04$ and -10.61 ppm; 5.3 mol%).

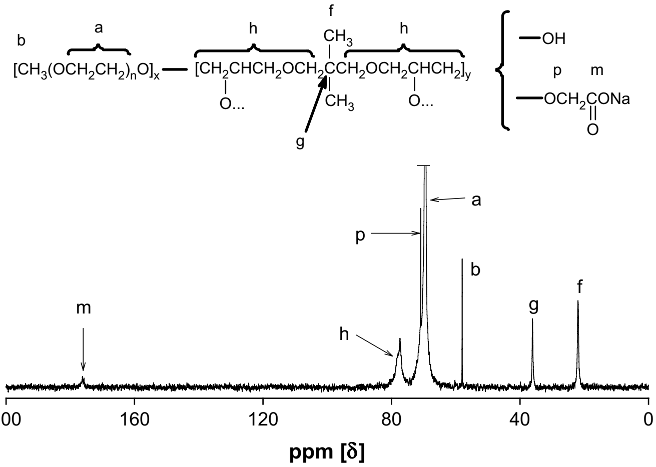
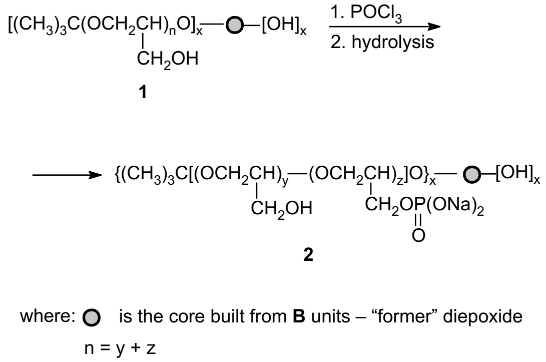
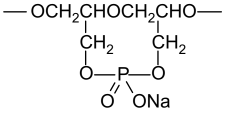


Fig. 3. ^{13}C (inverted gate) NMR spectrum of carboxymethylated PEO star polymer ($\mathbf{A_xB_y(Y)_x}$, **Y** = –OC(=O)ONa, Table 1, entry 4) in D$_2$O. Structure of star molecule is shown schematically.



Scheme 3.

Two signals observed at $\delta = 1.76$ and 0.85 ppm could be ascribed to cyclic diester (e.g. **3** – the smallest possible 9-membered ring created from two neighboring –CH$_2$OH groups), and the diester structure **4** formed between two PGL chains.



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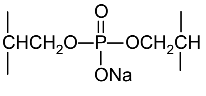


4

Two signals at $\delta = -10.04$ and -10.61 ppm, could be assigned to the pyrophosphate structures as side groups (**5**) and/or as "a bridge" between two PGL chains (**6**; analogous to the structure **4**).

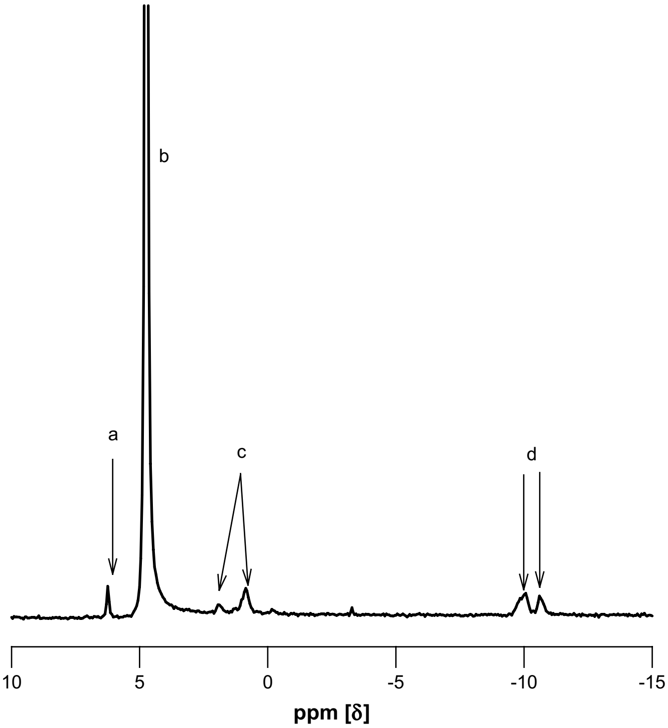
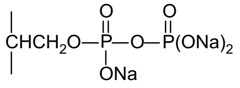
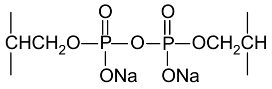


Fig. 4. ^{31}P NMR spectrum of phosphorylated PGL star polymer (Table 1, entry 9) in D$_2$O (pH = 10). Description of signals: a: residue of Na$_3$PO$_4$, b: monoesters (**2**), c: diesters (**3** and **4**), d: pyrophosphates (**5** and **6**).



$$\text{-CHCH}_2\text{O-P(=O)(ONa)-O-P(=O)(ONa)}_2$$

5



$$\text{-CHCH}_2\text{O-P(=O)(ONa)-O-P(=O)(ONa)-OCH}_2\text{CH-}$$

6

The degree of phosphorylation was determined from the quantitative ^{13}C (inverted gate) NMR spectra (Fig. 5) by comparing integrations of the c ($\delta = 63.25$) and c′ ($\delta = 65.84$ ppm) signals derived from the unsubstituted and substituted $-\underline{CH_2}OH$ groups, respectively.

PGL star polymer having only hydroxyl groups (**1**; Table 1, entry 6) should have a quite compact structure because of the stabilization by strong internal hydrogen bonds between PGL chains mediated by water molecules [17]. With the increase of the degree of phosphorylation, the increase of molar masses (M_n) of the resulted star polymers was observed (Table 1, entries 7–9). In Fig. 6 SEC traces (RI) of the initial and phosphorylated PGL stars are shown. They are monomodal and have similar retention times. The respective trace for the arm precursor is shown additionally.

3.5. PEO star-shaped polymers having phosphate groups

PEO star-shaped polymers with phosphate groups ($\mathbf{Y} = -OP(=O)(ONa)_2$) placed on the core ($\mathbf{A_xB_y(Y)_x}$) and/or at the end of PEO arms ($\mathbf{A_xB_y(CY)_x}$) (Scheme 1) have interesting properties. They were applied as effective macroionophores in liquid membranes for the separation of Zn^{2+} or Cu^{2+} from a mixture containing the following cations: Cu^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+. It has been suggested that the selectivity of these macroionophores is conditioned both by the properties of ionizable groups, its placement in the star-shaped macromolecule, and the molecular mass of the attached polyether arms. Thus, these macroionophores can be considered as the bi-functional macromolecular carriers of cations [18,19].

PEO star-shaped polymers with hydroxyl and phosphate end groups were also studied as polymer electrolytes. Interesting properties were observed for electrolytes formed by the addition of salt to the branched matrix. The value of conductivity was much higher than in the case of similar system based on linear PEO. Therefore, the star branched PEO seems to be promising for application in "polymer in salt" systems [20].

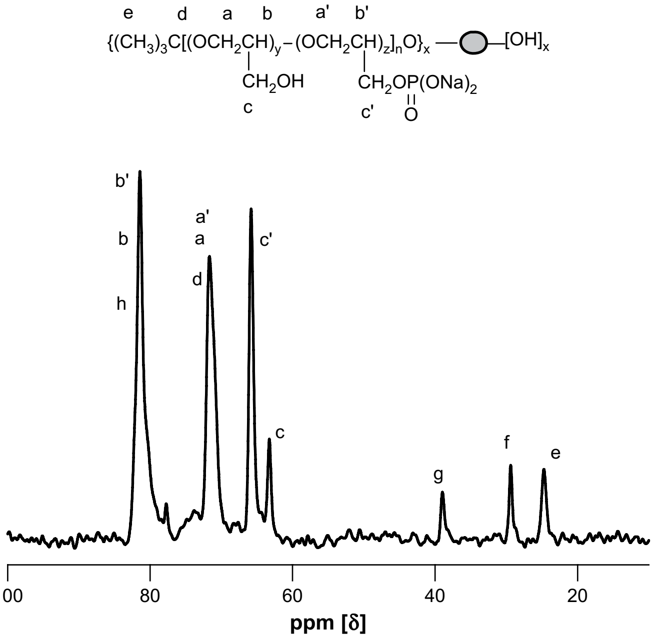


Fig. 5. ^{13}C (inverted gate) NMR spectrum of phosphorylated PGL star polymer (Table 1, entry 9) in D_2O. Signals f, h, and g ($>\underline{C}(CH_3)_2$) are derived from the core as shown in Fig. 3.

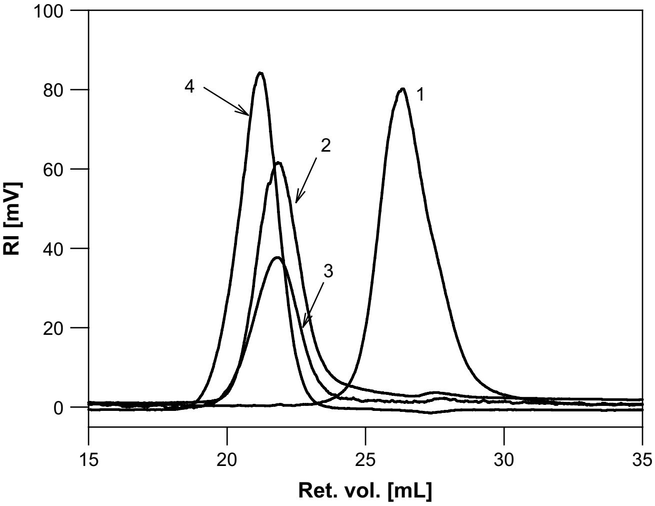


Fig. 6. SEC traces (RI) of arm precursor (1) and the first generation of PGL stars: (2) starting star with only hydroxyl groups, (3) phosphorylated star (57.9%) and (4) phosphorylated star (74.5%) (Table 1, entries 6, 8, 9).

3.6. Thermal analysis of star-shaped polymers

The melting and crystallization behaviors of star-shaped polymers were investigated by DSC. The endothermic and exothermic peak temperatures were taken as the melting (T_m) and crystallization (T_c) temperatures.

The degree of crystallinity (X_c) was estimated from the following equation:

$$X_c = \Delta H_m / \Delta H_m^o \tag{1}$$

where $\Delta H^o{}_m$ is the heat of melting of 100% crystalline linear PEO polymer, 196.8 J/g [21–23] and ΔH_m is the heat of melting of the analyzed star-shaped polymer.

The analysis was performed for the homo-arm star polymers with PEO arms (Table 1, entries 1, 3–5 and Table 2, entries 10–14) or with PGL arms (Table 1, entries 6–9) and for hetero-arm stars with PGL and PEO arms (Table 2, entries 15–18). These stars have different end (or functional) groups: hydroxyl, phosphate, carboxylic, and/or methoxy. The results of their thermal analysis are collected in Table 3. In Table 4 data of phosphorylated MPEG

Table 2
Molecular characteristics of star-shaped polymers analyzed by DSC.

No.[a]	MPEG (1st arm)	M_n (1st star)	M_n (2nd star)	M_n (2nd arm) (PEO)	Number of arms (f)	End groups
10	2000	78 800	–	–	26.8	–OH
11	2000	66 400	–	–	25.9	Phosphate[c]
12	2000	–	125 400	1950	2 × 26.8	–OH
13	2000	–	61 200	2000	2 × 14.8	–OH
14	2000	–	70 600	2000	2 × 14.8	Phosphate[c]
15	2450[b]	–	89 500	6850	2 × 17.9[d]	–OH
16	2450[b]	–	100 200	6850	2 × 17.9[d]	$-OCH_3$[e]
17	2450[b]	–	136 500	14 970	2 × 17.9[d]	–OH
18	2450[b]	–	133 000	14 970	2 × 17.9[d]	$-OCH_3$[e]

[a] Star-shaped polymers with PEO arms (entries 10–14) and with PGL and PEO arms (entries 15–18).

[b] PGL; the synthesis was previously described [13].

[c] $-OP(=O)(ONa)_2$.

[d] PGL: $f = 17.9$; PEO: $f = 17.9$.

[e] $-OCH_3$ group at the end of PEO chain.

Table 3
Thermal properties of star-shaped polymers.

No.[a]	T_m[b] [°C]	T_m[c] [°C]	T_c[d] [°C]	ΔH_m[b] [J/g]	ΔH_m[c] [J/g]	X_c [%]	T_{on}[e] [°C]	T_D[f] [°C]
1	46.5			122.3		62	369.3	393.5
		40.0	17.9		92.10	47		
3	50.6			136.9		70	366.4	397.9
		46.6	29.8		102.4	52		
4	–	46.9	26.4	–	105.4	54	374.8	396.8
5	–	47.8	30.4	–	101.9	52	368.9	396.2
10	51.4	49.5	27.1	–	115.2	59[c]	370.3	403.2
11	–	44.8	21.8	–	99.3	50	383.4	406.5
12	49.0			127.2		65	366.0	392.6
		43.1	24.1		97.99	50		
13	53.78			144.0		73	371.5	401.2
		48.6	29.5		112.7	58		
14	45.8			101.9		52	366.1	395.3
		41.7	15.5		79.46	41		
15	–	54.5	35.4		96.76	49	382.7	408.1
16	–	53.3	32.9		91.78	47	377.5	403.8
17	–	59.4	39.3		123.7	63	380.6	407.1
18	–	59.4	39.8		121.4	62	380.1	407.2

[a] Star-shaped polymers with PEO arms (entries 1, 3–5, 10–14) and with PGL and PEO arms (entries 15–18).
[b] The first heating run (10 °C/min).
[c] The second heating run (5 °C/min).
[d] Crystallization temperature: T_c [°C].
[e] T_{on} – onset temperature – heating run (10 °C/min).
[f] T_D – derivative peak temperature – heating run (10 °C/min).

2000 are reported for the comparison. The results are given for the first and the second heating cycles.

DSC analysis disclosed that the structure of arms, their length and the presence of end groups influence on T_m, T_c, and the degree of crystallinity (X_c) of star-shaped polymers.

Star polymers with PGL arms (cf. entries 6–9 in Table 1) do not crystallize and therefore for these polymers T_g was determined. In Fig. 7 the dependence of the degree of the phosphorylation of polyglycidol arms on T_g in PGL stars is shown. With increasing degree of the phosphorylation the increase of T_g was observed: from −18.7 °C for unsubstituted PGL star (entry 6), containing only –OH groups, to 2.5 °C for star with PGL arms where hydroxyl groups were substituted in 74.5% by phosphate groups (entry 9). When in PGL star (entry 6) –OH groups placed on the core were replaced by $-OCH_3$ groups the decrease of T_g up to −37.0 °C was observed. That could mean that methoxy groups diminish the possibility of the hydrogen bonding formation within the macromolecule.

T_g measured for the linear PGL ($M_n = 100\ 000$) was equal to −31.4 °C, that is close to the reported literature data: −37.9 °C [24].

The lower T_m, T_c, and the degree of crystallinity (X_c) were observed for all star-shaped polymers because of their less regular crystalline structure (thinner lamellar crystals) than their linear analogs (~66 °C) [22,23,25] with comparable molar masses.

Table 4
Thermal properties of MPEG 2000 derivatives.

Sample	T_m[a] [°C]	T_m[b] [°C]	T_c[c] [°C]	ΔH_m[a] [J/g]	ΔH_m[b] [J/g]	X_c [%]	T_{on}[d] [°C]	T_D[e] [°C]
MPEG	55.4			181.0		92	368.5	399.3
		53.6	34.3		167.7	85		
MPEG–PONa[f]	55.3			160.3		81	366.2	399.1
		53.2	31.5		133.9	68		
MPEG–POH[g]	58.3			183.8		93	352.7	391.8
		54.5	33.4		161.2	82		

[a] The first heating run (10 °C/min).
[b] The second heating run (5 °C/min).
[c] Crystallization temperature: T_c [°C].
[d] T_{on} – onset temperature – heating run (10 °C/min).
[e] T_D – derivative peak temperature – heating run (10 °C/min).
[f] MPEG–OP(=O)(ONa)$_2$; the synthesis was previously described [31].
[g] MPEG–OP(=O)(OH)$_2$.

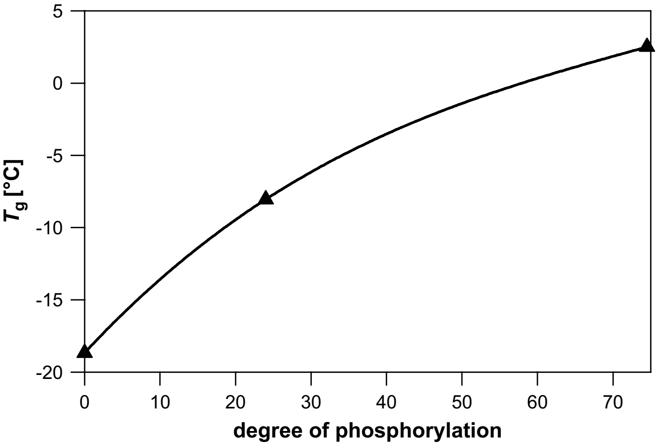


Fig. 7. The influence of the degree of the phosphorylation polyglycidol arms on T_g of PGL stars.

The exemplary DSC second heating runs for star-shaped polymers are shown in Figs. 8 and 9.

The presence of the shorter arms: MPEG 550 (Table 1, entry 1) instead MPEG 2000 (Table 1 and 2, entries 1, 3, 10, 12, 13) and phosphate end groups in stars with the first and second generation of arms (Table 2, entries 10, 11, 13 and 14) decrease the ability of the material to crystallize that is reflected in the lowering of T_m, T_c, and the crystallinity (X_c) of PEO star-shaped polymers. Introduction of carboxylic groups into star polymers do not change T_m and X_c because of their much lower size in comparison to bulky phosphate groups (Table 3, entries 3–5, 13).

Hetero-arm star-shaped polymers with PGL and longer PEO arms ($M_n = 14\,970$) exhibited high melting temperature ($T_m = 59.4$ °C). In Fig. 9 no difference was observed for polymers

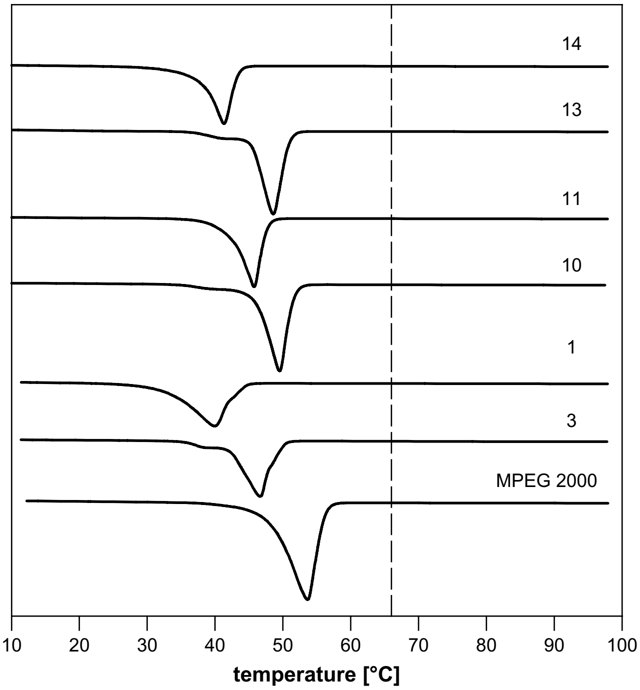


Fig. 8. DSC curves for the second heating (5 °C/min) for PEO star-shaped polymers and for MPEG 2000 (shown for comparison). Above the lines number of samples (entries from Tables 2 and 3) is given. Broken line corresponds to $T_m = 66$ °C for linear PEO [22,23,25].

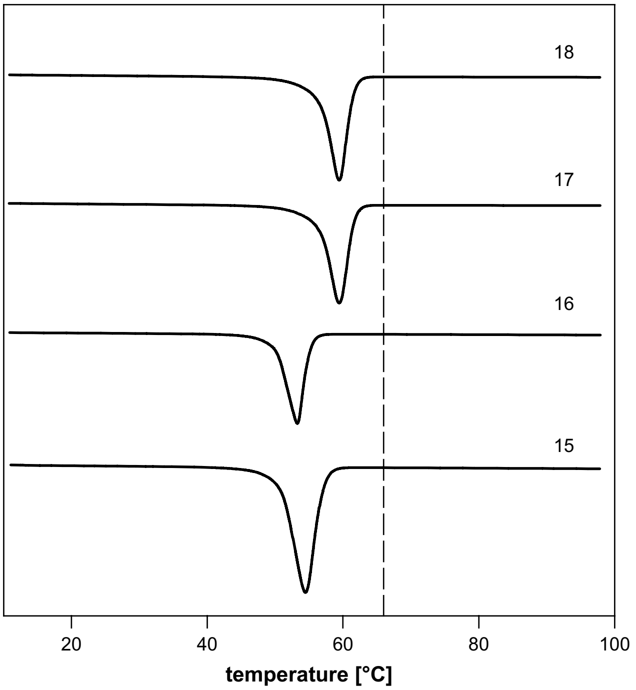


Fig. 9. DSC curves for the second heating (5 °C/min) for star-shaped polymers with PEO and PGL arms. Above lines numbers of samples (entries from Tables 2 and 3) are given. Broken line corresponds to $T_m = 66$ °C for linear PEO [22,23,25].

with hydroxyl and methoxy end groups (Tables 2 and 3, entries 17 and 18). Slightly lower T_m and T_c were recorded for similar stars with shorter PEO chains ($M_n = 6850$; entries 15 and 16 in Tables 2 and 3). In this case the slightly lower T_m = 53.3 °C was observed for star with –OCH$_3$ than with –OH (T_m = 54.5 °C) end groups at the end of PEO chains. The calculated degree of crystallinity was higher for stars with longer PEO arms (~62 to 63%) than for shorter ones (~47 to 49%), as it was observed for linear PEG/PEO [25–28].

In Fig. 10 the influence of the number of arms, in the range from 15 to 54, on T_m and X_c in star-shaped polymers is shown. In the sequence of experiments the sizes of the cores could not differ considerably (similar conditions of the reaction were applied). Therefore, the distances between PEO arms in every star molecule are influenced by the number of arms connected to the hard core. Buckley and Kovacs [27] suggested that low molecular weight PEO ($M_n < 3000$) formed extended-chain crystals. In our star-shaped polymers arms have $M_n = 2000$ and therefore PEO chains could be considered to be present in extended forms. Observed in Fig. 10 a maximum of T_m (49.5 °C) and X_c (59%) for $f \approx 27$ suggested the occurrence of an optimum for the alignments of PEO chains. For star polymers with lower and higher number of arms lower values of T_m and X_c were observed that could be interpreted as the difficulties in the formation of the relative thick extended-chain lamellar crystals. The measured values of T_m for samples 3, 10 and 13, and 12, equal to 45.6, 48.6-49.5, and 43.1 °C are close to T_m, reported previously for PEG 1500, ~1750, and 1000, and equal to 46.0, ~49.3, and 43.3 °C, respectively [27]. Thus, it means that in star-shaped polymers the thickness of extended-chain lamellar crystals depends on the number of arms.

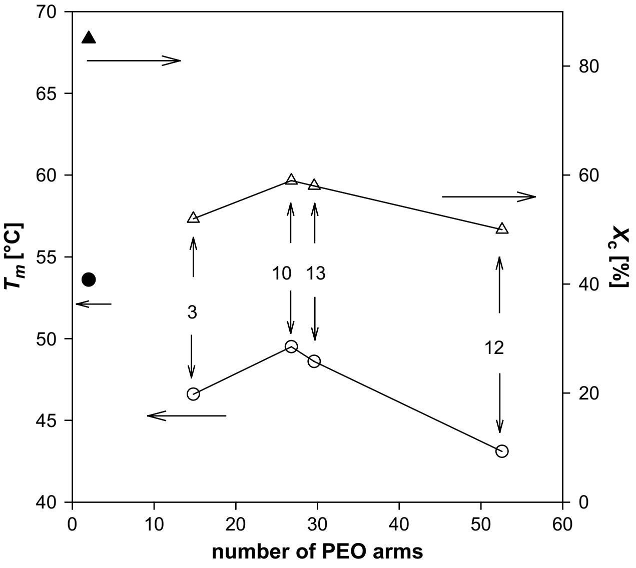


Fig. 10. The influence of the number of arms on T_m and X_c in PEO star-shaped polymers (the second heating run: 5 °C/min). Numbers correspond to star polymers described in Tables 2 and 3. Data for MPEG 2000 are given for comparison: ● for T_m and ▲ for X_c.

The decrease of T_m and X_c with the increase of the number of arms from 3 to 8 was reported previously for PEO star polymers [29,30].

TGA thermograms are featured by single peaks. DTGA peaks (T_D) and onset temperatures (T_{on}) are the highest for hetero-arm stars, most probably due to the strong hydrogen bonding between PGL and longer PEO chains, that increase their thermal stability in comparison to PEO homo-arm stars.

The similar DSC relationships were observed for linear MPEG 2000 and its phosphorylated derivatives: monoester of phosphoric acid (MPEG-POH) and its sodium salt (MPEG-PONa) (cf. Table 4). The highest T_m were observed for acid. That could be explained by the formation of more stronger hydrogen bonds in MPEG-POH than in MPEG alone. On the other hand the presence of acidic group lowers the thermal stability and facilitates degradation of polymer. Thus, the acid (MPEG-POH) decomposes earlier (at ~ 392 °C) than its salt derivative (MPEG-PONa) and MPEG alone, both at ~ 399 °C. MPEG-PONa has the lowest degree of crystallinity because the bulky neutral phosphate groups impede the alignment of MPEG chains.

4. Conclusions

Various functional groups (phosphate, carboxylic and methacrylic) were introduced into the star-shaped polymers with PEO and PGL arms. The resulted polymers were characterized by NMR and SEC analysis and their structure was confirmed by ^{1}H and ^{13}C NMR spectra.

Star-shaped PEO polymers with phosphoric or carboxylic groups could be considered e.g. as solid polymer electrolytes and/or soluble carriers for biologically active compounds.

The lower melting (T_m) and crystallization (T_c) temperatures and the degrees of crystallinity (X_c) were observed for star-shaped polymers than for their linear analogs with comparable molar masses. The increase of the length of PEO arms causes increasing of T_m, T_c, and X_c. The presence of phosphate and/or methoxy end groups lowers T_m and X_c because of hindering the ability of star-shaped polymers to crystallization. It was also observed a maximum of melting temperature ($T_m = 49.5$ °C) and the degree of crystallinity ($X_c = 59\%$) for PEO star-shaped polymers having ~27 arms.

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